

Summary of literature review on measurement of ions in PM_{2.5}

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REPORT

**SUMMARY OF LITERATURE REVIEW ON
MEASUREMENT OF IONS IN PM2.5**

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1. Summary

Directive 2008/50/EC on ambient air quality and Cleaner Air for Europe set limit values for particulate matter PM10 and fine particulate matter PM2.5. The reference measurement methods have already been standardized by CEN, the European Committee for Standardization (EN 12341:1998¹ and EN 14907:2005²). Both methods are currently under revision and will be merged (prEN 12341:2012³).

The Directive also requires the measurement in the PM2.5 fraction of inorganic components (anion and cations) and elemental and organic carbon (EC/OC) with the objective to support air quality assessment and management. In order to ensure better data comparability, validated standard methods for these measurements are equally required.

This report represents the summary of the literature review required for the validation of the method for anions and cations in PM2.5 or more specific the water soluble fraction of nitrate, sulphate, chloride, ammonium, sodium, potassium, calcium and magnesium. Quartz fiber and Teflon filters are considered. Major uncertainty aspects of the method, the inlet system, evaporation from the filter, reactive gas retention, storage, blanks and extraction are reviewed. In addition equivalence with the EMEP method is considered and guidelines for laboratory tests are given.

It is concluded that the contribution of artefacts induced by inlet system, the storage of the filters and the extraction procedure, to the uncertainty of the individual components is negligible. The filter blanks and the retention of precursor gases contribute to a minimum extent to the uncertainty. Blanks (field and laboratory) need to be taken into consideration on a continuous basis. Evaporation leads to considerable uncertainty contribution for nitrate and ammonium, and to a lesser extent for chloride.

Table 1 *Individual sources of uncertainty*

	SO4	NO3	Cl	NH4	Na	K	Ca	Mg
Inlet System	-	-	-	-	-	-	-	-
Evaporation	-	C	M	C	-	-	-	-
Retention	-	M	-	-	-	-	-	-
Storage	-	-	-	-	-	-	-	-
Blanks	-	-	M	-	M	-	M	M
Extraction	-	-	-	-	-	-	-	-
Analysis	NC	NC	NC	NC	NC	NC	NC	NC

C = considerable, M = minimal, - = negligible, NC = not considered

Nitrate is a major component of PM2.5 in terms of mass fraction and exhibits a considerable artifact potential. This potential is due to evaporation of ammonium nitrate (NH₄NO₃) from the filter by changes in the temperature, humidity, timing and precursor gases ammonia and nitric acid. The volatilization may lead in exceptional cases to complete evaporation. Mid and south of Europe are most vulnerable for this artifact. On the other hand overestimation may occur by the substitution of chloride associated with sodium by nitric acid. This effect is less

¹ EN 12341:1998, Air quality – Determination of the PM₁₀ fraction of suspended particulate matter – Reference method and field test procedure to demonstrate reference equivalence of measurement methods

² EN 14907:2005, Ambient air quality – Standard gravimetric measurement method for the determination of the PM_{2.5} mass fraction of suspended particulate matter

³ prEN 12341:2012, Ambient air – Standard gravimetric measurement method for the determination of the PM₁₀ or PM_{2.5} mass concentration of suspended particulate matter

effective in terms of PM_{2.5} mass. The quantity of evaporated or absorbed mass is strongly dependent on start and stop time of the sampling period.

The major fraction of ammonium is associated with nitrate and sulphate. Ammonium sulphate has no vapour pressure and will therefore remain entirely on the filter. Ammonium associated with nitrate may entirely evaporate. It is concluded that ammonium is considerably vulnerable for artefacts but less than nitrate. Furthermore ammonium represents a much smaller PM_{2.5} mass fraction than nitrate.

Chloride is predominantly present as sea salt. Chloride may be substituted by nitrate on filters in polluted coastal areas. This process usually takes place by changing wind directions during sampling. Already collected sea salt chloride being part of marine originated air can get exposed later on to nitric acid being part of polluted continental air mass. In general this effect is very limited for Europe. And most certainly when the effect on the PM_{2.5} mass fraction is considered.

Blanks are considered from two different angles, the anions and cations levels extracted from unused filters and the standard deviations of these levels. Both are of importance concerning the quality of the method. Teflon exhibits very low blank levels for all components, but will not be used for the method because of practical reasons (CEN/TC 264/WG34, document N75). Various quartz fiber brands were tested and showed on average satisfying results. All components when converted into PM_{2.5} concentrations below 0.1 µg/m³, except for Na in Whatman filters (0.5 µg/m³) and Cl in Albet filters (0.2 µg/m³). As the laboratory averaged blank concentration is subtracted from sample result the uncertainty is dependent on the standard deviation of the blank rather than the blank level itself. Considering the standard deviations all components remained below 40 ng/m³. This is sufficient for background areas throughout Europe, even in Finland. Brand related restrictions cannot be made, because brand specific qualities are bound to change in time. Currently the use of Whatman QMA should be discouraged because of the high Na blanks and the uncertainty to what level the water soluble Na per batch may vary.

In conclusion, considering all artefacts only the impact of the loss of nitrate by evaporation is severe and not well understood. Therefore Laboratory tests (Work Package 2) (7) will focus on parameterization of this phenomenon.

Comparison of the standard with the EMEP (SPM) reference method is difficult since the difference in size cut off makes it hard to assess the potential differences. In addition, the Teflon filter used for collecting aerosols in the filterpack method is not necessarily comparable with the single filter PM_{2.5} when it comes to positive and negative bias like evaporating and absorption of gases. These differences are dependent on chemical composition and meteorology, and the comparability between these methods will therefore vary between sites.

2. Scope

This review comprises knowledge on the possible artefacts that can arise when CEN/TR 16269:2011 Guide for the measurement of anions and cations in PM_{2.5} (1) is used. More specific, the determination of the mass of the water soluble of anions

NO₃, SO₄, Cl and the cations NH₄, Na, K, Mg and Ca. The Guide was derived from EN 12341, the gravimetric method for PM_{2.5}. EN 12341 offers already an uncertainty assessment for the PM_{2.5} mass determination. The method for ions is divided into 3 main parts: the sampling, the storage and the analytical procedure in the laboratory. The analytical procedure is basically covered by the required accreditation and tested by Statistical Evaluation (Work Package 4) (7). Artefacts caused by blank filters and the extraction efficiency of water soluble ions are considered in this review. The filter weighing procedure and the calibration of physical measuring devices such as flow rate meters and temperature sensors are dealt with in EN 12341 and therefore not considered as part of this review. More details on this can be found in Field Validation Report of EN 14907 (3). In order to narrow down the field of interest here the investigated filter material is limited to Teflon and quartz fiber. The concentration range of the standard (3) is set to 1 to 120 µg/m³ mass PM_{2.5}. Priority given to the concerned anions and cations will be dominated by the mass fraction that the ion represents regarding European PM_{2.5} concentrations. The final report of COST Action 633 (6) is considered as a useful document in this respect. The application is limited to the area of the EU member states.

An assessment of the impact of expected artefacts is made, the impact to the objective of the standard. The main objective (7) is to ensure that adequate information is made available on levels in the background. This information is essential to judge the enhanced levels in more polluted areas, assess the possible contribution from long-range transport of air pollutants, support source apportionment analysis and for the understanding of specific pollutants. It is also essential for the increased use of modeling in urban areas.

The method for ions has to be developed in harmonization with CEN/TC264/WG35 (developing a similar method for organic and elemental carbon) and EMEP (5). The European Monitoring and Evaluation Program (EMEP) is a scientifically based and policy driven program under the Convention on Long-range Transboundary Air Pollution (CLRTAP) for international co-operation to solve transboundary air pollution problems. The EMEP monitoring network consists of about hundred rural sites measuring chemical composition in rain and aerosols in Europe, including several countries beyond the EU members states. The monitoring obligations are defined by the EMEP Monitoring strategy (UNECE,2009). A comparison between the method and the EMEP procedure is made.

3. Terms and definitions

For the purposes of the review, the following terms and definitions apply.

- Ambient Air – outdoor air in the troposphere excluding workplace air (2)
- High Volume Sampling Method, HVS – method for sampling particulate matter with a flow rate of 30 m³/h (2)
- Low Volume Sampling Method, LVS – method for sampling particulate matter with a flow rate of 2.3 m³/h (2)
- PM2.5 – fraction of suspended matter which passes through a size-selective inlet with a 50% cut-off efficiency at 2.5 µm aerodynamic diameter (2)
- PM10 – fraction of suspended matter which passes through a size-selective inlet with a 50% cut-off efficiency at 10 µm aerodynamic diameter (2)
- Suspended particulate matter SPM – notion of all particles surrounded by air in a given, undisturbed volume of air (2)

Other abbreviations:

- EMEP – Co-operative program for monitoring and evaluation of the long range transmission of air pollutants in Europe

4. Artefacts

Artefacts can be induced by the inlet system, the storage and extraction procedure of the filters. The filter blanks and the retention of precursor gases may also contribute to the uncertainty in the actual concentration of the collected components. We first consider the artifacts induced by the sampling and the effect that the inlet can have on the stability of the PM collected on the filter

4.1 Inlet System

The sampling is done according to the standard method described in EN 12341. This method involves (for both LVS and HVS) an inlet design, connecting pipework, filter holder and filter, sampling period, and maintenance of the sampling system. EN 12341 sets out the criteria for the inlet system.

- The temperature of the connecting pipe work shall be kept as close to the ambient temperature as possible in order to avoid contact of the sampled air with cold surfaces which could cause condensation, for instance by flowing a sheath of ambient air around the pipe work.
- The pipework shall have no bends and be vertical.
- The length of the connecting pipework shall be no longer than 3m.
- The pipe work shall be made of inert, non-corroding, electrically conducting material such as stainless steel or anodized aluminum.
- The pipe work shall be designed to minimize the effect of solar heating so that the air sample is kept as close as possible to ambient temperature.

