Sources and concentrations of gaseous and particulate reduced nitrogen in the city of Münster (Germany)

Esther Vogt, Andreas Held, Otto Klemm*

Institute of Landscape Ecology, Climatology, University of Münster, Robert-Koch-Str. 26, 48149 Münster, Germany

*Corresponding author. Tel +49-251-83-33921; Fax +49-251-83-38352. E-mail address: otto.klemm@uni-muenster.de (O. Klemm).

Abstract

Atmospheric ammonia mixing ratios and the main inorganic ions NH_4^+, NO_3^- and SO_4^{2-} of size-resolved particles in the range from 0.05 µm to 10 µm were measured at an urban site in Münster, Germany. High mixing ratios of ammonia with a median of 5.2 ppb and a maximum of 50 ppb were detected. The mass fraction of submicron particles was much higher during the day than at night. At night, a greater particle mass and an increased presence of particulate nitrate was measured. Recurring patterns of particle distribution were distinguished and their characteristics analysed. In half of the measurements, the accumulation mode was clearly dominating, which is an indication of aged aerosol. In some measurements, higher concentrations of fine particles were found indicating particle formation. In these cases, a smaller particle mass and about four times greater ratios of ammonia versus ammonium concentrations were observed. These data show that ammonia contributes considerably to the formation of secondary particulate material.

Keywords: atmospheric ammonia, ammonium, accumulation mode, coarse mode, particle formation, particle mass, urban aerosol

1 Introduction

Ammonia (NH_3) is the predominant alkaline gas in the atmosphere and thus plays a significant role in atmospheric chemistry (e.g. Finlayson-Pitts and Pitts, 1986; Seinfeld and Pandis, 1998). In Europe, the major sources of ammonia emissions are agricultural activities (Van der Hoek, 1998). Because of its alkaline properties, ammonia neutralizes acid substances such as sulphuric acid (H_2SO_4) and nitric acid (HNO_3) to form ammonium (NH_4^+), sulphate (SO_4^{2-}) and nitrate (NO_3^-) on particles (Krupa, 2003). Therefore, ammonia is an important precursor of secondary particles (Erisman and Schaap, 2004).

Particulate matter up to 10 µm in diameter (PM_{10}) exerts harmful effects on human health. The smaller the particles the deeper they reach into the human respiratory system. Due to deposition, particles of 10 µm in diameter do not pass the throat, whereas particles smaller than 0.1 µm can penetrate deeply into the lung. Consequently, the European Union introduced novel limits to particle concentrations from the year 2005 on. A threshold for PM_{10} concentrations of 50 $\mu g\ m^{-3}$ (24 hour limit) must not be exceeded more than 35 times per year (Council directive 1999/30/EC). These limits are stepwise reduced until 2010. In many regions of central Europe the concentrations still exceed these limits (Spindler et al., 2004). Therefore, the need to reduce particle concentrations and their precursors remains an important task for local and state authorities. Various sources contribute to particulate material in urban areas: wind erosion from streets and other surfaces, tyre debris, combustion emissions including street traffic, advection of material on the mesoscale, and secondary particle formation from VOC, ammonia, and other precursors. Previous studies have shown that the contribution of organic compounds to particulate matter varies. According to Turpin et al. (2000), fine particles consist of 10 to 70 % of organic matter. It is unknown what contribution ammonia has on secondary aerosols and therefore on PM_{10} concentrations.

In this study, concentrations of gaseous NH_3 and NH_4^+, NO_3^- and SO_4^{2-} of size-resolved particles were measured. By comparing various typical patterns of particle distribution and their characteristics, the key factors leading to particle formation were analysed. In this article, the term particle formation refers to the growth of particle mass due to condensation. New particle formation through nucleation events cannot be observed by the instrument used in this study as it does not capture particulate matter smaller than 50 nm. The goal of this work is to improve the understanding of particle dynamics at an urban site.

2 Site and methods

2.1 Site

The measurements took place on the roof of the Institute of Landscape Ecology in the city of Münster in Northwestern Germany. Münster has a population of about 260 000. The city is not highly industrialized and the traffic impact is relatively low for a German urban location. Münster is surrounded by intensive agriculture, mainly by cattle and pig farms, therefore ammonia emissions are relatively high.

The Institute of Landscape Ecology is located approximately one kilometre west of the centre of Münster. The green roof of the institute is flat and at a height of 17 m a.g.l. The site is situated at 78 m a.s.l. at 51° 57’ 37’’ N and 7° 36’ 27’’ E.

2.2 Aerosol sampling

Size-segregated aerosol particles were measured with a five-stage Berner low-pressure impactor (LPI 80/0.05). The five size classes of the impactor are shown in Table 1.

> **Table 1**

The impaction surfaces were covered with aluminium foils for particle collection. A critical orifice restricts the air flow through the impactor to 75.4 l min^{-1}. Samples were taken either at daytime from 9 a.m. to 5 p.m. (CET) or at night from 10 p.m. to 5 a.m. (CET). Aerosol was collected in two periods, from 3 to 11 May 2004 and from 20 to 30 June 2004. In this study, 30 measurements of good data quality were considered. Measurements were excluded when obvious contaminations such as insects were found in the impactor or when indications of impurity were detected in the blank samples taken before every measurement.

The reduced pressure in the impactor can lead to evaporation of NH_4NO_3 during sampling, though the measurements are expected to be not severely effected by this artifact.

2.3 Analysis of NH_4^+, NO_3^- and SO_4^{2-}

Each aluminium foil, including the blank samples, was extracted with 10 ml of deionised water which was analysed for ammonium, nitrate and sulphate in the laboratory of the Institute of Landscape Ecology at the University of Münster. Ammonium was analysed by flow injection analysis with the Aquatec Analyser 5400. Nitrate and sulphate were analysed with the ion chromatograph Dionex DX-100.

2.4 Gas sampling

Atmospheric ammonia concentrations were measured by a horizontal continuous-flow wet denuder (AMANDA). Ammonia is collected in a 3.6 mM $NaHSO_4$ absorption solution and separated from other compounds by diffusion through a gas-permeable PTFE membrane. Finally, the ammonia concentration is determined by measuring the conductivity. For more details about the sampling system see Wyers et al. (1993).

