REPORT

EMEP Intensive Measurement Periods 2008/09 at Råö

(Paper presented at the 10th TFMM meeting in Paris, 15-17 June 2009)

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Report Summary

Project title

Intensivmätningar av gas-partikelfördelning för oorganiska komponenter inom EMEP

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EMEP Intensive Measurement Periods 2008/09 at Råö. Paper presented at the 10th TFMM meeting in Paris, 15-17 June 2009

Summary

IVL has participated in the intensive measurement periods 2008/2009 within EMEP by performing denuder measurements of NH_3/NH_4^+ and HNO_3/NO_3^- on a 24 h basis. Measurements were performed at Råö on the Swedish west-coast. In earlier investigations the denuder for HNO_3/NO_3^- was coated with carbonate in order to also obtain the SO_2 concentration. A small positive interference in the HNO_3 determination from other oxidized nitrogen compounds can then occur. To avoid that interference the denuder was coated with chloride instead of carbonate.

The EMEP station Råö is performing filter pack sampling since 1986. Since the filter pack results are reported as gas and particle phases separately, the results from the denuder measurements were compared to the filter pack results. The total (gas + particle) concentrations agreed very well between the two sampling techniques. However, the filter pack overestimated the ammonia concentration and underestimated the particulate ammonium concentration. The filter pack was surprisingly good at separating gaseous nitric acid from particulate nitrate.

Keyword

Ammonia, Nitric acid, Denuder, Filter pack

Bibliographic data

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1 Introduction

The EMEP Task Force on Measurements and Modelling (TFMM) has recommended repeating earlier intensive measurement periods during two contrasting measurements periods in 2008/09. The first campaign was set to 17 September 06:00 GMT to 17 October 06:00 GMT 2008 and the second one 25 February 06:00 GMT to 27 March 06:00 GMT 2009. EMEP has presented a "wish list" of monitoring activities containing 11 items for these two periods. IVL got funding from the Swedish EPA for one item on this list "More sites with concomitant measurements of inorganic gas concentrations (HNO_3, NH_3, HCl, SO_2), with particular emphasis on HNO_3 and NH_3".

Very few denuder measurements have been carried out in Sweden. HNO_3/NO_3^- was, however, measured during one year 1981/82 (Ferm *et al.*, 1984) at Rörvik, the earlier EMEP site is very close to Råö. In connection with an intercomparison both NH_3/NH_4^+ and HNO_3/NO_3^- was measured at Rörvik in 1984 (Ferm 1986a). The results were evaluated with respect to formation of ammonium nitrate as well as scavenging ratios for precipitation. Ammonium nitrate formation was also studied 60 km from the coast (east of Gothenburg) at a forest site (Ferm 1992 and Ferm 1993).

2 Experimental

Sampling was made at the EMEP station Råö (57º 23.62' N, 11º 54.85' E), see Fig. 1.

Ammonia was sampled using a 50 cm long cylindrical denuder made of Pyrex glass (Ferm, 1979). 35 cm of the denuder was coated with 1 % citric acid in acetone. Behind the denuder a filter holder was attached with a 25 mm cellulose filter impregnated with the same solution as the denuder. The air flow was 2.1 l/min.

Nitric acid was sampled was sampled with a cylindrical denuder made of sodium glass (Ferm 1986b). Instead of using a carbonate coating, sodium chloride was used. Interference from nitrous acid (HNO_2) and nitrogen dioxide is avoided with sodium chloride coating (Allegrini *et al.*, 1987). This denuder was also 50 cm long with an uncoated inlet of 15 cm that was also leached and analysed. Behind the denuder a 25 mm cellulose filter was impregnated with sodium chloride. The air flow was 1.2 l/min.

The denuders were mounted in a plastic box covered on the outside with aluminium foil. In the bottom an aluminium plat with a 100 W heat source (electric resistant) was mounted, see Fig. 2. This increases the air temperature in the box with ca 5 ºC. The inlets of the denuders are protected from rain by 50 mm funnels turned upside down and slipped over the denuders. The inlets were at the same level as the wide end of the funnel in order to avoid HNO_3 losses.

These two denuders have been developed at IVL and have earlier participated in two denuder intercomparisons with good results. One intercomparison was organised for nitric acid/nitrate (Allegrini *et al.*, 1988 and Febo *et al.*, 1993) and one for ammonia/ammonium (Allegrini *et al.*, 1990).

In parallel with these measurements, filter packs were used to measure the total (gas + particle) concentrations of ammonia and nitric acid. This method has been in use at Rörvik/Råö since 1986. The filter pack consists of three filters in series. The first is a Teflon filter (Zefluor) to remove particulate matter. The second filter (cellulose) is impregnated with potassium hydroxide and

glycerine. Denuders and filter packs have earlier been compared to one another with good result (Ferm *et al.*, 1988). From 2009 Na^+, Mg^{2+}, K^+ and Ca^{2+} will also be measured on the particle filter and Cl^- on the second filter (representing HCl). All 24h measurements are carried out from 06:00 GMT at Råö, similar to all other EMEP sites.