Even when these criteria are met artefacts affecting the determination of ions can be expected. For example, before collection on the filter, air containing PM2.5 particles as well as precursor gases like HNO₃, hydrochloric acid, sulfur dioxide and NH₃ travel from the inlet to the filter through the pipe work. The reactive gases are in equilibrium with PM2.5 ions (4). Both PM2.5 and the precursor gasses may react with wall material (cut off outlet, connecting pipe work and filter holder inlet). The particles and surrounded air can get disturbed. The definition of SPM may therefore not be valid anymore. Furthermore temperature deviations change the heterogeneous equilibria. Kinetic, thermal and electrostatic process may lead to impaction of PM2.5 subfractions.

Are these effects significant for the determination of the individual ions? EN 12341 expects losses due to premature PM2.5 impaction to be less than 0.1%. With the flow rates (1.1 m/s for LVS and 0.6 m/s for HVS) and ambient temperature range (-10 °C to 40 °C) the Particle Reynolds Number (9) remains just below 0.1, threshold for laminar flow conditions. Diffusion losses per size fraction vary. As also the composition differs per size fraction, it may affect the individual ion concentrations. Mineral dust and sea salt are usually found in the fraction above 1 micron whereas NH₄ salts (NO₃ and SO₄) are more abundant below 1 micron (6). The losses under the described condition are however less than 0.1% (9) for particles larger than 0.1 micron making this artifact negligible for both sampler types.

In 2011 Weijers et al. (10 and Annex B) investigated these artefacts by determination with an hourly time resolution of the composition of the original ambient air simultaneous with the air behind the filter. Measurements were carried out with a MARGA2S (47) (detection limit 0.1 µg/m³) for the PM ions and the precursor gases. During periods without a filter in the holder no significant wall effects on the composition in the passing air were observed. Actually the concentrations for HCl and HNO₃ appeared to increase marginally. The tests were performed with a Leckel LVS.

Komazaki (11) investigated transmittance losses of hydrochloric and HNO₃ in stainless steel tubing. Approximately 80% of HNO₃ and 70% of HCl was lost. The test was carried out with a flow rate of 1 l/min and tubing of 1.5 m length and 3 mm i.d. representing laminar flow conditions. Regarding the residence time the chance for a gas

molecule to impact on the wall is 50 times higher in Komazaki's set up compared to the standard reducing the loss for standard to about 1%.

The concentration of the precursor gases may be reduced, the reduction is zero at the entrance and the largest just before the filter surface. Taking into account that the evaporation of gases from the particle surface is a matter of minutes rather than seconds (12), it is concluded that the loss of reactive gases on the wall of the connecting pipe work will not disturb the composition of the PM_{2.5} mass collected on the filter significantly.

4.2 Filter Sampling

During sampling chemical reactions may affect the levels of the already sampled particulate matter. The complex matrix here comprises: increasing load of PM, exposure to changing concentrations of precursor gases, retention or reactions with the filter material, liquid water, water vapor and temperature effects.

The standard EN 12341 recognizes this artifact stating that substantial fractions of PM_{2.5} can be composed of semi-volatile components, which can volatilize at any time between entry to the sample and weighing of the loaded filter, at a rate predominantly determined by the temperature in the system. Losses of semi-volatile material are expected when the European Standard is followed and the loss may differ between the different location, day and SM values. However, the definition of PM_{2.5} for the purpose of the European Standard incorporates these losses. Therefore, average effect of volatilization losses on the measurement of PM_{2.5} is considered to be zero by convention, when the constraints in the European Standard are followed.

The main objectives (7) however for the determination of ions in PM_{2.5} are to ensure that adequate information is made available on levels in the background. This information is essential to judge the enhanced levels in more polluted areas, assess the possible contribution from long-range transport of air pollutants, support source apportionment analysis and for the understanding of specific pollutants. It is also essential for the increased use of modeling also in urban areas.

Obviously, it is essential to assess the deviation between the concentrations of PM_{2.5} ions measured according to the European Standard and those actually present in ambient air. This issue was already addressed by the AEROSOL-community in Eurotrac (13) in the measurement of PM₁₀. Laboratory and field campaigns were conducted to quantify various influencing processes leading to a series of papers published in 2004 in a special issue of Atmospheric Environment and referred to in this report.

4.2.1 Evaporation

4.2.1.1 Ammonium nitrate

Sampled NH₄ NO₃ (being one of the major components of PM_{2.5} (6)) may evaporate from the filter during sampling. This phenomenon is observed by many researchers (e.g. 18, 19, 20, 33). Evaporation can occur when it becomes unstable due to e.g. changing ambient conditions during sampling, differences between ambient conditions and those inside the sampler or a pressure drop over the filter (pack). This artifact was investigated by Schaap et al. (17) for European conditions as part of the INTERCOMP2000 campaign (13). Field and laboratory tests were conducted to investigate the artifact under various conditions and with a wide range of filter types. A main conclusion from this study is that under European conditions quartz fiber is a suitable filter material for sampling NO₃ as long as the temperature does not exceed 20 °C during sampling. Cellulose-type filters quantitatively collect aerosol NO₃ and HNO₃, but negligible amounts of nitrous acid. Teflon filters were more vulnerable for evaporation losses than quartz. Indications for losses from Teflon below 10 °C (at the field campaign Melpitz, Germany) were not obtained, probably due to the high relative humidity.

Hering et al. (20) investigated the evaporation effect of NH₄ NO₃ from Teflon filters as a function of temperature and of reduced HNO₃ and NH₃ concentrations as well as combinations of these parameters. Derived implication for US standard (back in 1999) was a yearly average loss of 30% for PM_{2.5}.

Keck et al (28) conducted a 10-month test period with cellulose acetate- NO₃ (CA), quartz fiber (QF), Teflon (Tf) and glass fiber (GF) filters to collect 19 ambient PM_{2.5} aerosol samples at mean temperatures between -1 °C and 25 °C. For comparison measurements were also carried out using a denuder filter system. At mean temperatures below 0 °C, CA, QF and Tf filters were found to properly collect particulate NH₄, NO₃ and Cl. Above 0 °C the salts were already lost from QF and Tf, more so the higher the temperature and with no significant difference between QF and Tf. The salts were lost completely from denuded QF filters above 20 °C and from undenuded QF and Tf filters above about 25 °C. In contrast, the losses from CA filters were negligible or small up to 25 °C, but positive artefacts due to gas retention could occur at high concentrations of HNO₃ and NH₃. With the exception of GF, the filter face velocity had no significant effect on the measured PM concentrations on front filters. Keck et al concluded that without additional means, inert QF and Tf filters are not suited for routine sampling of particulate NH₄ NO₃ and Cl at temperatures exceeding ~0 °C. It was noted that the observed losses at low temperatures were significantly higher than reported by other groups (17, 19). Two reasons were suggested. First, the employed QF filters (QF20 Scheicher & Schuell) by Keck feature a very low retention efficiency for HNO₃. In contrast the QF filters (Munktell MK 360 and Pallflex) used by (17,19) exhibiting a significant retention for HNO₃. Secondly Keck sampled 24h from afternoon to afternoon whereas other researchers sample from morning to morning leading to additional losses by Keck's sampling protocol (see chapter Time of Sampling).

More recently Vecchi et al (37) conducted a field study in Milan (Po-valley). Artefacts for both organic and inorganic matter were observed. Results showed that positive artefacts due to organic carbon adsorption on quartz filters accounted for 39% of the OC measured concentration in summer and 23% in winter. Negative artifact due to NO₃ volatilization by the filters was 51% on Teflon and 22% on quartz filters in summer and no or negligible losses were observed in the winter. Vecchi used Pall Teflon and quartz filters. This study was devoted to PM₁₀.

Wieprecht et. al. (8) noticed that PTFE filters are very thin and an electrostatic charge build-up can result in loss of coarse particles during transport. They recommend quartz for routine sampling.

Finally, in 2012 Weijers et al (10) investigated the artefacts associated with PM₁₀ filter sampling in the Netherlands at a rural background station. The novelty was the high time resolution measurement of the volatile species before and behind the filter (Quartz, Whatman QMA). This experiment visualized the effects of temperature, humidity, cNH₃, cHNO₃ and cHCl on the evaporation rate. The tests were conducted with a Leckel and a MARGA-2S. See Annex B for the details. Main conclusions drawn were that despite the statement of the manufacturer losses of NO₃ and Cl were seen. In the long term (i.e., for a yearly average) the effect on PM mass appears to be limited. For the measurement period of one month the average loss of NH₄ NO₃ was less than 0.5 µg/m³. On a daily basis the loss of mass can be substantial. It was found that the evaporation of NO₃ varied between 0.8 and 1.8 µg/m³ even on days with moderate temperatures, for example at 20 °C.

Though the evaporation velocity of NH₄NO₃ is a function (4) of temperature, humidity, cNH₃xCHNO₃ and Y (the SO₄ fraction) researchers do not keep track of these parameters for individual samples making it hard to derive the magnitude of losses.

The optimum method to collect NH₄ NO₃ is to stabilize it after collection against evaporation, by impregnating filters with a reagent or to use a reactive type of filter. However, such substrates also collect gaseous HNO₃. Gas-denuders are therefore applied to remove the interfering HNO₃. Over thirty years of experience has shown that these denuder filter combinations are very suitable for aerosol NO₃ collection (35). However, applying such relatively complicated systems is expensive and labor intensive (36). At the EMEP sites in Montelibretti in Italy, CNR performs continuous measurements using the reference EMEP method using denuders. During the EMEP intensive monitoring campaigns in June 2006 and January 2007 (45), the fine and coarse fraction from denuder measurements were compared with speciation in PM₁₀ and PM_{2.5}. Sulfate shows very small difference between these methods and most of the sulfate is in the fine fraction in both winter and summer. For NO₃ and NH₄ on the other hand, there are substantial differences, i.e NO₃ is more than 2 and 5 times higher in the fine fraction using denuders compared to PM_{2.5} in summer and winter respectively; for NH₄ the differences are 1.3 and 3 times higher. In the same campaign, speciation from gravimetric PM₁ measurements at Payern in Switzerland were compared to measurements with an Aerosol Mass Spectrometer (AMS) also showing clearly a loss of NH₄NO₃ (45).