Measurements took place continuously between 30 March and 2 July 2004 with a time resolution of 10 min. For comparison with the impactor measurements, the ammonia concentrations were averaged over the respective 7 or 8 hour impactor sampling intervals. Occasional loss of data occurred due to blockage of the denuder by soil material.

3 Results and discussion

3.1 NH_3, NH_4^+, NO_3^- and SO_4^{2-} concentrations

The median and maximum concentrations of NH_3 over the whole measuring period in spring 2004 clearly show the influence of the agricultural surroundings of Münster (Table 2). Typical concentrations of 0.23 µmol m^{-3} (5.2 ppb) are similar to those measured in other studies at sites nearby agricultural activities in the Netherlands (Sutton et al., 1994). As shown in Table 2, NH_3 concentrations in the city of Münster can reach very high levels up to 2.24 µmol m^{-3} (50 ppb) under certain conditions.

> **Table 2**

Unlike in other studies (e.g. Yamamoto et al., 1995; Horvath and Sutton, 1998), there was no clear correlation observed between NH_3 concentrations and air temperature or relative humidity. The atmospheric equilibrium between NH_3, HNO_3 and NH_4NO_3 favours increased gaseous concentrations at higher temperatures. Such an equilibrium should therefore result in a diurnal cycle of e.g. NH_3 concentrations. The fact that this has not been observed in this study indicates a great influence of local emittents (Burkhardt et al., 1998). It also indicates that NH_3, HNO_3 and NH_4NO_3 have not yet reached equilibrium at the measurement site.

As an example of variations in NH_3 mixing ratios, three days of continuous data are shown in Figure 1.

> **Figure 1**

While concentrations of particulate ammonium are typically much lower than those of gaseous NH_3, NH_4^+ still dominates the particle mass together with NO_3^-. Sulphate contributes only a small percentage of the particle mass due to the effective reduction of SO_2 emissions in Europe over the past 20 years (Klemm and Lange, 1999; Erisman and Schaap, 2004). As all ammonium found in the atmosphere originates from ammonia (Asman et al., 1989), high ammonia concentrations may be expected at the site and nearby.

3.2 Ion charge balance

Figure 2 shows the equivalent concentrations of ammonium ions compared to the sum of nitrate and sulphate ions. Additionally shown is a straight line of the function y = x which represents a closed ion charge balance.

> **Figure 2**

The ion charge balance of NH_4^+, NO_3^- and SO_4^{2-} is almost closed. This indicates that these three ions are the main constituents of the inorganic particle mass as shown in various studies (Lee et al., 1999; Held et al., 2002).

On individual impactor stages the ion charge balance varies. Especially on large particle stages (stage 4 and 5) the analysed anions have higher concentrations than the analysed cations. This cation deficit can be explained by the fact that nitrate is enriched on particles in the coarse mode by reactions with Na^+, Ca^{2+} and Mg^{2+} from sea salt and soil particles (Zhuang et al., 1999).

3.3 Day- and nighttime patterns of particle composition

Differences were found between day- and nighttime median concentrations. In Figure 3 the circle areas represent the overall concentration of NH_4^+, NO_3^- and SO_4^{2-} during day and night, respectively. The percentages indicate the contributions of the single ions to the overall concentration.

> **Figure 3**

Obviously, particle concentrations at night are higher than during the day. Median particle concentrations of 0.15 µmol m^{-3} during the day and 0.22 µmol m^{-3} at night were found. Also, the chemical composition varies. Absolute sulphate concentrations remain the same during day and night. Ammonium concentrations increase from 0.09 µmol m^{-3} during the day to 0.12 µmol m^{-3} at night. Nitrate concentrations reach 0.04 µmol m^{-3} at daytime and 0.08 µmol m^{-3} at nighttime. Nitrate has a much greater relative contribution during the night.

The constant sulphate concentrations during day and night are probably a result of much ealier formation originating from distant sources and therefore they represent aged aerosol.

Boundary layer dynamics could contribute to higher particle concentrations at night. In this study, this might only apply for individual cases, as trace gas measurements at the site indicate that a low boundary layer did not form regularly.

Greater particle mass at night can be explained by the meteorological conditions. At night, lower temperatures and higher humidity lead to a shift of the equilibrium between the gaseous and particulate phases towards the particulate phase, and consequently to a greater particle mass.

Another factor contributing to greater particle mass and, in addition, to a change in the chemical composition at night, is an effective nighttime production of the nitrate radical. The nitrate radical leads to the production of N_2O_5 which itself reacts with water molecules on the surface of particles (Seinfeld and Pandis, 1998). The adsorption of HNO_3 takes place directly on the surface of the particle, therefore, all of the HNO_3 passes on to the particulate phase. Thus, the adsorption of HNO_3 on particles is very efficient at night.

Similar results were found in previous investigations. Lee et al. (1999) observed increased nitrate concentrations at night. Increased ammonium concentrations were also found but with a smaller difference between day and night. Sulphate concentrations remained the same during day and night. They explained their results by the nitrate radical and the N_2O_5 production during nighttime. Particulate nitrate was mainly found in the coarse mode which they concluded is due to the reaction of N_2O_5 and NaCl at night.

In the present study, particulate nitrate was also found in relatively high concentrations in the coarse mode (see Figure 4). These high concentrations were measured at night, but also during the day. The greater contribution of nitrate to the coarse mode may be explained by its reactivity with sea salt and soil particles (Zhuang et al., 1999). These reactions with coarse particles can occur both during day- and nighttime, either with HNO_3 or N_2O_5.

Makar et al. (1998) found a rapid increase of particles in the accumulation mode at night. They came to the conclusion that the overnight production of HNO_3 in the presence of local NH_3 emissions and pre-existing particles leads to a rapid formation of particulate NH_4NO_3.