Figure 1. EMEP station at Råö with boxes for NH_3/NH_4^+ and HNO_3/NO_3^-. The filter packs as well as samplers for PM_{10} and $PM_{2.5}$ can also be seen on the photo.

Figure 2. Heated box with 8 denuders and impregnated filters.

2.1 Calculation of concentrations

The sampling efficiency of the denuders increases with length of denuder and decreases with sampling flow. The concentration of gas that is not trapped inside the denuder is trapped in the impregnated particle filter. A correction for this was therefore made. The sampling efficiency, η for NH3 was 94 % at the flow and length used. If the amounts in μg N are denoted m, and the air volume in m3, V, the following two equations can be used,

$$[NH_3] = \frac{m_{NH_3}}{V \cdot \eta} \quad (1)$$

$$[NH_4^+] = \frac{m_{NH_4^+}}{V} - [NH_3] \cdot (1 - \eta) \quad (2)$$

Analogously with the ammonia denuder, corrections were also made for the nitric acid denuder. An efficiency of 94 % was also used for the calculation of HNO_3/NO_3^- concentrations.

3 Results

The results from the denuder measurements are presented in Table 1 and 2 in the appendix.

3.1 Quality control

Neither the denuder technique nor the filter pack sample a well defined aerodynamic size fraction of the particles. Despite this fact, a good agreement of the total (gas + particulate) concentrations obtained with the two techniques has earlier been observed for both NH_3/NH_4^+ and HNO_3/NO_3^- (Ferm *et al.*, 1988). In the earlier study the same coating/impregnation were used in denuders and filter pack. A carbonate coating was used to trap HNO_3 because it also traps SO_2. It has also earlier been found (Ferm 1987)that a positive interference in the HNO_3 denuder occurs when the carbonate coated denuder is used in an urban area with high NO_2 concentrations (11 μg NO_2-N m^{-3}).

In order to avoid this interference, A neutral coating (sodium chloride) instead of basic coating (sodium carbonate) was used in this study.

The total (gas + particulate) concentrations filter pack are plotted against the total concentration obtained with the denuder and impregnated filter. The first period for total ammonium is shown in Fig. 3 and the second period in Fig. 4. The correlation coefficients are high and the slope close to 1.

The sodium chloride coated denuder was compared to the filter pack (carbonate impregnated). During the first period, the average NO_2 concentration was 1.0 μg NO_2-N m^{-3} and during the second, 1.3 μg NO_2-N m^{-3}. The first period for total nitrate is shown in Fig. 5 and the second period in Fig. 6. The correlation coefficients are high and the slope close to 1.

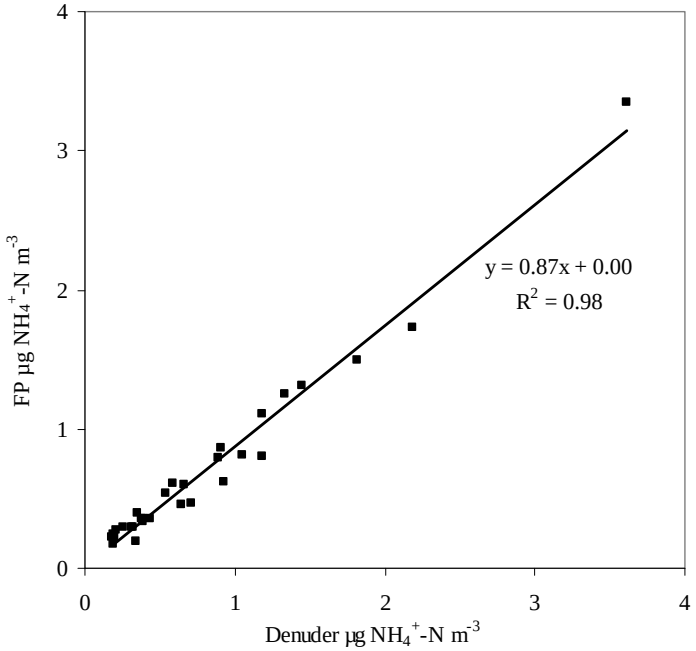

Figure 3. Total NH_4^+ measured with filter pack as a function of the same parameter measured with denuder + impregnated filter during the first campaign (Sept – Oct. 2008).