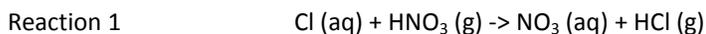
To overcome sampling artefacts and the coarse temporal resolution associated with filters the Steam Jet Aerosol Collector (SJAC) has been devised (33), which enables to sample and analyse the inorganic aerosol composition as well as the gas phase on an hourly basis. The sampling of aerosols is based on droplet formation. After passage through a wetted annular denuder stripping the NH_3 and HNO_3 , steam is injected in the air. Due to the super saturation the aerosols will grow to droplets, which are subsequently removed from the air by a cyclone. The resulting sample solutions are analyzed for their ion concentrations (36). This system (MARGA) has been extensively tested and approved by the US EPA (47) and applied by CASTnet (48).

4.2.1.2 Ammonium chloride

NH_4Cl may exist in ambient air as part of particulate matter, though it can hardly be formed by the nucleation reaction between NH_3 and HCl (4). Even though Pio et al. (15) derived an equilibrium constant of $K = 1.5 \text{ ppb}^2$, suggesting that it is likely that NH_4Cl aerosol exists at temperatures below 10°C in the accumulation mode depending on concentration levels of NH_3 and HCl . Du et al (16) demonstrated significant levels of NH_4Cl with on line instrumentation (MARGA) in the city of Shanghai with K going up to 10 ppb^2 at 26°C . Apart from other sources HCl may well be generated by the depletion of sea salt aerosol in marine air by HNO_3 explaining the covariance of both acids in diurnal patterns (personal observations). NH_4Cl is likely to be present in NW Europe (significant levels of NH_3 , HNO_3 and sea salt) in the winter season at night times in aged marine air. Evaporation from the filter material may well take place according to the mechanisms described for NH_4NO_3 .

4.2.1.3 Chloride substitution by nitrate

Sea salt (mainly NaCl) is usually present in coastal areas. It is a remainder of sea spray and is dominantly found in the coarse aerosol mode $\text{PM}_{10}\text{-PM}_{2.5}$. For example in the Netherlands: 69% (25). While collected on the filter the Cl may be substituted by the NO_3 of HNO_3 leading to evaporation of hydrochloric acid.



At 25°C Reaction 1 has an equilibrium constant of 1.27 (27). The reaction is sensitive to the relative humidity when observed in ambient air. The outgassing of HCl is slightly favored at high humidity and greatly favored at lower humidity (26).

Weijers et al. (10) investigated the sea salt depletion during PM_{10} filter sampling in the Netherlands at a rural background station. The tests were conducted with a Leckel and a MARGA-2S. A near-complete loss of Cl (more than 70%) occurred on 6 days (out of 21). See Annex 2 for the details.

For Cl in $\text{PM}_{2.5}$ this effect may be significant, for NO_3 in $\text{PM}_{2.5}$ it is almost negligible as NO_3 is mainly present as NH_4NO_3 .

4.2.1.4 Time of Sampling

In the standard for the determination of mass $\text{PM}_{2.5}$ (2) the requirement is 24 ± 1 hour sampling with an accuracy of 5%. The starting time of the sampling is not regulated. Daily practice is to sample from midnight to midnight when automatic samplers are applied. For most EMEP sites the daily sampling starts at 08:00 local time because of the importance of similar measurement period as the co-located precipitation collector and the fact that the sampling has been done manually for many years. Now when many of the precipitation collectors and air samplers are getting automatic, there are several EMEP sites which measure from midnight to midnight (29). In the US CASTNET weeklong samples are collected. They are exchanged every Tuesday morning around 9:00. For IMPROVE, two 24-hour samples are collected each week, on Wednesday and Saturday from midnight to midnight local time (30).

The timing of the sampling can make a large difference in the analytical result for NH_4 , NO_3 and Cl (28, 36). The evaporation of volatile matter (both in ambient air and on filters) takes place during day time, when the temperature is relatively high and the humidity low. This effect is therefore most apparent in mid and southern

Europe. The equilibrium constant for NH_4NO_3 (and NH_4Cl) increases rapidly, leading to evaporation of night time NH_4NO_3 . Although the daytime NH_3 and HNO_3 concentration will rise in result, the K ($c\text{HNO}_3 \times c\text{NH}_3$) is rarely achieved. In agricultural areas like in the Netherlands the high NH_3 concentration often compensates this effect. Given the fact that the NH_4NO_3 evaporation rate is a function of temperature, it is obvious that the resulting mass of NH_4NO_3 on the filter is dependent on the sampling stop time. The highest yield is obtained when sampling is stopped, in the morning when $c\text{HNO}_3 \times c\text{NH}_3$ drops below K . Likewise the lowest yield is obtained in the evening when $c\text{HNO}_3 \times c\text{NH}_3$ equals K again and formation of NH_4NO_3 commences.

The driving forces of the sea salt depletion process on the filter are the humidity and the HNO_3 concentration. With on average the highest HNO_3 concentration and the lowest humidity at high temperature conditions, the sea salt artifact shows the same diurnal cycle as the evaporation of NH_4NO_3 .

The magnitude of effect on the concentration measurement of the concerned ions at the member states remains unclear. No literature was found making an estimate of impact. In order to address the main objectives (7) of the method, an attempt to assess the impact of these artefacts should be made. The laboratory study may shed light on this issue. Main area of research should be the evaporation characteristics of NH_4NO_3 as this component represents a main fraction of $\text{PM}_{2.5}$ in Europe (6). Once NH_4NO_3 is collected on a filter the evaporation rate is likely to be dependent on the actual deviation of $c\text{NH}_3 \times c\text{HNO}_3$ to the equilibrium constant K (4). If ambient evaporation mechanisms apply than K can be calculated from temperature, humidity and SO_4 content for example by the ISORROPIA II model (21).

4.2.2 Retention of precursor gases

Artefacts may be caused by precursor gases like HCl or HNO_3 , which are very reactive and adsorptive gases. Reactions with previously collected aerosol material or filter substrate have been reported (34). Adsorption of these gases may lead to overestimation of the NO_3 and Cl levels. Keck et al (38) investigated this artifact for various type of filter materials. They exposed the filters to artificial concentrations of pure HNO_3 , HCl and NH_3 . In contrast to other filter materials for quartz (Scheicher and Schuell QF20) and Teflon (Pall) retention efficiencies were essentially zero. The statement by Keck concerning the significant retention for HNO_3 for Munktell MK 360 quartz filters could not be verified. Schaap et al (17) identified considerable retention of NO_3 , but that was in the form of NH_4NO_3 due to the high NH_3 background concentration during testing. This effect was however not seen with Teflon filters, which may suggest formation of NH_4NO_3 on quartz surfaces under the condition of $c\text{NH}_3 \times c\text{HNO}_3 > K$.

4.2.3 Spatial inhomogeneity of sampled particulate matter on filter surfaces

Inhomogeneous loading of particulate matter on filters may occur by preferent flow patterns through filter body. This is usually not an important issue as the filter handled for further analysis as a whole. It becomes an issue when parts of the filters taken for various analytic reasons like inter laboratory comparisons or for multicomponent analysis.

Chiappini et al. (42) reported a test with a Digital DA80 sampler which was checked at INERIS by comparing TC, EC and OC concentrations on central and surrounding filter punches. A total number of 18 punches were taken. The overall relative standard deviation (RSD) was below 5% for TC and ranged between 2 and 6% for OC and between 3 and 4% for EC. Observed samples were taken on PM_{10} quartz fiber filters of 150 mm diameter with a flow rate of $30 \text{ m}^3/\text{hr}$.

Brown et al. (40) investigated the phenomenon for anions. Two approaches were followed, one revealing the variation between equal sectors of the filter and the other the variation of a function of the distance to the centre of the filter. The first approach was performed with daily PM_{10} samples on 47 mm PTFE bonded glass filters and the second on daily and weekly PM_{10} and $\text{PM}_{2.5}$ samples on 47 mm Cellulose ester filters. Relatively large differences were observed between the filter sectors, ranging from 0.75 to in excess of 1.4 times the average level observed on each filter. These values were found for 1/8 sector cuts. The second approach revealed an average

mass distribution being 1.1 times higher in the centre decreasing to approximately 0.8 at the outer edges of the filter.

Though the 1/8 filter sector cuts analysis was performed with PM10 samples collected on Teflon coated glass 47 mm filters, the observed effects can have according to Brown serious implications for the CEN PM2.5 validation work for ions and carbonic matter. According to Chiappini this effect is very limited for 150 mm filters.

4.3 Storage

After sampling the filter will be stored until it will be processed in the laboratory. The storage is divided into 3 periods, the post sampling storage in the sampler, the transportation to the laboratory and the storage at the laboratory prior to the analytical processing. The method (1) refers to standard for PM10 and PM2.5 with respect to this procedure. The standard emphasizes to protect the samples from being contaminated and excessive heating without being explicit. Only a few researchers investigated the effect of temperature on loaded filters.

In 2002 Lumpp et al. (41) investigated the evaporation of NH_4 on filters PM10. At 2 stations 2 Digital DHA80 samplers were operated in parallel. One sampler was operated automatically for 14 days. Afterwards the filters were brought to the weighing room, equilibrated and weighed and subsequently analyzed on NH_4 . The other sampler at each station was managed without sample changing. Every day, the sampled filter was transported in a cooling box $<8^\circ\text{C}$ to the laboratory. The filters were stored in a refrigerator. At the end, all filters (cooled and routine) were analyzed on. One station was in Karlsruhe, the other station was rural back ground. No evaporation of NH_3 was observed.