In this study, the increase of particle mass at night was also found mainly in the accumulation mode. Figure 4 shows the size-resolved chemical composition of the particles during the day (a) and during the night (b). The size of particles increases from stage 1 to 5.

> **Figure 4**

In both figures, the greatest particle mass occurs on impactor stage 3, reflecting particles with diameters between 0.42 and 1.2 µm. However, stage 3 is more dominant at night than it is during the day. At daytime, the particle mass of stage 2 is more than half of the particle mass of stage 3, whereas at nighttime it drops to 20 %.

Because of higher concentrations on stage 2 at daytime, it is assumed that processes of particle formation occur mainly during the day.

This corresponds with results of previous studies. Kulmala et al. (2004) summarise the observations of the formation and growth of particles over the last decade. They found that almost all nucleation events occur during daytime.

Secondary formation of particles in the atmosphere takes place through chemical transformation of gases to low volatility products (Penkett et al., 2003). Important atmospheric oxidants are the OH radical and ozone. They are influenced by photochemical reactions (Penkett et al., 2003) and are therefore controlled by shortwave radiation. Boy & Kulmala (2002) conclude that solar UV-radiation indirectly influences the formation and growth of particles because it controls the photochemical reactions. Therefore, nucleation events are more likely to occur at daytime than at night.

3.4 Characteristic patterns of particle distribution

Four different types of particle distribution are defined by the following criteria:

Type *Dominance*: impactor stage 3 is dominant (i.e., its mass contributes more than 50 % of the total mass and no other stage contributes more than 60 % of its mass).

Type *Particle formation*: impactor stage 2 exhibits the highest particle mass.

Type *Intermediate stage*: impactor stage 3 exhibits a greater mass than other stages, but is not dominant.

Type *Coarse particles*: impactor stage 3 is dominant and stage 4 exhibits a greater mass than stage 2.

In the following, examples of the four different types of distribution are presented.

> **Figure 5**

Type Dominance

Figure 3a shows the size-resolved chemical composition of the particle population in the night from 7 to 8 May 2004. Stage 3 is clearly dominant. It exhibits 82 % of the total particle mass. The total NH_4^+ concentration including all stages reaches 0.10 µmol m^{-3}. The average NH_3 concentration during the impactor measurement was 0.03 µmol m^{-3}. Thus, the NH_4^+ concentration is more than three times as high as the NH_3 concentration. Due to the small amount of NH_x in the gaseous phase, the potential to form particle mass from NH_3 condensation was relatively low.

Accumulation mode particles "accumulate" over a certain period of time. The dominance of stage 3, i.e. the accumulation mode, indicates an aged particle population. Most of the particles were probably transported into the area. During the day on 7 May, precipitation occurred and consequently particles were removed by wet deposition. The effect of dry deposition is selective, so that the loss of particles in the accumulation mode is less effective than of smaller particles (stages 1 and 2) and larger particles (stages 4 and 5). Diffusion processes lead to high deposition of small particles whereas the high deposition rate of large particles is due to sedimentation processes. Because of the absence of considerable particle formation in the local area, only accumulation mode particles of stage 3 are found.

Type Particle formation

Figure 3b shows the subsequent daytime measurement of 8 May 2004. The total particle mass is very low, but the mass on stage 2 is relatively high. The total NH_4^+ concentration reaches 0.02 µmol m^{-3}, which is five times lower than the night before. The average NH_3 concentration is 0.15 µmol m^{-3} and thus five times higher than the night before. Hence, the relation between NH_x in the gaseous and the particulate phase has turned around.

This was probably caused by a change in the wind direction. From the evening of the 7th to the morning of the 8th, the wind direction changed gradually from 250° to 100°. Air masses from westerly directions advected aged aerosol to Münster. After the change to easterly winds, air masses with low particle concentration arrived in Münster. In the morning, increasing NH_3 concentrations and the onset of solar radiation initiated particle formation.

In almost every measurement of the type “Particle formation”, there is much more reduced nitrogen in the gaseous phase compared to the particulate phase. In some cases the NH_3 concentration was up to nine times higher than the NH_4^+ concentration.

Kulmala et al. (2000) found two conditions promoting particle formation. First, low concentrations of pre-existing particles facilitate particle formation by making homogeneous nucleation more likely than heterogeneous nucleation. Raes et al. (2000) often observed high concentrations of small particles when the total aerosol surface area was low. Second, high concentrations of condensable gases, such as ammonia, encourage further growth of newly formed particles.

In this study, the average particle mass of the type "Particle formation" was found to be less than a third of the average particle mass of all other types.

Type Intermediate stage

Shown in Figure 3c is the chemical composition of the five impactor stages during the day of 3 May 2004. Stage 3 exhibits the greatest particle mass but is nevertheless not dominant because of the relatively high concentration of stage 2. The average concentration of NH_3 is 0.39 µmol m^{-3} which is more than twice as high as the total NH_4^+ concentration of 0.17 µmol m^{-3}.

The characteristics of the type "Particle formation" are also visible in the type "Intermediate stage" though not as distinctively. In the "Intermediate stage" the ratio between reduced nitrogen in the gaseous and the particulate phase is clearly smaller than in the "Particle formation", but it is still greater than the average ratio of the other types. In the "Intermediate stage", there is on average 2.4 times as much NH_x in the gaseous phase than in the particulate phase. In comparison, in the types "Dominance" and "Coarse particles" there is on average 1.7 times as much NH_x in the gaseous phase than in the particulate phase.

The particle mass of the "Intermediate stage" is clearly higher than in the type "Particle formation", but still smaller than in the other two types "Dominance" and "Coarse particles". Therefore, it may be concluded that the types "Particle formation" and "Intermediate stage" show similar characteristics. But the characteristic features are much more apparent in the type "Particle formation".

Type Coarse particles

Figure 3d shows the results of the measurement during the night from 10 to 11 of May 2004. The total particle mass is large. Stage 3 is dominant and stage 4 exhibits a higher concentration than stage 2. The NH_3 and NH_4^+ concentrations are both relatively high at 0.61 µmol m^{-3} and at 0.51 µmol m^{-3}, respectively.