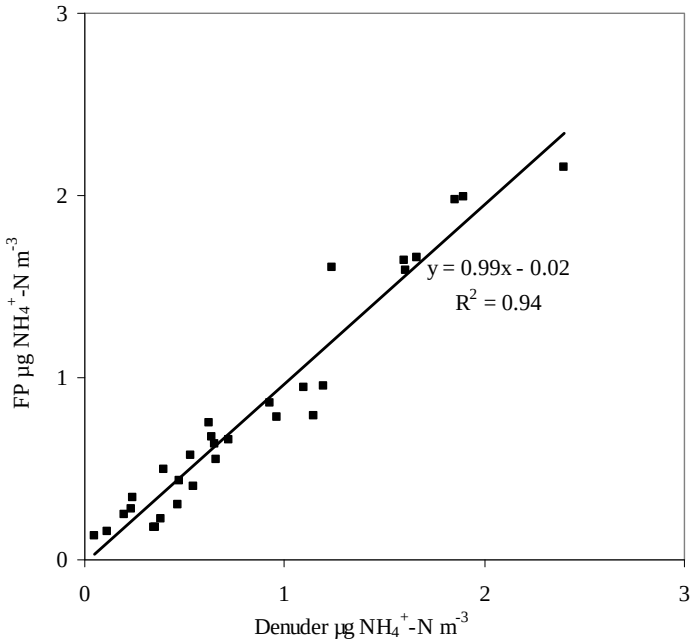

Figure 4. Total NH_4^+ measured with filter pack as a function of the same parameter measured with denuder + impregnated filter during the second campaign (Feb – March 2009).

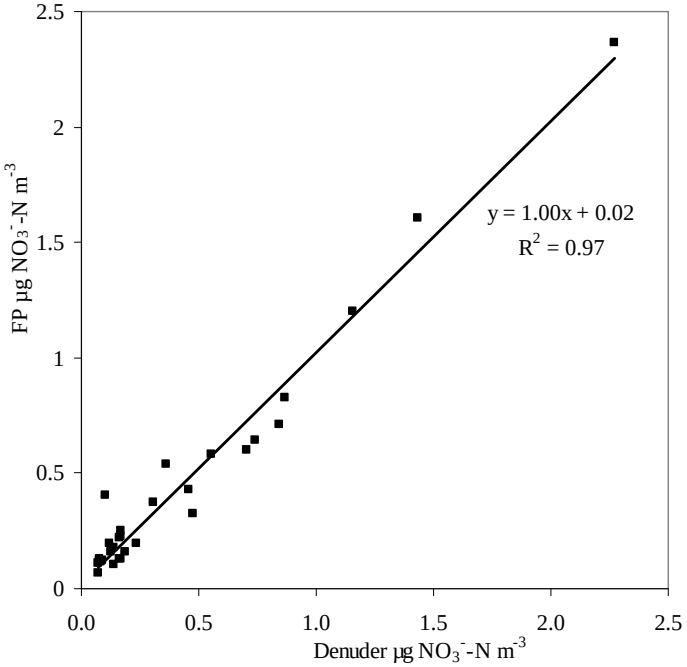

Figure 5. Total NO_3^- measured with filter pack as a function of the same parameter measured with denuder + impregnated filter during the first campaign (Sept – Oct. 2008).

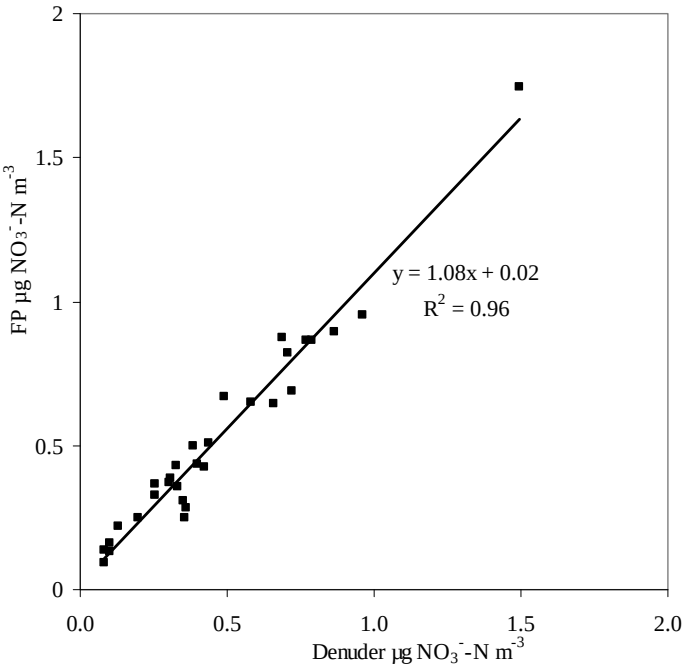

Figure 6. Total NO_3^- measured with filter pack as a function of the same parameter measured with denuder + impregnated filter during the second campaign (Feb – March 2009).

3.2 Concentration variation with time

For ammonium as well as for nitrate, the gaseous concentrations were lower than the particulate. 20 % of the total ammonium concentration was gaseous in the first period and 10 % in the second period, see Fig. 7 and 8.

For total nitrate 18 % was gaseous in the first period and 18 % in the second period see Fig. 9 and 10. The highest total concentration occurred on October 13 for both ammonium and nitrate.