Furthermore Lumpp et al. (41) investigated the evaporation of pure NH_4NO_3 (Merck, polymorph II) in a drying chamber. Up to 130°C no loss of weight was found, even after one week of exposure.

Wittmaack et al (39) exposed identical samples of PM2.5, PM10 and TSP collected on quartz fiber to elevated temperatures. They observed the evaporation of salts as function of temperature. The thermograms show volatilization of NH_4NO_3 at 80°C or lower temperatures. The researchers used 80°C as a first setpoint, therefore the effect at lower temperatures remain unsolved. Above 120°C evaporation of more NH_3 was seen, which was likely attached to the SO_4 fraction.

4.4 Blanks

The filter material itself contributes to a certain extent ions to the sample solution, mainly during the sample extraction procedure. Obviously the contribution is dependent on the type of filter material, ion and brand, but may vary also immensely per batch (8). Blanks are generally divided into two types, the laboratory and the field blank. The laboratory blank is obtained by analysis after extracting a new, not used filter. The field blank is obtained by extraction and analysis of a new filter that went into the field and was treated the same way as the regular sample filters but without air drawn through or in some cases a negligible quantity of air. The field filter blank is used only for quality assurance purposes. If the field filter blank exceeds significantly the average laboratory filter blank, the reasons should be investigated and corrective action should be taken (1). The field blank values are not subtracted from the sample analysis results. As they are site and procedure dependent they are not considered in this survey.

Laboratory blanks are dependent on the quality of the filter material per batch and per brand. As quality per brand may also vary in time most actual information was needed to review the impact of the laboratory blanks. For that matter the CEN/TC 264/WG 34 members were requested for available information on blanks (lab and field) for Teflon and quartz fiber filters. Teflon and quartz fiber are considered by CEN/TC 264/WG 34 as the only suitable filter material types for the standard.

Information below was obtained from 7 institutes (see acknowledgement) and reference (8) on:

Quartz Fiber

Pallflex Tissuequartz
Munktell MK360
Whatman QMA
Albet

Teflon

Millipore FSWL
Pall Teflo

It concerns both laboratory and field blank data.

The interpretation of the various data sets was done according to EN 14211, EN 14212, EN 14625, EN 14626⁴ and the AQUILA recommendation (22). For the interpretation field blanks were only used in case only one dataset was available for the specific filter and available field blanks were in range with the laboratory blanks. In those cases the concentrations are marked as < (smaller than). As the data set for Teflon was too limited (one set per brand), the 2 data sets were combined and presented as Teflon. Also the standard deviation per component per measurement series was determined. In case measurement series with only values below the detection limit were presented, the detection limit itself was taken as a value for the standard deviation. The average standard deviations over the available data series are presented.

The derived data set is presented in Annex A. The unit shown in Annex A is in $\mu\text{g}/\text{filter}$ (47mm). Data of filters with different diameters were proportionally corrected to 47mm. The unit shown in Figures 1 and 2 are in ng/m^3 , representing the effects in terms of air concentration in case 2.3 m^3 per hour was sampled for a period of 24 hours.

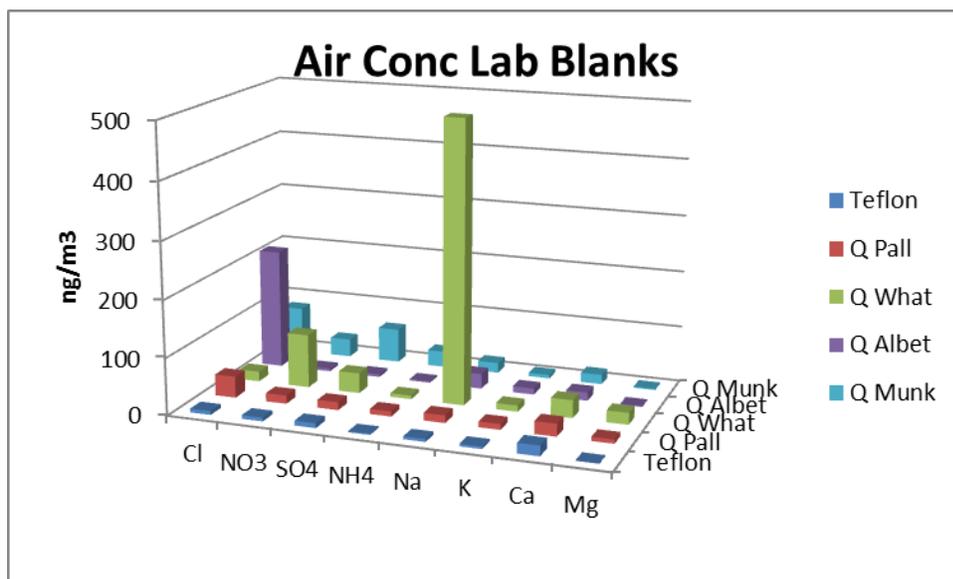


Figure 1 Blanks values converted into air concentrations

⁴ EN 14211:2012, Ambient air quality - Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence
 EN 14212:2012, Ambient air quality - Standard method for the measurement of the concentration of sulphur dioxide by ultraviolet fluorescence
 EN 14625:2012, Ambient air quality - Standard method for the measurement of the concentration of ozone by ultraviolet photometry
 EN 14626:2012, Ambient air quality - Standard method for the measurement of the concentration of carbon monoxide by nondispersive infrared spectroscopy

Clearly Na ($0.5 \mu\text{g}/\text{m}^3$) for Whatman QMA and Cl ($0.2 \mu\text{g}/\text{m}^3$) for Albet are relatively high in comparison to the other concentrations remaining below $0.1 \text{ ng}/\text{m}^3$. In general Teflon appears to be cleaner than quartz. It is important to realize that these values are based on very limited data series and blanks between batches may vary strongly (8). Whatmans average Na concentration is derived from two data series ($0.28 \pm 0.01 \mu\text{g}/\text{m}^3$ and $0.71 \pm 0.03 \mu\text{g}/\text{m}^3$). Albet's average Cl concentration was based on one data series of 2 individual determinations ($0.212 \pm 0.007 \mu\text{g}/\text{m}^3$).

Considering the standard deviation per batch per component the result is much better. In terms of air concentrations all components remain below a standard deviation of $40 \text{ ng}/\text{m}^3$ (see figure 2). As the laboratory averaged blank concentration is subtracted from sample result the uncertainty is dependent on the standard deviation of the blank rather than the blank level itself.

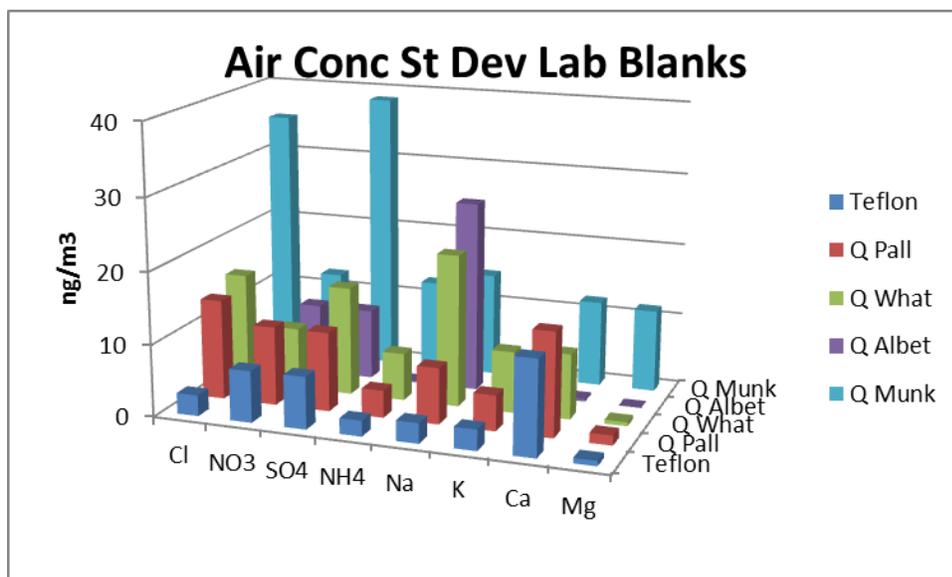


Figure 2 Standard deviation of laboratory blanks presented as air concentrations

How does the laboratory blank compare to background concentrations in Europe? In the outskirts of Europe Finland may represent one of lowest background concentrations levels for PM2.5 in Europe. FMI (the Finnish Meteorological Institute) conducts at the station Hyytiälä continuous measurements of PM2.5 ions by MARGA and were willing to make this data set available for this review. The averaged concentration for 2012 (January to August) is derived from the data set.

Table 2 Average concentrations at Hyytiälä (F)

Concentrations in $\mu\text{g}/\text{m}^3$							
Cl	NO3	SO4	Na	NH4	K	Mg	Ca
0.019	0.218	0.724	0.050	0.190	0.026	0.007	0.016

Table 3 Ratio blank concentration to background Hyytiälä to (B/H)

	Cl	NO3	SO4	Na	NH4	K	Mg	Ca
Teflon	0.2	0.0	0.0	0.1	0.0	0.1	0.1	0.3
Q Pall	0.9	0.1	0.0	<0.2	0.0	<0.3	<0.4	<0.4
Q What	0.4	0.4	0.0	7.9	0.0	0.3	1.1	0.6
Q Albet	5.2	0.0	0.0	0.4	0.0	0.3	0.1	0.3
Q Munk	2.0	0.1	0.1	0.3	0.1	0.2	0.1	0.3

Table 4 Ratio standard deviation blank concentration to background Hyytiälä to (B/H)

	Cl	NO3	SO4	Na	NH4	K	Mg	Ca
Teflon	0.2	0.0	0.0	0.1	0.0	0.1	0.1	0.8
Q Pall	0.7	0.1	0.0	<0.2	0.0	<0.2	<0.2	<0.9
Q What	0.8	0.0	0.0	0.4	0.0	0.3	0.1	0.6
Q Albet	0.0	0.0	0.0	0.5	0.0	0.0	0.0	0.0
Q Munk	1.9	0.1	0.1	0.3	0.1	0.1	1.8	0.8

Influence of filter blanks on the determination of low background levels of PM2.5 ions (Arbitrary appreciation) is shown in Table 5.