In this measurement, the overall nitrate concentration is relatively high, especially on stage 3 and 4. As explained above, at night the effective production of the nitrate radical leads to more particulate nitrate. In this process, mainly NH_4NO_3 in the accumulation mode and $NaNO_3$ in the coarse mode are produced.

Correspondingly, all measurements of the type "Coarse particles" occurred at night. On average, the particle mass of this type is very high compared to all other types.

4 Conclusions

The city of Münster is clearly affected by the surrounding agricultural activities. Even in the city centre high ammonia concentrations occur. In every direction, Münster is surrounded by ammonia sources, therefore, ambient ammonia concentrations do not depend on the wind direction. In contrast to the NH_3 concentrations, the NH_4^+ concentrations seem to have their origin in distant sources. 70 km to the West, the neighbouring Netherlands have the highest ammonia emission density in Europe, in the year 1990 with an average of more than 4000 kg km^{-2} (Buijsman et al., 1998; Lekkerkerk, 1998). Since then, NH_3 emissions have been reduced in the Netherlands by more than 20 %, though it still is the European country with the highest ammonia emissions relative to the area (Erisman et al., 2003). Therefore, back trajectories calculated by the HYSPLIT-model (Draxler and Rolph, 2003) were used to compare ammonium concentrations to the time that air masses spent over the Netherlands before arriving in Münster. A tendency towards higher ammonium concentrations in air masses that spent a long time over the Netherlands was found. These data indicate that ammonium originating in the Netherlands contributes considerably to the particle mass in Münster.

Table 3 summarises the main differences between the four types of particle distribution "Dominance", "Particle formation", "Intermediate stage" and "Coarse particles"

> **Table 3**

The absolute ammonia concentration was not higher when particle formation occurred. The key factor leading to particle formation was found to be the difference in particle mass and therefore in pre-existing particles. When the mass of particulate NH_4^+, NO_3^-, and SO_4^{2-} was small, also the ratio between ammonia and ammonium was greater and particle formation was more likely to occur.

The conclusion can be drawn that there is probably always enough NH_3 in the atmosphere to contribute to particle formation in the city of Münster. Therefore, the ambient NH_3 concentration is not a key factor for particle formation. Other factors such as small particle mass and at the same time a great difference between ammonia and ammonium concentrations are necessary to trigger particle formation.

For further investigation of particle formation and growth, the simultaneous use of instruments capable of high resolution measurements of the particle size spectrum, such as the Scanning Mobility Particle Sizer (SMPS), and instruments for analyzing the chemical composition of size-resolved particles, such as the Electrical Low Pressure Impactor (ELPI), would be desirable. By coordinated measurements of key particle properties and of gaseous ammonia concentrations, the formation and growth of particles as well as the simultaneous composition in the gaseous and in the particulate phase could be studied in detail.

Acknowledgements

We gratefully acknowledge the Bayreuth Institute for Terrestrial Ecosystem Research (BITÖK) of the University of Bayreuth for lending us the AMANDA NH_3-analyser. We also like to thank the laboratory of the Institute of Landscape Ecology at the University of Münster for the chemical analysis.

References

Asman, W. A. H., Pinksterboer, E. F., Maas, H. F. M., Erisman, J.-W., Waijers-Ypelaan, A., Slanina, J., Horst, T. W., 1989. Gradients of ammonia concentration in a nature reserve: model results and measurements. Atmospheric Environment 23, 2259-2265.

Boy, M., Kulmala, M., 2002. Nucleation events in the continental boundary layer: Influence of physical and meteorological parameters. Atmospheric Chemistry and Physics 2, 1-16.

Buijsman, E., Aben, J. M. M., Van Elzakker, B. G., Mennen, M. G., 1998. An automatic atmospheric ammonia network in the Netherlands. Atmospheric Environment 32, 317-324.

Burkhardt, J., Sutton, M. A., Milford, C., Storeton-West, R. L., Fowler, D., 1998. Ammonia concentrations at a site in Southern Scotland from 2 yr of continuous measurements. Atmospheric Environment 32, 325-331.

Draxler, R. R., Rolph, G. D., 2003. HYSPLIT (Hybrid Single-Particle Langrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4.html). NOAA Air Resources Laboratory, Silver Spring, USA.

Erisman, J. W., Grennfelt, P., Sutton, M., 2003. The European perspective on nitrogen emission and deposition. Environment International 29, 311-325.

Erisman, J. W., Schaap, M., 2004. The need for ammonia abatement with respect to secondary PM reductions in Europe. Environmental Pollution 129, 159-163.

Finlayson-Pitts, B. J., Pitts, J. N., 1986. Atmospheric chemistry: Fundamentals and experimental techniques. John Wiley & Sons, New York.

Held, A., Wrzesinsky, T., Mangold, A., Gerchau, J., Klemm, O., 2002. Atmospheric phase distribution of oxidized and reduced nitrogen at a forest ecosystem research site. Chemosphere 48, 697-706.

Horvath, L., Sutton, M. A., 1998. Long-term record of ammonia and ammonium concentrations at K-puszta, Hungary. Atmospheric Environment 32, 339-344.

Klemm, O., Lange, H., 1999. Trends of air polluion in the Fichtelgebirge mountains, Bavaria. Environmental Science and Pollution Research 6, 193-199.

Krupa, S. V., 2003. Effects of atmospheric ammonia (NH_3) on terrestrial vegetation: a review. Environmental Pollution 124, 179-221.

Kulmala, M. , Pirjola, L., Mäkelä, J. M., 2000. Stable sulphate clusters as a source of new atmospheric particles. Nature 404, 66-69.

Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W., McMurry, P. H., 2004. Formation and growth rates of ultrafine atmospheric particles: a review of observations. Journal of Aerosol Science 35, 143-176.

Lee, D. S., Dollard, G. J., Derwent, R. G., Pepler, S., 1999. Observations on gaseous and aerosols components of the atmosphere and their relationships. Water, Air and Soil Pollution 113, 175-202.