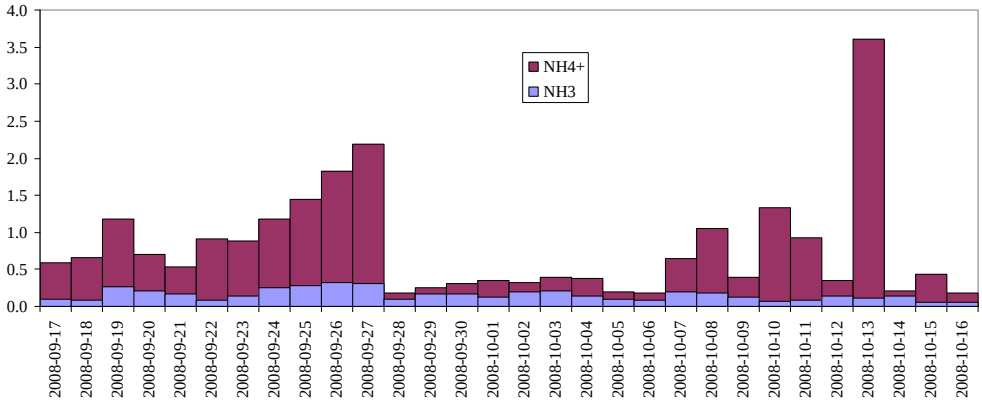

Figure 7. Gaseous NH_3 and particulate NH_4^+ measured with denuders during the first campaign (Sept – Oct. 2008).

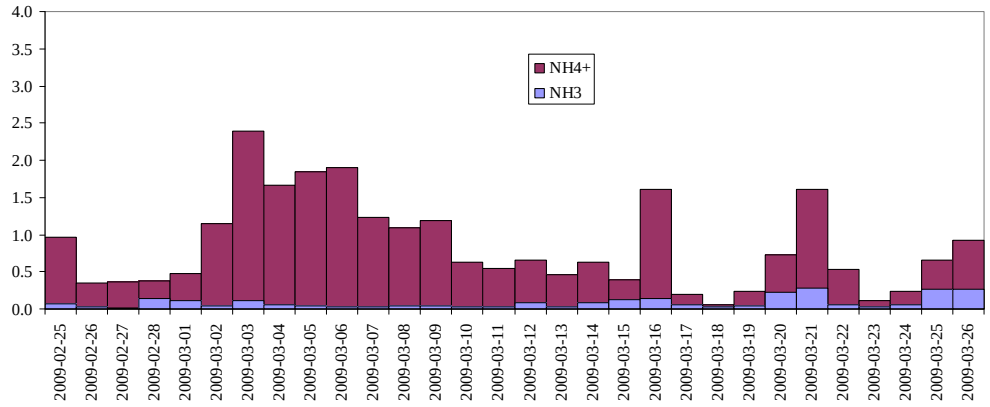

Figure 8. Gaseous NH_3 and particulate NH_4^+ measured with denuders during the second campaign (Feb – March 2009).

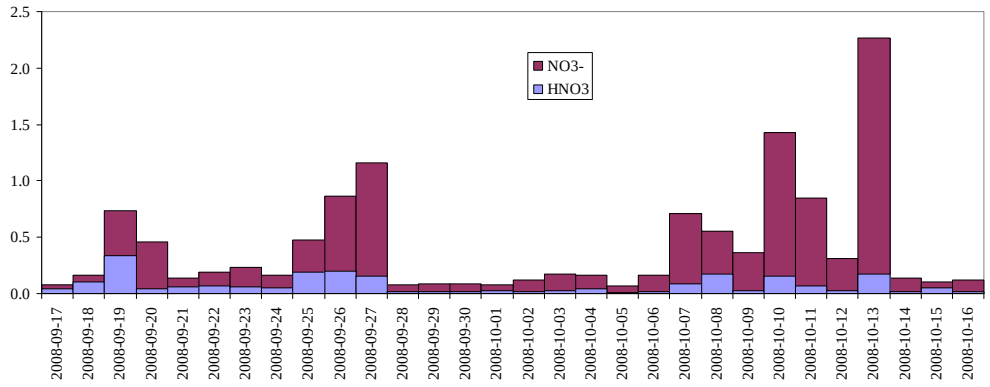

Figure 9. Gaseous HNO_3 and particulate NO_3^- measured with denuders during the first campaign (Sept – Oct. 2008).

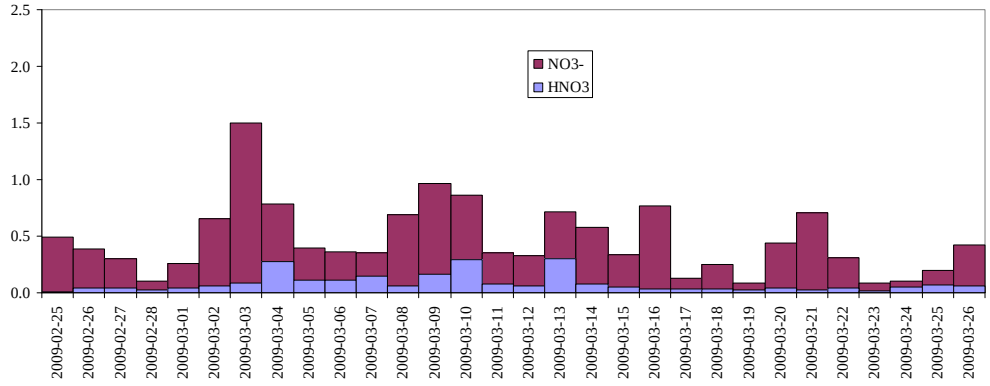

Figure 10. Gaseous HNO_3 and particulate NO_3^- measured with denuders during the second campaign (Feb – March 2009).