Table 5 Influence of filter blanks on low background levels

	Cl	NO3	SO4	Na	NH4	K	Mg	Ca
Teflon								
Q Pall								
Q What				>c			>c	
Q Albet	>c <n	<n	<n	<n	<n	<n	<n	<n
Q Munk	>c							

	good
	moderate
	doubtful
	bad
>c	high blank concentration
<n	small data set

In conclusion based on used dataset for blanks Teflon and quartz fiber filters may be used for the method. Brand related restrictions cannot be made, because brand specific qualities are bound to change in time. Currently the use of Whatman QMA should be discouraged because of the high Na blanks and the uncertainty to what level the water soluble Na per batch may vary.

4.5 Extraction of water soluble ions

The concentration of ions in PM2.5 is defined as the water soluble fraction. Depending on the chemical matrix and extraction procedure variability in fractions can be expected. Therefore additional guidelines for the extraction procedure are required. In the method (1) it is stated that the extraction volume should be as small as possible but enough to completely cover the sample, typically at least 10 ml for 47 mm filters. The sample tubes should be exposed in an ultrasonic bath for at least 30 minutes to obtain complete extraction. Brown et al. (23) researched an new extraction technique and commented on extraction parameters of concern. Brown et al. extracted the anions using the IC eluant as extraction medium rather than deionised water. They showed full extraction after 10-15 minutes compared to 15-20 minutes for deionised water. The full extraction criteria were defined as no extra anions were obtained after longer extraction times. On an average 5% higher extraction efficiency was obtained with the IC eluant. The appealing method is however not applicable for cations and does not truly reveal just the water soluble fraction, but the IC eluant soluble fraction. Usually recommended is an extraction time of 1 hour (24). The effect of elevated temperatures on extraction rate was also tested (23) but did not give a significant enough improvement to warrant the extra complication of heating the samples in the sonic bath. As the elevated temperature did not extract significantly more anions, it was concluded that room temperature sonication is

sufficient to extract fully the water soluble anions from PM. It is likely but not tested that elevated temperatures are also not required for the full extraction of cations. The definition of the water soluble fraction may however be extended with the comment 'at room temperature'.

5. Guidelines for a laboratory study on the evaporation artefacts of NH_4NO_3

In order to be able to assess the loss of NH_4NO_3 from filters the evaporation rate needs to be measured as a function of temperature, humidity, c_{NH_3} , c_{HNO_3} and Y ($\text{NO}_3^- / \text{NO}_3^- + \text{SO}_4^{2-}$ ratio). The range should apply to sampling conditions valid for the various member states in order to assess the potential magnitude of loss of NH_4NO_3 .

The laboratory study should be conducted with the method selected filter material in a standard (EN 12341) setting. On the filter a sufficient amount of artificial NH_4NO_3 should be collected to supply enough matter for the evaporation test. Furthermore under the actual conditions the NH_4NO_3 should be in equilibrium with its precursor gases. This should be demonstrated by simultaneous measurements of HNO_3 and NH_3 before and after the filter. These concentrations need to be equal. Once the equilibrium is installed one of the K determining parameters (T , RH , c_{xc}) can be changed, bringing the system out of equilibrium. The evaporation rate can then be determined by measuring the flux of NH_3 and HNO_3 (equal molar concentrations) evaporating from the filter. To conduct laboratory tests a matrix of parameter settings can be derived from daily temperature ranges, lowest temperature observed for evaporation losses, variation in humidity, c_{xc} and Y (4, 6, 21, 28, 31, 32).

- c_{xc} – set between 0 and K and vary to a minimum of 0 ppb^2
- Temp - set between 0 and 25 and vary to a maximum of 35°C
- RH – set between 40 and 100 and vary to a minimum of 30%
- Y – set between 0.2 and 1

6. EMEP Equivalence

6.1 The EMEP method

The monitoring obligations in the UNECE Cooperative Program for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) are defined by the monitoring strategy for 2010-2019 (UNECE, 2009)(44). At the basic level 1 sites, the measurement program includes tropospheric chemistry of substances involved in the atmospheric cycling of particulate matter, hence PM10 and PM2.5 mass and inorganic compounds in air (SO_2 , SO_4 , NO_3 , HNO_3 , NH_4 , NH_3 , (sNO_3 , sNH_4), HCl , Na , K , Ca , Mg) with no defined cut off. The measurements should have a daily temporal resolution (24 hours). The reference method and methodologies are described in the EMEP manual for sampling and chemical analysis (EMEP/CCC) (43). The sampling of inorganic ions in aerosols should be done using a filterpack sampler or a denuder-filter system for better partitioning of the gas and aerosol phases. The preferred denuder-filter EMEP method is artifact free (46), but labor intensive. This method is only deployed by one EMEP station (IT01) on a regular basis and is therefore not representative as commonly used EMEP method.

The filterpack system is the commonly used method. There are three filters, the first filter in the air stream is a membrane filter, e.g. Teflon, for collecting the airborne particles. This is followed by an alkaline (usually potassium hydroxide) and then acid (usually citric or oxalic acid) impregnated filters, e.g. cellulose, for sampling volatile acidic and alkaline substances. After sampling, the ions are extracted from the aerosol filter with deionized water. The aerosol filters should be given an ultrasonic treatment to obtain a complete extraction. The recommended and most commonly used method for analytical detection is ion chromatograph. Other methods can also be used when proven comparable.

6.2 Assessment

The first filter will collect particulate matter containing NO_3 , Cl , SO_4 , NH_4 , Na , K , Ca and Mg . The second filter collects acidic gases like HNO_3 , HCl , SO_2 , HNO_2 . The third collects the alkaline gases like NH_3 . As shown before NH_4 , NO_3 and Cl may evaporate from the first filter and add as HNO_3 and HCl to the second filter and as NH_3 to the third filter. Airborne HNO_3 may add to the first filter as NO_3 due to sea salt depletion. So in conclusion SO_4 , Na , K , Ca and Mg are determined by analysis of the first filter, SO_2 and HNO_2 by analysis of the second filter, the sum of HNO_3 + NO_3 and the sum of HCl + Cl by adding up the results of the first and second filter and finally the sum of NH_4 + NH_3 by adding up the first and the third filter.

As EMEP doesn't prescribe the use of any cut off system SPM (also referred to as TSP, total suspended matter) is sampled and analyzed. The fraction above 2.5 micron also known as the coarse PM fraction may contain significant levels of the mentioned components. Usually the major fraction of Cl , Na , K , Ca and Mg is present in this coarse mode (6).

So comparison of the standard (designed for PM2.5) with the EMEP reference method with no defined cut off is difficult, and the differences are dependent on the site, chemical composition and the meteorology.

7. Uncertainty Assessment

The uncertainty of the method is too complex to quantify in this context. The standard is a method to determine the concentration of the water soluble anions NO₃, SO₄, Cl and cations NH₄, Na, K, Mg and Ca in PM_{2.5}. PrEN 12341 (2) offers the relative uncertainty for the gravimetric measurement of PM_{2.5} being 5.8% for a level of 30 µg/m³. The weighing and conditioning of the filter contributes largely to the uncertainty, but these activities are not part of the PM_{2.5} method for anions and cations. Furthermore the effect of the loss of semi-volatiles is set to zero by convention and the interaction with gases is not considered (2). These effects may however represent a considerable contribution to the uncertainty, which is valid concerning the objectives of the method. The effects on the uncertainty per individual ion may differ largely.

Here in this report major uncertainty aspects of the method, the inlet system, evaporation from the filter, reactive gas retention, storage, blanks and extraction are reviewed. Validation of the method including analysis uncertainty is to be provided by Field Tests (Work Package 3) and Statistical Evaluation (Work Package 4) (7) and not considered in this assessment. The uncertainty assessment is based on Quartz fiber filters.

Table 6 Individual sources of uncertainty

	SO4	NO3	Cl	NH4	Na	K	Ca	Mg
Inlet System	-	-	-	-	-	-	-	-
Evaporation	-	C	M	C	-	-	-	-
Retention	-	M	-	-	-	-	-	-
Storage	-	-	-	-	-	-	-	-
Blanks	-	-	M	-	M	-	M	M
Extraction	-	-	-	-	-	-	-	-
Analysis	NC	NC	NC	NC	NC	NC	NC	NC

C = considerable, M = minimal, - = negligible, NC = not considered

NO₃ is a major component of PM_{2.5} in term of mass fraction and exhibits a considerable artifact potential. The potential is due to evaporation of NH₄NO₃ from the filter by changes in the temperature, humidity, timing and precursor gas concentrations of NH₃ and HNO₃. The volatilization may lead in exceptional cases to complete evaporation. Mid and south of Europe are most vulnerable for this artifact. On the other hand overestimation may occur by the substitution of Cl associated with Na by HNO₃. This effect is less effective in terms of PM_{2.5} mass as Cl (M=34.5) is substituted by NO₃ (M=62), while NH₄NO₃ represents M=80 (M is molecular weight). Polluted, coastal areas like Barcelona are most vulnerable for sea salt depletion on filters. The quantity of evaporated or absorbed mass is strongly dependent on start and stop time of the sampling period.