Lekkerkerk, L. J. A., 1998. Implications of Dutch ammonia policy on the livestock sector. Atmospheric Environment 32, 581-587.

Makar, P. A., Wiebe, H. A., Staebler, R. M., Li, S. M., Anlauf, K., 1998. Measurement and modelling of particle nitrate formation. Journal of Geophysical Research 103, 13095-13110.

Penkett, S. A., Law, K. S., Cox, T., Kasibhatla, P., 2003. Atmospheric photooxidants. In: Brasseur, G. P., Prinn, R. G., Pszenny, A. A. P. (Eds.). Atmospheric chemistry in a changing world: An integration and synthesis of a decade of tropospheric chemistry research. pp 73-124. Springer, Berlin.

Raes, F., Van Dingenen, R., Vignati, E., Wilson, J., Putaud, J.-P., Seinfeld, J. H., Adams, P., 2000. Formation and cycling of aerosols in the global atmosphere. Atmospheric Environment 34, 4215-4240.

Seinfeld, J. H., Pandis, S. N., 1998. Atmospheric chemistry and physics: from air pollution to climate change. John Wiley & Sons, New York.

Spindler, G., Müller, K., Brüggemann, E., Gnauk, T., Herrmann, H., 2004. Long-term size-segregated characterization of PM_{10}, $PM_{2.5}$, and PM_1 at the IfT research station Melpitz downwind of Leipzig (Germany) using high and low-volume filter samplers. Atmospheric Environment 38, 5333-5347.

Sutton, M. A., Asman, W. A. H., Schjoerring, J. K., 1994. Dry deposition of reduced nitrogen. Tellus 46B, 255-273.

Turpin, B. J., Saxena, P., Andrews, E., 2000. Measuring and simulating particulate organics in the atmosphere: problems and prospects. Atmospheric Environment 34, 2983-3013.

Van der Hoek, K. W., 1998. Estimating ammonia emission factors in Europe: summary of the work of the UNECE ammonia expert panel. Atmospheric Environment 32, 315-316.

Wyers, G. P., Otjes, R. P., Slanina, J., 1993. A continuous-flow denuder for the measurement of ambient concentrations and surface-exchange fluxes of ammonia. Atmospheric Environment 27A, 2085-2090.

Yamamoto, N., Nishiura, H., Honjo, T., Ishikawa, Y., Suzuki, K., 1995. A long-term study of atmospheric ammonia and particulate ammonium concentrations in Yokohama Japan. Atmospheric Environment 29, 97-103.

Zhuang, H., Chan, C. K., Fang, M., Wexler, A. S., 1999. Formation of nitrate and non-sea salt sulfate on coarse particles. Atmospheric Environment 33, 4223-4233.

Figure Captions

Fig. 1: Mixing ratios of atmospheric NH_3 from 27 May 2004 at 12 a.m. to 29 May 2004 at 12 a.m. (CET)

Fig. 2: Ion charge balance of NH_4^+, NO_3^- and SO_4^{2-} for each measurement

Fig. 3: Relative contribution of NH_4^+ (grey), NO_3^- (white) and SO_4^{2-} (striped) to the total mass of these ions. Shown are medians of daytime (a) and nighttime (b) data. The relative circle areas reflect the total concentrations.

Fig. 4: Median concentrations of NH_4^+ (grey), NO_3^- (white) and SO_4^{2-} (striped) on each impactor stage (for size ranges see Table 1) at daytime (a) and at nighttime (b).

Fig. 5: Concentrations of NH_4^+(grey), NO_3^- (white) and SO_4^{2-} (striped) on each impactor stage (for size ranges see Table 1): a) Type "Dominance", night from 7 to 8 May 2004, 10 p.m. to 5 a.m. b) Type "Particle formation", day on 8 May 2004, 9 a.m. to 5 p.m. c) Type "Intermediate stage", day on 3 May 2004, 9 a.m. to 5 p.m. d) Type "Coarse particles", night from 10 to 11 May 2004, 10 p.m. to 5 a.m.

Table 1: Impactor stages and their size ranges

Stages	**Size range**
Stage 5	3.46 – 10.0 µm
Stage 4	1.20 – 3.46 µm
Stage 3	0.42 – 1.20 µm
Stage 2	0.14 – 0.42 µm
Stage 1	0.05 – 0.14 µm

Table 2: Median and maximum concentrations of gaseous NH_3 and of the three main inorganic ions NH_4^+, NO_3^- and SO_4^{2-} in the city of Münster.

	Median [µmol m^{-3}]	**Maximum** [µmol m^{-3}]
NH_3	0.230	2.240
NH_4^+	0.105	0.514
NO_3^-	0.060	0.364
SO_4^{2-}	0.024	0.080

Table 3: Characteristics of the different patterns of particle distribution “Dominance”, “Particle formation”, “Intermediate stage” and “Coarse particles”.

	Dominance	**Particle formation**	**Intermediate stage**	**Coarse particles**
Mean particle mass [µg m^{-3}]				
Stage 5: 3.46 – 10.0 µm	0.35	0.32	0.80	0.45
Stage 4: 1.20 – 3.46 µm	0.95	0.74	1.13	4.17
Stage 3: 0.42 – 1.20 µm	7.46	1.03	4.01	13.78
Stage 2: 0.14 – 0.42 µm	2.03	1.39	2.81	1.18
Stage 1: 0.05 – 0.14 µm	0.31	0.33	0.48	0.29
All stages	11.10	3.81	9.23	19.87
Median concentration [µmol m^{-3}]				
NH_3	0.21	0.18	0.35	0.22
NH_4^+	0.11	0.04	0.12	0.21
NO_3^-	0.07	0.02	0.06	0.15
SO_4^{2-}	0.03	0.01	0.03	0.02
Daytime measurements	5	5	4	0
Nighttime measurements	6	4	2	4