3.3 Quality of gas/particle partitioning as measured with filter pack

The ammonia denuder was developed to prevent acidic particles from being neutralized by ammonia on the filter and thereby give an underestimation of the concentration. When the first ammonia denuder was developed, the opposite phenomenon was observed (Ferm 1979). The particles collected on the filter released ammonia probably due to the pressure drop across the filter. This is also seen here in Fig. 11 and 12. If the ammonia concentration is overestimated with the filter pack, the particulate ammonium concentration must be underestimated. This can be seen in Figures 13 and 14. The relative error of the underestimation of the particulate fraction is, however, rather small since the gaseous fraction is much smaller than the particulate one.

The separation of gas and particle phases by the filter pack is, however, fairly good for HNO_3/NO_3^-, see Figures 15 - 18.

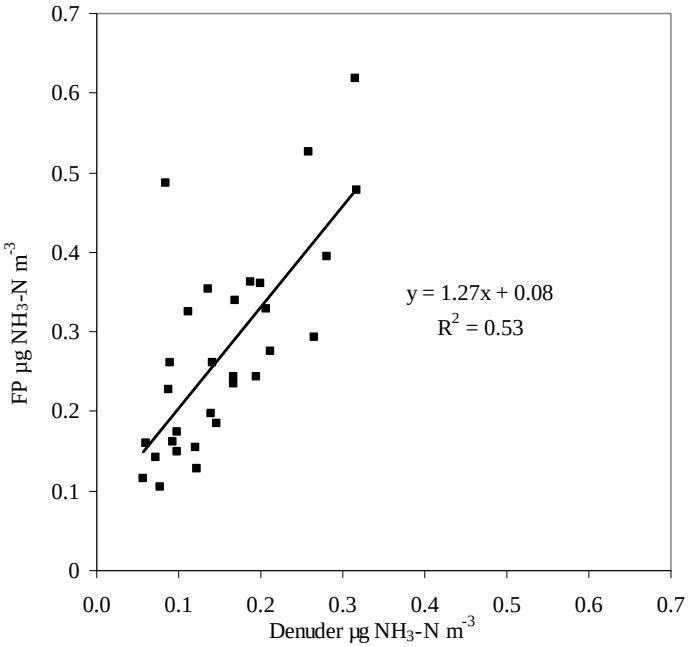

Figure 11. Gaseous NH_3 concentration measured with the filter pack as a function of the same fraction measured with the denuder during the first measurement period (Sept – Oct. 2008).

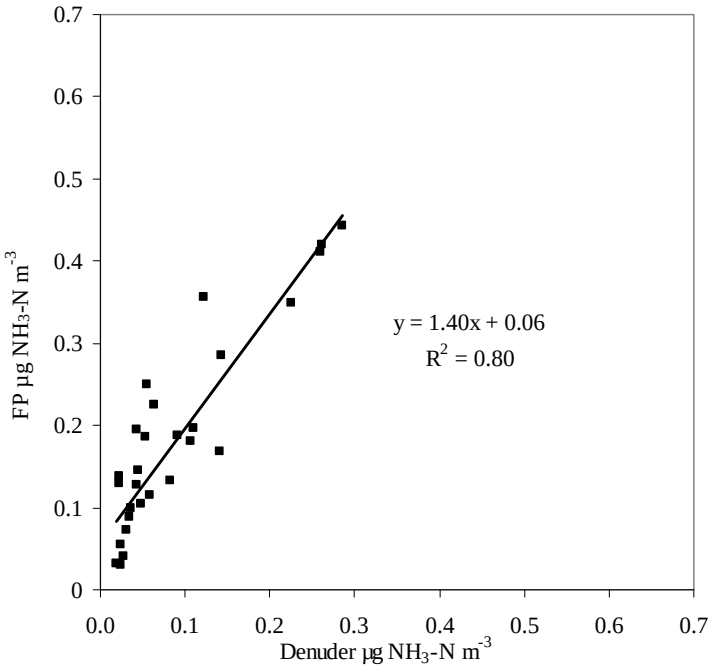

Figure 12. Gaseous NH_3 concentration measured with the filter pack as a function of the same fraction measured with the denuder during the second measurement period (Feb – March 2009).