NH₄ may exist in PM as counterpart of NO₃, SO₄, Cl and carbonic acids. The major fraction is associated with NO₃ and SO₄. (NH₄)₂SO₄ has no vapor pressure and will therefore remain entirely on the filter. NH₄ associated with NO₃ as mentioned before may entirely evaporate. As PM_{2.5} is commonly pH neutral (6) due to CLTRAP and other SO₂ reduction programs and the elevated NH₃ concentration in the EU, atmospheric NH₃ is not likely to react with already collected PM_{2.5} on the filter. It is concluded that NH₄ is considerable vulnerable for artefacts but less than NO₃. Furthermore NH₄ represents a much smaller PM_{2.5} mass fraction than NO₃.

Cl is predominantly present as sea salt. NH₄Cl may exist in PM_{2.5} under severe cold weather conditions and is not seen a component of importance in PM_{2.5} in Europe. So most of the Cl found in PM_{2.5} is associated with Na. As mentioned before Cl may be substituted by NO₃ on filters in polluted coastal areas. This process usually takes place

by changing wind directions during sampling. Already collected sea salt Cl being part of marine originated air can get exposed later on to HNO₃ being part on polluted continental air mass. In general this effect very limited for Europe. And most certainly when the effect on the PM mass fraction is considered.

Blanks are considered from two different angles, the anions and cations levels extracted from not used filters and the standard deviations of these levels. Both are of importance concerning the quality of the method. Teflon exhibits very low blank levels for all components, but will not be used for the method because of practical reasons (CEN/TC 264/WG 34, document N75). Various quartz fiber brands were tested and showed on average satisfying results. All components when converted into PM_{2.5} concentrations below 0.1 µg/m³, except for Na in Whatman filters (0.5 µg/m³) and Cl in Albet filters (0.2 µg/m³). As the laboratory averaged blank concentration is subtracted from sample result the uncertainty is dependent on the standard deviation of the blank rather than the blank level itself. Considering the standard deviations all components remained below 40 ng/m³. This is sufficient for background area's throughout Europe, even in Finland. Brand related restrictions cannot be made, because brand specific qualities are bound to change in time. Currently the use of Whatman QMA should be discouraged because of the high Na blanks and the uncertainty to what level the water soluble Na per batch may vary.

In conclusion, considering all artefacts only the impact of the loss of NO₃ by evaporation is severe and not well understood. Therefore Laboratory tests (Work Package 2) (7) will focus on parameterization of this phenomenon. See the section on "guidelines for a laboratory study on the evaporation artefacts of NH₄NO₃".

8. Acknowledgement

Special thanks to the institutes that provided valuable information on blanks to the author. Information was made available by CNR, FMI, RIVM, IUTA, NILU, LUBW, CSIC and ECN, all members of CEN/TC 264/WG 34. Also many thanks to FMI for offering the Hyytiälä MARGA PM2.5 data set. Thanks to Ralph Lumpp (LUBW) for offering the information concerning their NH_4NO_3 evaporation studies. Also gratitude to Wenche Aas (NILU) for contributing to the EMEP section. Wenche Aas (NILU) and Ernie Weijers (ECN) are also thanked for checking the report as a whole. Finally Harry ten Brink's contribution to this report is highly appreciated.

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Annex A. Results laboratory blanks

Table 7 Results for laboratory filter blanks. The concentration is in $\mu\text{g} / \text{filter}$ (47mm) and represents the dissolved fraction.

	Cl	NO3	SO4	NH4	Na	K	Ca	Mg	
Munktell	4.5	1.8	3.3	1.6	1.0	0.3	0.9	0.12	average concentration
	1.9	0.7	2.1	0.7	0.8	0.2	0.7	0.6	average stdev labs
	70	66	70	68	68	51	68	51	total # of analysis
	3	3	3	3	3	2	3	2	# labs
Albet	12	0.3	0.3	0.14	1.5	0.6	0.8	0.08	
	0.04	0.5	0.5	0.01	1.5	0.00	0.02	0.00	
	2	2	2	2	2	2	2	2	
	1	1	1	1	1	1	1	1	
Pall	2.1	0.8	0.8	0.5	<0.7	<0.6	<1.2	<0.4	
	0.8	0.6	0.6	0.2	<0.4	<0.3	<0.8	<0.08	
	159	160	160	98	155	155	155	155	
	3	3	3	3	2	2	2	2	
Whatman	1.0	5.2	2.0	0.3	27.3	0.6	1.7	1.1	
	0.9	0.5	0.8	0.4	1.2	0.5	0.5	0.03	
	44	26	44	44	7	7	7	7	
	3	3	3	3	2	2	2	2	
Teflon	0.4	0.4	0.5	0.12	0.3	0.2	1.0	0.06	
	0.2	0.4	0.4	0.12	0.2	0.2	0.7	0.04	
	5	5	5	5	5	5	5	5	
	2	2	2	2	2	2	2	2	

Annex B. Excerpt of Measurements of secondary inorganic aerosols in the Netherlands (ref. 10)

This text has been derived from the following report: Measurements of secondary inorganic aerosols in The Netherlands.

Weijers, E.P., G.P.A. Kos, M.J. Blom, R.P. Otjes, M. Schaap, E. van der Swaluw, ECN report ECN-E--12-003. (publication within the framework of the Netherlands Research Program on Particulate Matter II (BOPII), financed by the Ministry of Infrastructure and Environment).

B.1. Loss of particulate matter in filter measurements

B.1.1. Introduction

Whereas the LVS-RIVM instrument has been built in the '90s and reflects the state-of-the-art at that time, similar questions might be posed in relation to modern measurement devices. As mentioned earlier, filter instruments suffer from artefacts like evaporation or adsorption. In the past, several studies were performed to investigate sampling artefacts by the use of different filter types and samplers (Dasch et al (1989), Harrison and Kitto (1990), Hering and Cass (1999), Schaap et al (2004) and others). Many of these studies have been performed in the US, where other filters are in use than in Europe. Those performed in northern Europe are less relevant because the NO_3 found there is mainly present in the form of stable compounds, like NaNO_3 (Pakkanen et al (1999)).

In the study reported here we investigate how the chemical composition of PM (specifically NO_3 and Cl) collected on the filter alters due the artefacts mentioned earlier. We further discuss the role of meteorological variables during sampling. An important question here is to what extent the PM values produced by a reference Leckel instrument are affected by the chemical reactions taking place on the filters.

B.1.2. Experimental setup

A (very) schematic setup is given in Figure 3. The experimental determination of loss of PM from the Leckel filter goes as follows: the Marga analyses two airflows (on an hourly basis). One of them is PM_{10} in outdoor air. The second flow contains air after filtration by the filter. Comparing the chemical composition of both air flows allows to quantify adsorption on or loss from the filter. By measuring simultaneously the meteorology the influence of temperature and relative humidity can be established.

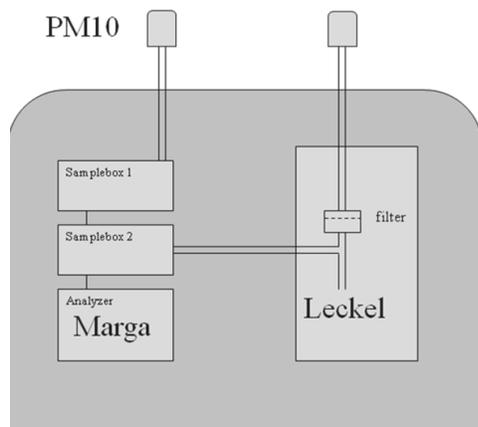


Figure 3 Schematic experimental setup

The instruments have been installed at the site of Wieringerwerf. One important reason for selecting this site was of a scientific nature: an accurate chemical analysis of the reactive gasses evaporated from a filter will be hampered by strongly varying background concentrations of these gases. This would be the case in areas where strong emissions of these gases occur (for example, NH₃ emissions at the Vredepeel site). Another reason was practical: no deviation occurs with routines and procedures in the continuous SIA measurements performed by LML.

The measurement data presented were acquired during the summer campaigns of 2010 and 2011. The motivation for choosing the summer periods was that a maximum volatilization effect could be expected then. The Leckel filters have afterwards been analysed for NO₃, SO₄, NH₄ and Cl. On the site also continuous monitoring of SIA takes place with another Leckel. The data from this instrument is used to ensure that the technical intervention (the connection between Leckel and Marga) did not yield a disturbance in the (reference) PM-measurements.

B.2. Marga time series

An illustration of a time series collected with the Marga instrument has been shown in Figure 4. This is a registration of SIA components (Cl, NO₃, SO₄ and NH₄) during the 2nd campaign at Wieringerwerf (July-August 2011). Clearly discernible are the periods with rather elevated concentrations for NO₃. At least 10 times the concentration value is larger than 5 µg/m³; twice its level rises well above 15 µg/m³ (4-7 August). It is further observed that during these days NH₄ and SO₄ concentrations are high as well indicating the presence of NH₄ NO₃ and NH₄ SO₄ salts. For the periods in between Cl appears somewhat enhanced (to some extent), for example on 15 and 23-24 July. This opposite variation reflects the transport of polluted air originating from different wind sectors already discussed in paragraph 2.1.