Figure 1

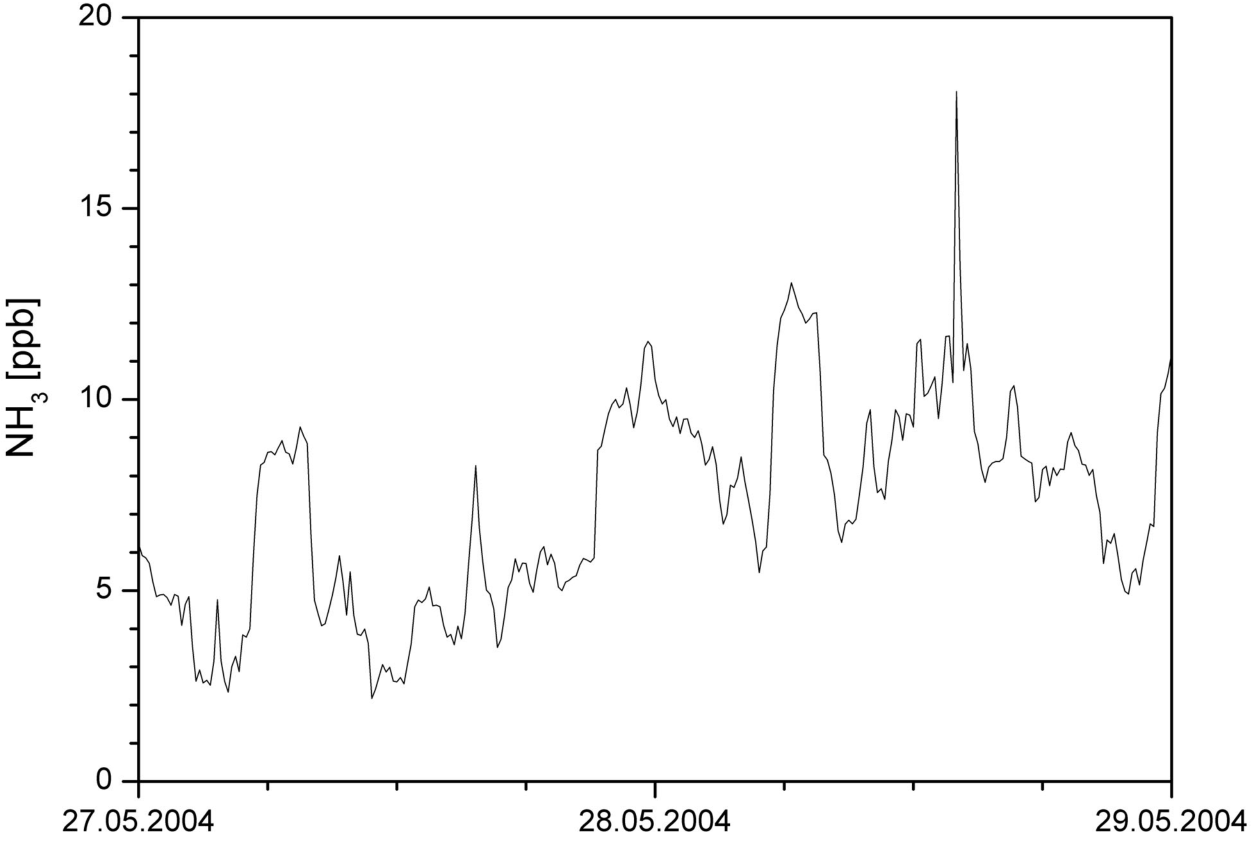


Figure 2

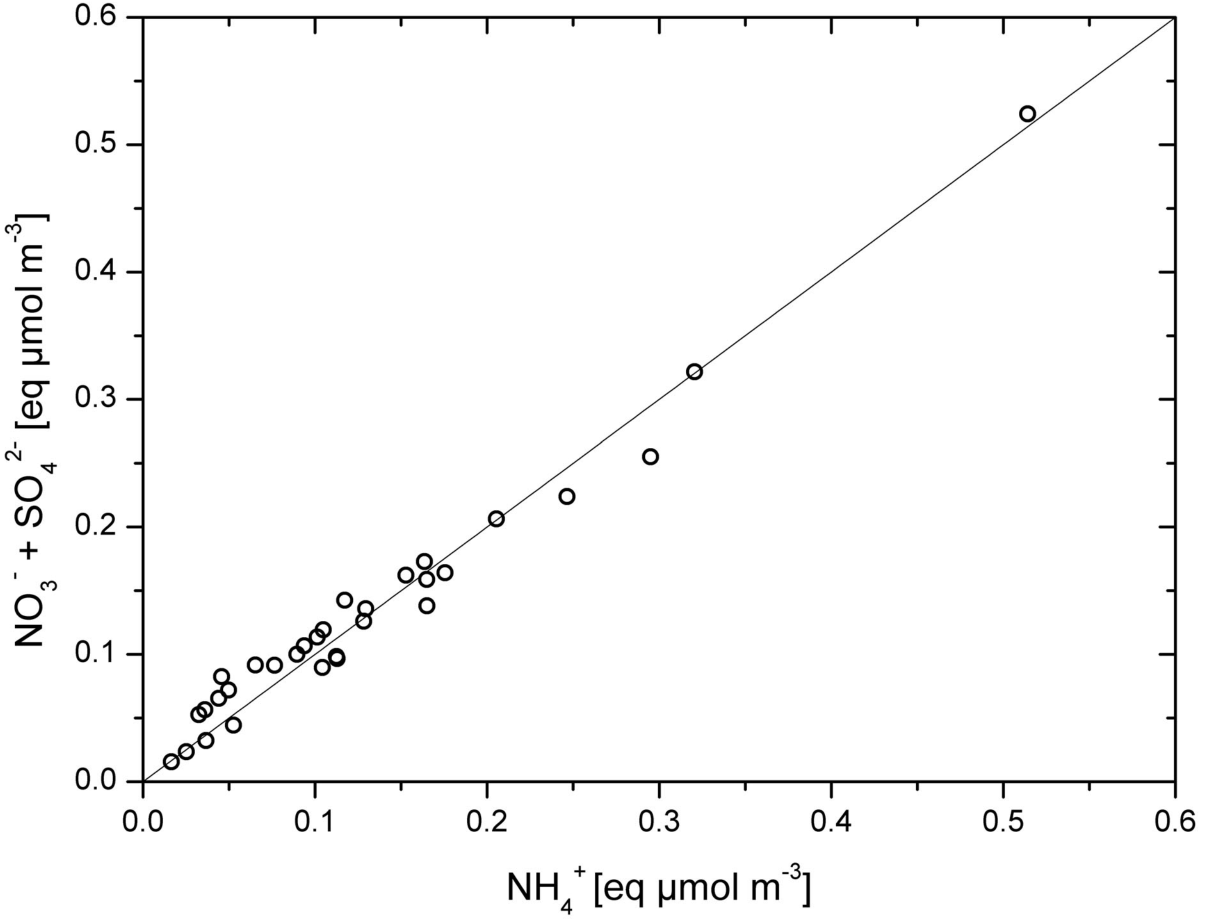

$NO_3^- + SO_4^{2-}$ [eq µmol m^{-3}]
0.0
0.1
0.2
0.3
0.4
0.5
0.6
NH_4^+ [eq µmol m^{-3}]
0.0
0.1
0.2
0.3
0.4
0.5
0.6