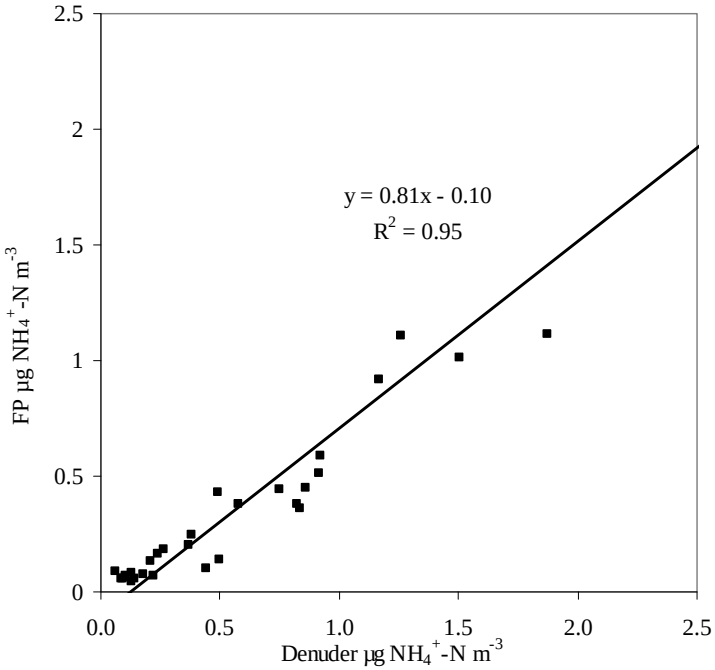

Figure 13. Particulate NH_4^+ concentration measured with the filter pack as a function of the same fraction measured behind the denuder during the first measurement period (Sept – Oct. 2008).

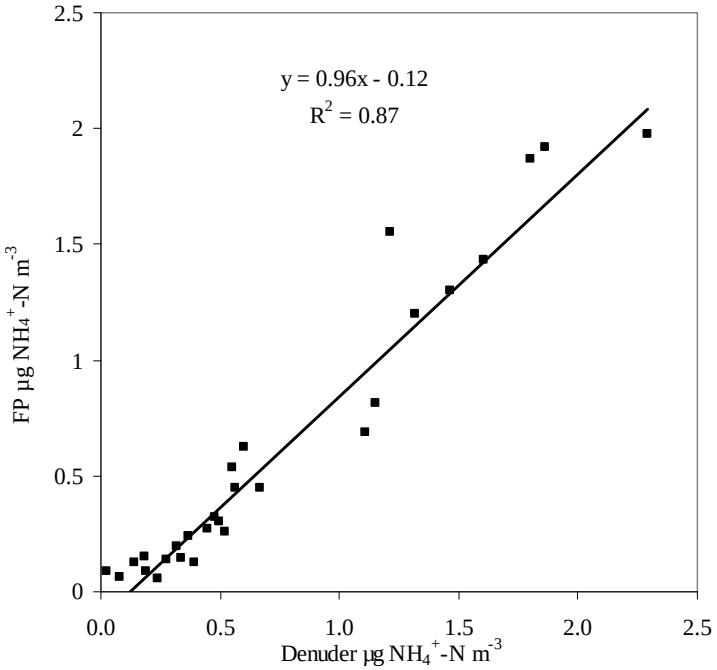

Figure 14. Particulate NH_4^+ concentration measured with the filter pack as a function of the same fraction measured behind the denuder during the second measurement period (Feb – March 2009).

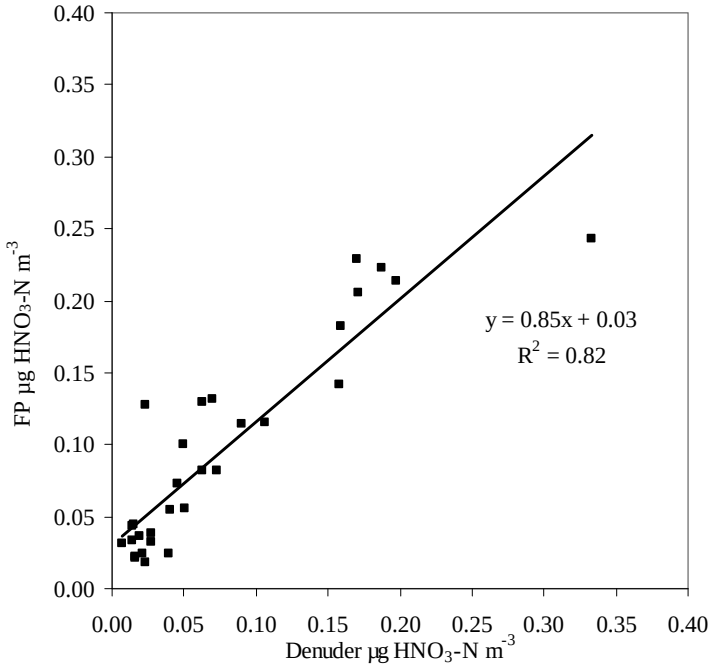

Figure 15. Gaseous HNO_3 concentration measured with the filter pack as a function of the same fraction measured with the denuder during the first measurement period (Sept – Oct. 2008).