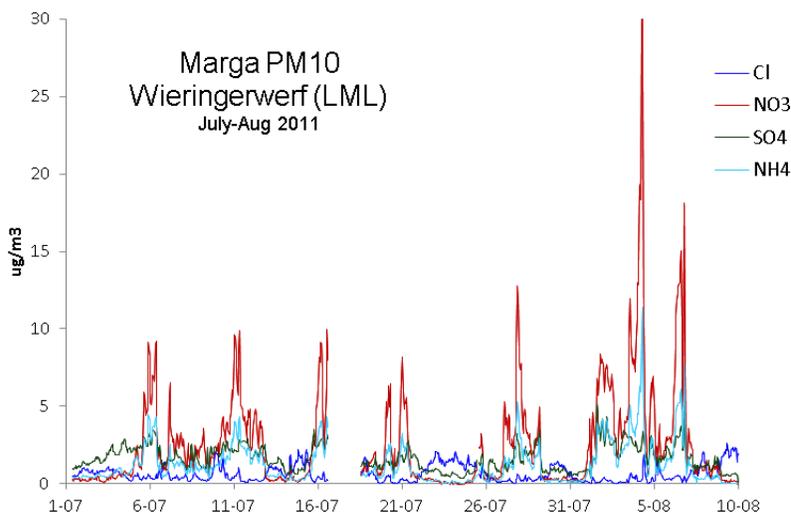
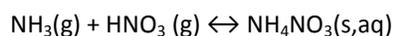


Figure 4 Time series of SIA components during the second BOP campaign at Wieringerwerf

B.3. Chemistry

B.3.1. Formation of ammonium nitrate

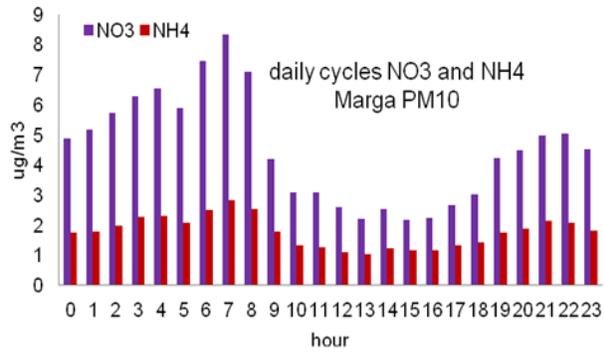
Gas-aerosol partitioning of NH₄ NO₃ (NH₄NO₃) in the atmosphere takes place between the gases NH₃ (NH₃) and HNO₃ (HNO₃) according to



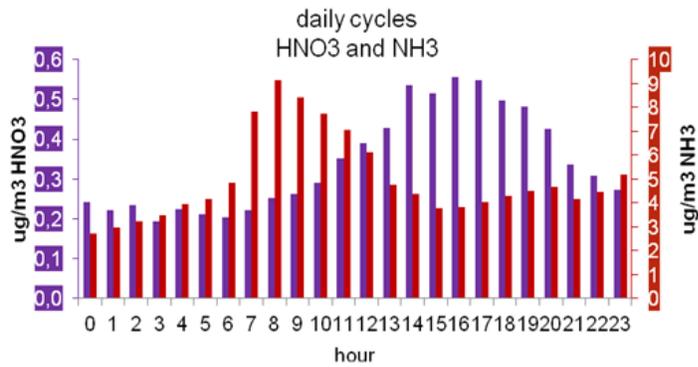
where 'g', 's' and 'aq' stands for gas, solid and aqueous (physical state), respectively. Due to intensified agriculture and large traffic volumes, NH_3 and nitrogen oxide are abundantly present in the ambient air in the Netherlands. An important role is played by HNO_3 which is a product of nitrogen oxide. In air, the formation continues until an equilibrium is depending on the levels of (precursor) concentrations, air temperature and relative humidity. When one of these parameters then changes NH_4NO_3 will be formed or evaporated. For example, when temperature rises the gas-phase precursors will be released from the aerosol (decreasing the NO_3 and NH_4 contributions) until a new chemical equilibrium has been attained. In the Netherlands, low temperatures and high relative humidities prevail most of the time having a positive effect on the formation and stability of the NH_4NO_3 aerosol.

The influence of temperature can be observed in the daily cycles of aerosol NO_3 and NH_4 as well as HNO_3 (see Figure 5.a-b). During the day the concentrations of NO_3 and NH_4 are considerably lower than in the night (roughly 50%). The pattern for HNO_3 is reverse with maximum levels between 14:00-16:00. In the case of NH_3 the pattern differs from HNO_3 for two reasons. The maximum level occurs in the early morning which is due to NH_3 deposited during the night (trapped in moisture) as temperatures rise. In addition, the absolute contribution from the aerosol partitioning reaction during the day is relatively small compared to ambient levels of NH_3 in the daytime.

(a)



(b)



(c)

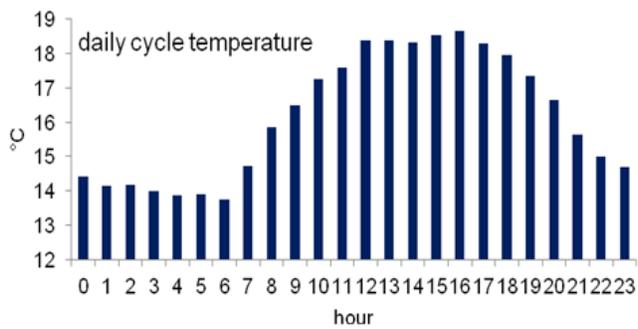
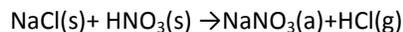


Figure 5 Daily cycles of (a) NO₃ and NH₄ salts, (b) gaseous precursors (HNO₃ and NH₃) and (c) temperature as derive from Marga measurements during the second Wieringerwerf experimental campaign

B.4. Depletion of chloride

The 'depletion of Cl' is another reaction of interest here. Again, HNO_3 plays an important role here. Coarse sea salt particles act as a reactive sink for HNO_3 . At first, HNO_3 adsorbs on sea salt aerosol. The Cl present is then removed from the aerosol under the formation of NaNO_3 and the release of gas-phase HCl (hydrogen Cl) according to



producing stable NaNO_3 . Part if not all of the solid Cl is lost while 'some' NO_3 is gained. Taking into account the molecular masses of Cl (35) and NO_3 (62), respectively, the reaction results in some additional solid (NO_3) mass that will arrive in the coarse fraction due to the binding with Na.

The reaction predominantly takes place in a marine/urban environment with an enhanced sea salt and NO_x presence in the air. Evidence that this is prevalent in the Netherlands could be derived from the BOPI program. Figure 6 shows the average daily cycles of the Cl deficit and gaseous HCl at the Schiedam site in the BOP campaign. In seawater, the Cl-to-Na ratio is 1.8. At Schiedam it is observed that this ratio is smaller and at a minimum in the late afternoon coinciding with the maximum in the daily variation of HCl measured at the same location.

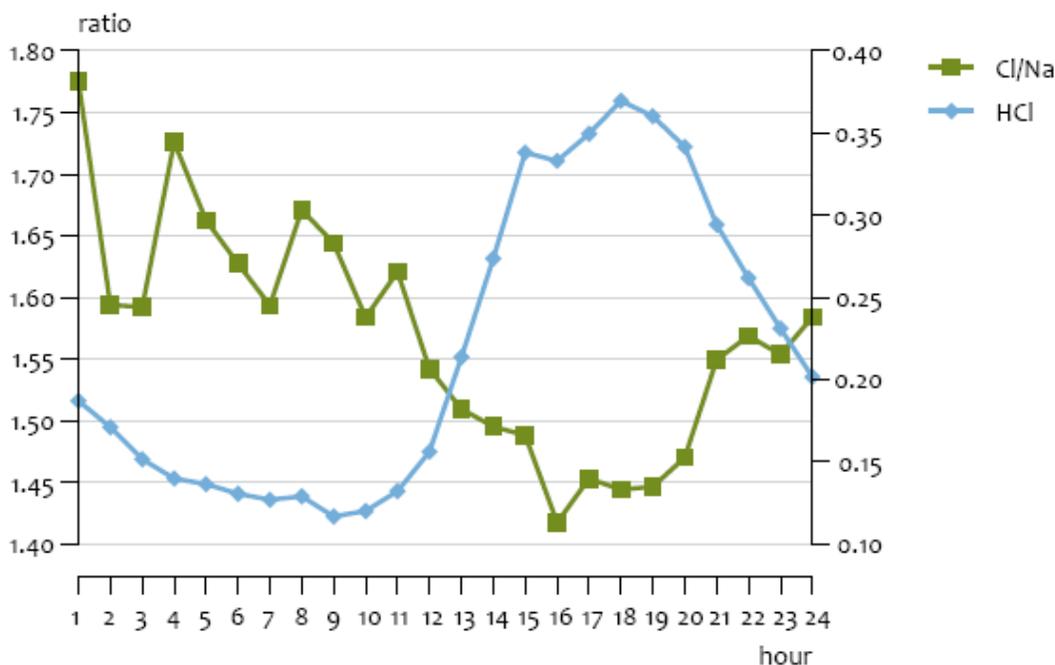


Figure 6 Daily cycles of Cl/Na and HCl, as measured with the MARGA system at Schiedam during the BOPI campaign

To end, all these reactions are known to take place in the atmosphere. The questions here are: what happens on the filters in the Leckel instrument? If these reactions take place in air why not on these filters when they become loaded with particulate matter? And if so, how will it affect the mass concentration values produced by the Leckel? The answers will be given in the next sections.

B.5. Results

That evaporation of gases from the filter indeed takes place can be seen in Figure 7, a registration taken from the campaign in 2011. Similar examples were observed in the 2010 campaign. Looking into detail it is concluded that in the early morning evaporation starts for both HNO_3 and HCl and becomes strongest in the afternoon. The pattern repeats every day with different amplitudes and a relation with ambient temperature seems evident. Peak values

in evaporation (on 2 and 4 August) coincide with the highest daily temperatures measured during the campaign. After the 5th of August the effect becomes less which corresponds with decreasing air temperatures.