Figure 3

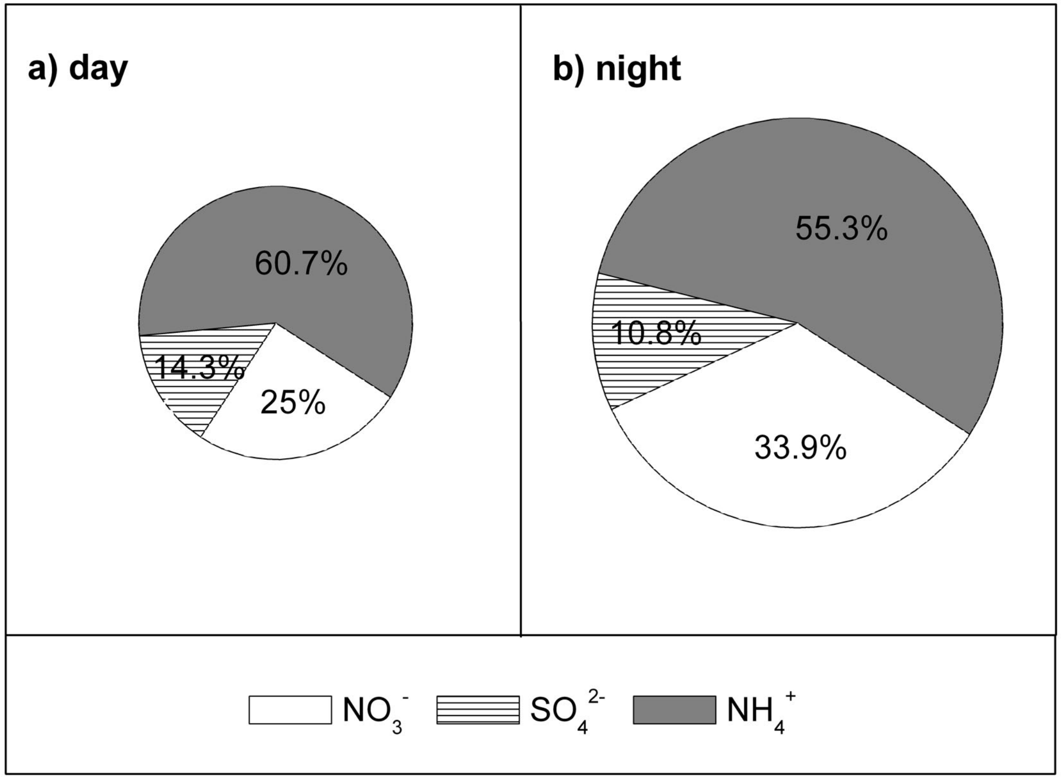


Figure 4

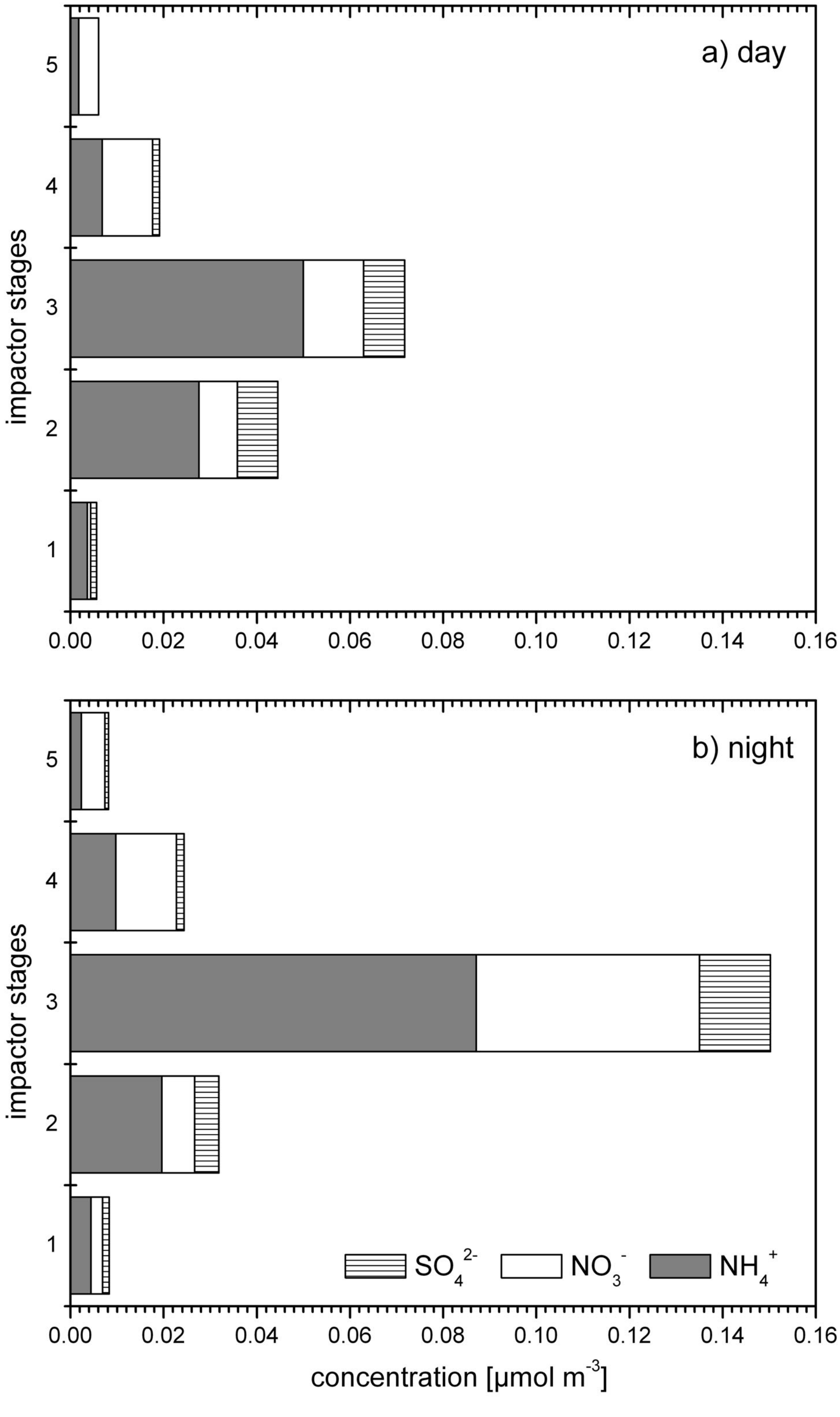
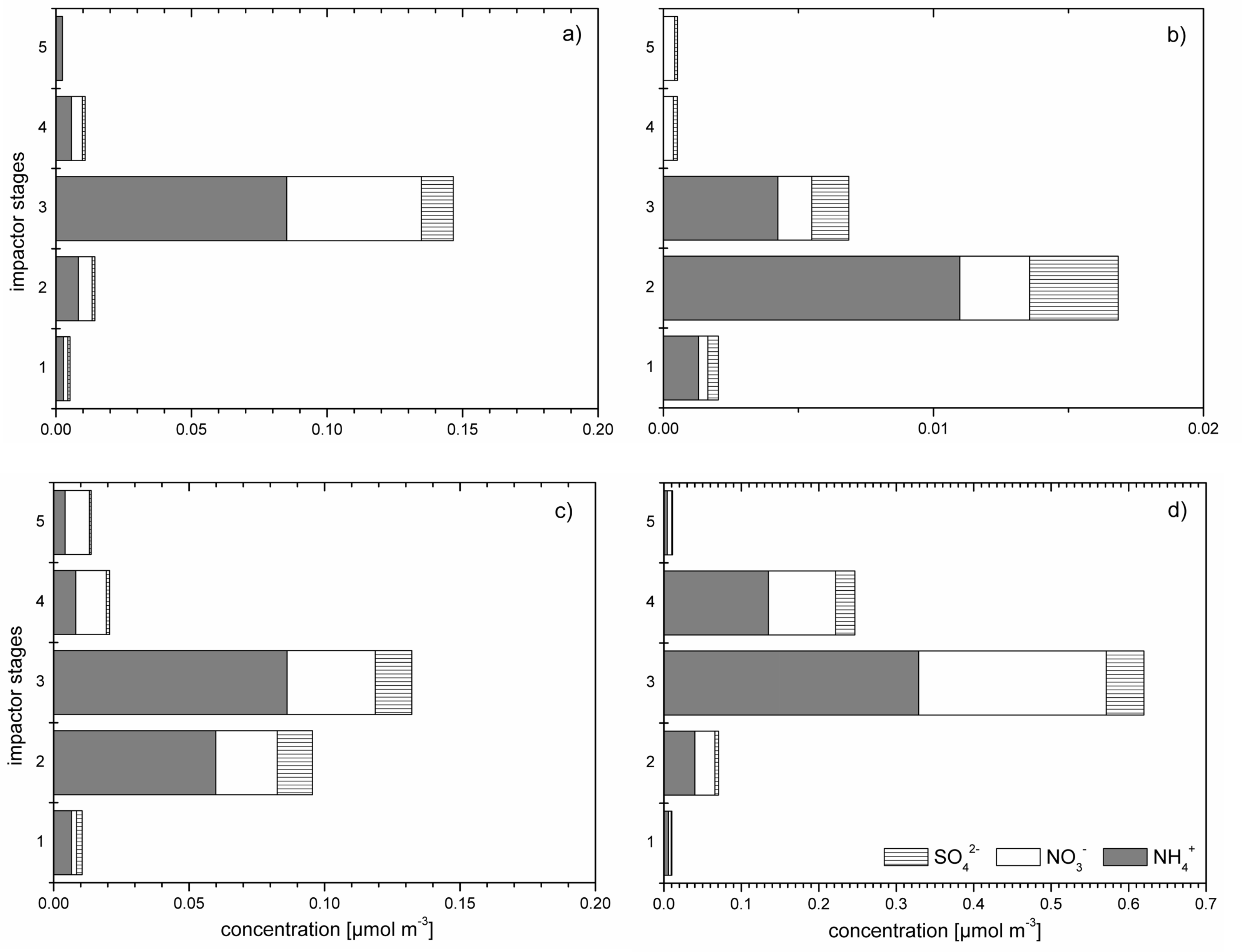

a) day
impactor stages
1
2
3
4
5
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
b) night
impactor stages
1
2
3
4
5
SO_4^{2-}
NO_3^-
NH_4^+
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
concentration [µmol m^{-3}]

Figure 5


a)
b)
c)
d)
impactor stages
impactor stages
5
4
3
2
1
0.00
0.05
0.10
0.15
0.20
0.00
0.01
0.02
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
concentration [µmol m^{-3}]
concentration [µmol m^{-3}]
SO_4^{2-}
NO_3^-
NH_4^+