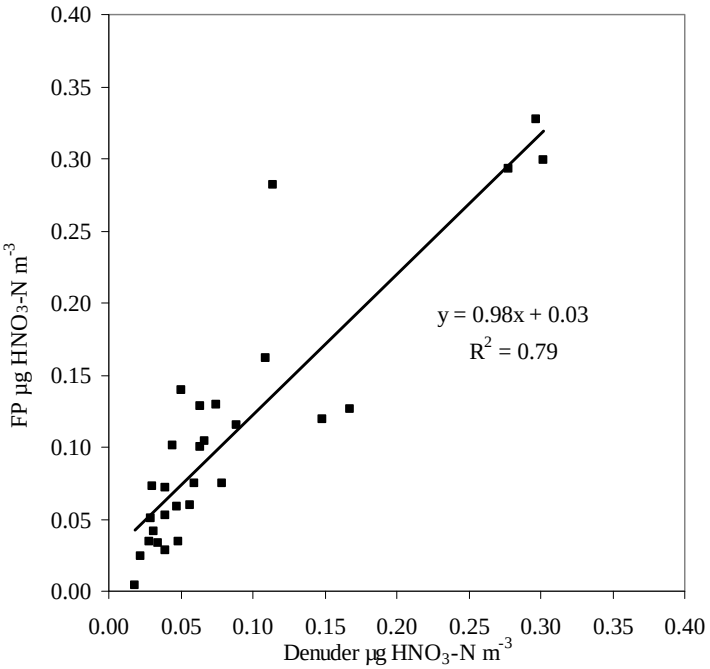

Figure 16. Gaseous HNO_3 concentration measured with the filter pack as a function of the same fraction measured with the denuder during the second measurement period (Feb – March 2009).

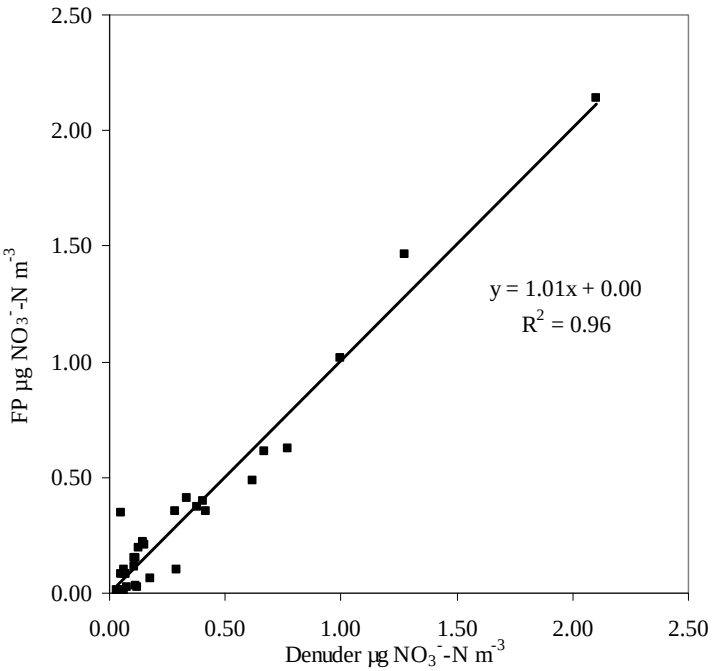

Figure 17. Particulate NO_3^- concentration measured with the filter pack as a function of the same fraction measured behind the denuder during the first measurement period (Sept – Oct. 2008).

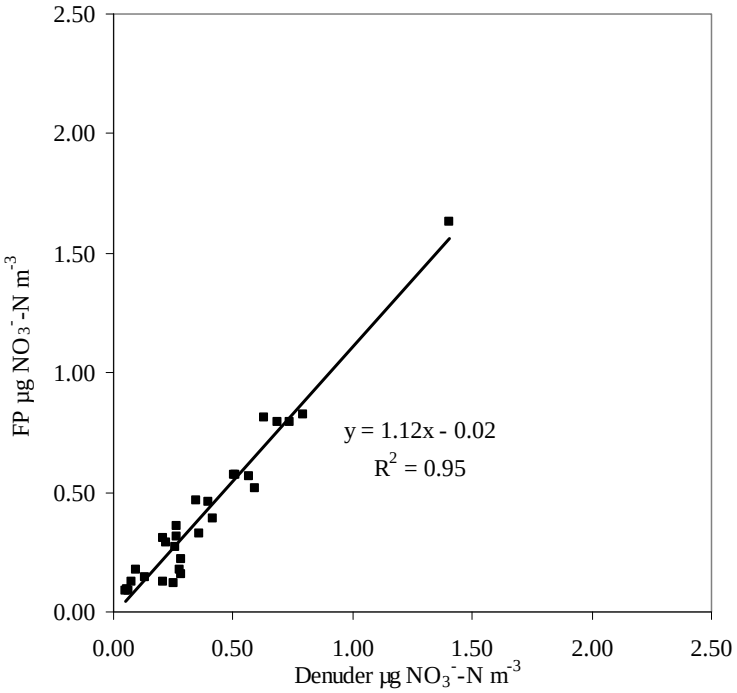

Figure 18. Particulate NO_3^- concentration measured with the filter pack as a function of the same fraction measured behind the denuder during the second measurement period (Feb – March 2009).

4 Conclusions

The filter pack method recommended by EMEP gives comparable results for total ammonium and total nitrate to a cylindrical denuder with an impregnated filter mounted behind. The interference caused by the use of carbonate in the filter pack is negligible for the HNO_3 determination at the EMEP station Råö. The filter pack also separates gas and particle phases, but the NH_3 fraction is overestimated and the particulate ammonium concentration underestimated. The filter pack was surprisingly good at separating gaseous nitric acid from particulate nitrate.

5 Acknowledgement

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Table 1. Concentrations obtained by the denuder technique during the first measurement period.

start date	NH_3 µgN/m^3	NH_4^+ µgN/m^3	HNO_3 µgN/m^3	NO_3^- µgN/m^3
det.lim.	0.02	0.05	0.002	0.007
2008-09-17	0.10	0.49	0.04	0.03
2008-09-18	0.09	0.57	0.11	0.06
2008-09-19	0.27	0.92	0.33	0.40
2008-09-20	0.21	0.50	0.05	0.41
2008-09-21	0.17	0.37	0.06	0.07
2008-09-22	0.08	0.82	0.07	0.12
2008-09-23	0.14	0.75	0.06	0.17
2008-09-24	0.26	0.92	0.05	0.11
2008-09-25	0.28	1.17	0.19	0.29
2008-09-26	0.32	1.50	0.20	0.67
2008-09-27	0.32	1.87	0.16	1.00
2008-09-28	0.09	0.09	0.02	0.06
2008-09-29	0.17	0.09	0.01	0.07
2008-09-30	0.17	0.14	0.02	0.07
2008-10-01	0.12	0.22	0.03	0.05
2008-10-02	0.19	0.13	0.01	0.11
2008-10-03	0.21	0.18	0.03	0.14
2008-10-04	0.14	0.24	0.04	0.12
2008-10-05	0.10	0.10	0.01	0.06
2008-10-06	0.08	0.11	0.02	0.15
2008-10-07	0.20	0.44	0.09	0.62
2008-10-08	0.19	0.86	0.17	0.38
2008-10-09	0.12	0.27	0.02	0.34
2008-10-10	0.07	1.26	0.16	1.27
2008-10-11	0.09	0.84	0.07	0.77
2008-10-12	0.14	0.21	0.02	0.29
2008-10-13	0.11	3.50	0.17	2.10
2008-10-14	0.15	0.06	0.02	0.12
2008-10-15	0.06	0.38	0.05	0.05
2008-10-16	0.06	0.13	0.02	0.11

Table 2. Concentrations obtained by the denuder technique during the second measurement period.

start date	NH_3 µgN/m^3	NH_4^+ µgN/m^3	HNO_3 µgN/m^3	NO_3^- µgN/m^3
det.lim.	0.02	0.04	0.002	0.002
2009-02-25	0.07	0.89	0.01	0.48
2009-02-26	0.02	0.32	0.04	0.35
2009-02-27	0.02	0.34	0.04	0.26
2009-02-28	0.14	0.24	0.03	0.07
2009-03-01	0.11	0.36	0.05	0.21
2009-03-02	0.04	1.11	0.06	0.59
2009-03-03	0.11	2.29	0.09	1.41
2009-03-04	0.06	1.60	0.28	0.51
2009-03-05	0.05	1.80	0.11	0.29
2009-03-06	0.03	1.87	0.11	0.25
2009-03-07	0.02	1.21	0.15	0.21
2009-03-08	0.04	1.05	0.06	0.63
2009-03-09	0.05	1.15	0.17	0.79
2009-03-10	0.02	0.60	0.30	0.57
2009-03-11	0.02	0.52	0.07	0.28
2009-03-12	0.09	0.56	0.06	0.27
2009-03-13	0.02	0.44	0.30	0.42
2009-03-14	0.08	0.55	0.08	0.50
2009-03-15	0.12	0.28	0.05	0.28
2009-03-16	0.14	1.46	0.03	0.74
2009-03-17	0.06	0.14	0.03	0.10
2009-03-18	0.03	0.02	0.03	0.22
2009-03-19	0.04	0.19	0.03	0.05
2009-03-20	0.22	0.50	0.04	0.40
2009-03-21	0.28	1.32	0.02	0.68
2009-03-22	0.06	0.48	0.04	0.27
2009-03-23	0.03	0.08	0.02	0.07
2009-03-24	0.05	0.19	0.05	0.05
2009-03-25	0.26	0.40	0.07	0.13
2009-03-26	0.26	0.67	0.06	0.36