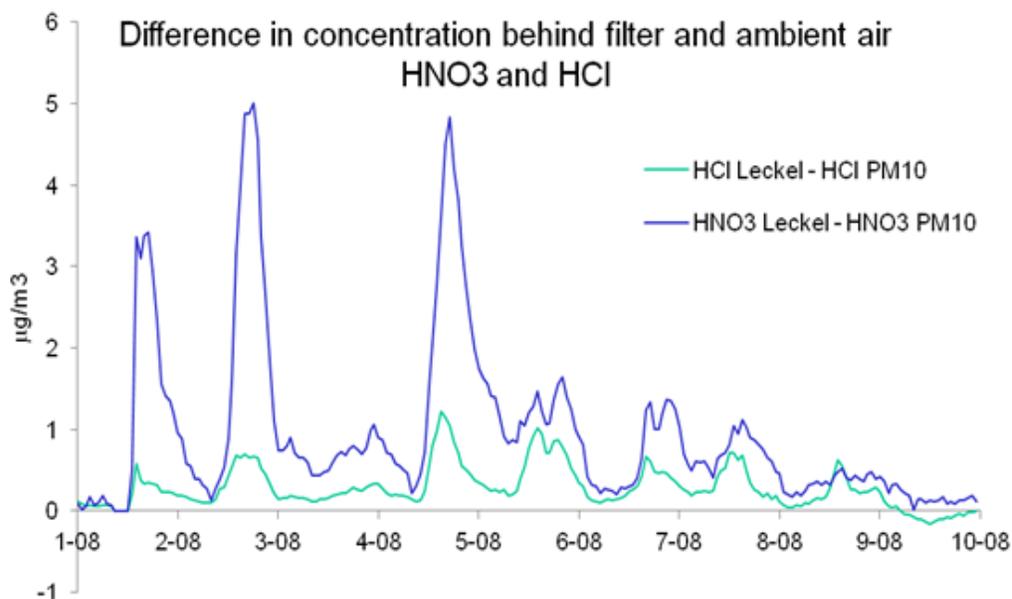
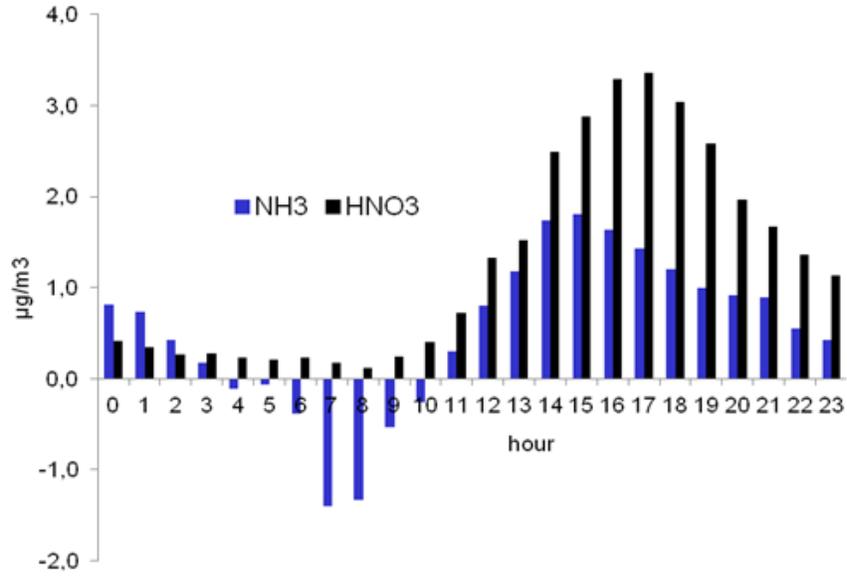


Figure 7 Registration of HNO₃ and HCl evaporated from the filter as measured in the Leckel instrument

To investigate some of the chemical characteristics we considered the hourly patterns during the day. After selecting six of the most pronounced events within the time series an average daily variation was calculated for HNO₃ and NH₃, and HCl with respect to differences in concentration before and after the filter. The result is given in Figure 8 a-b. Although the relatively small number of events may not be statistically robust, the role of the temperature seems evident. If temperature increases during the day both NH₃ and HNO₃ disappears from the filter. Because the NH₃ concentrations in ambient air are higher by several factors, the relative small amount due to volatilization from the filter is less accurate to determine. In the case of HNO₃ the concentration difference over the filter is well above the levels in ambient air (compare Figure 8a with Figure 5b). The disappearance of HCl from the filter seems to be a continuous process being at a maximum in the early afternoon.

Due to the relation with temperature one should expect a more common pattern for the both (precursor) gases. However, the maximum observed for NH₃ precedes the maximum in the HNO₃ registration. Similar to what happens in the free atmosphere in the (very) early morning (Figure 5b), inside the Leckel instrument condensation might take place when warmer and moist ambient air enters the instrument. This will capture part of the NH₃ and explains the negative values observed between 06:00 and 09:00 (meaning that the concentration behind the filter is actually lower than in the ambient air). When temperature further increases during the morning all of the NH₃ trapped in the condensation will be released in a relatively short period and producing a maximum before that of HNO₃. Part of the evaporated HNO₃ produced by the partitioning reaction might be used in the Cl depletion process which might explain the occurrence of a maximum value of gaseous HCl preceding the maximum seen in the HNO₃ series.

(a)



(b)

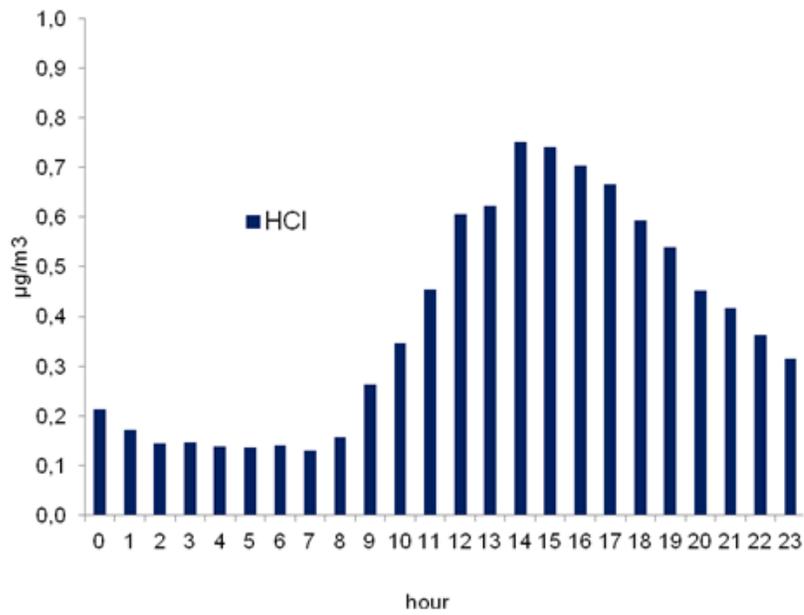


Figure 8 Daily cycle of the concentration differences before and after the Leckel filter for HNO and NH_3 (a), and HCl (b); averages over six events

Both reactions result in a loss of PM mass originally deposited on the filter. The next two questions are now of importance:

1. which parameter(s) influence these mass losses from the filter, and
2. how much mass will eventually disappear from the filter?

The influence of temperature is visualized in Figure 9 where all available data regarding the differences in HNO_3 concentrations as function of temperature are shown. For the 2010 data set a similar pattern has been observed. Clearly, the chance on evaporation of HNO_3 from the filter augments at higher temperatures, starting from around 13° onwards, and with the largest effect at the highest temperatures. However, the variation at a certain temperature is substantial. There may be considerable vaporization but the effect might also be entirely absent. Obviously, other factors play a role here as well. The fact that volatilization takes place below 20°C is contradictory to what was reported by Schaap et al (2004) who stated that only above this temperature volatilization takes place. More research is needed on this issue.

The dependence on the ambient relative humidity is given in Figure 10. Though being less straightforward than in the case of temperature it is clear that more evaporation occurs at a lower relative humidity. This was already expected as condensation results in a water mantle around the aerosol preventing the volatilization of material. It is concluded that the chance on mass loss from the filter is highest when higher temperatures (above 20°C) combine with lower relative humidity's (below 70%). In a similar manner the chemical reaction of hydrogen chloride can be considered. The results (shown in Figures 11 and 12) indicate, like in the case of HNO_3 , the dependence on temperature and relative humidity is evident.

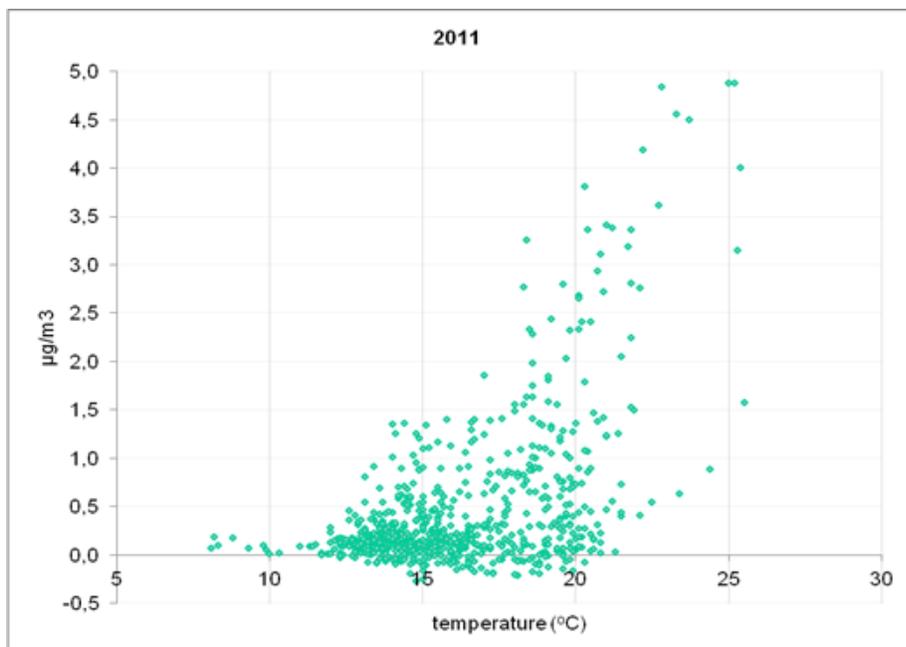


Figure 9 Difference in the hourly measured HNO_3 concentrations before and after the Leckel filter as function of ambient hourly temperature

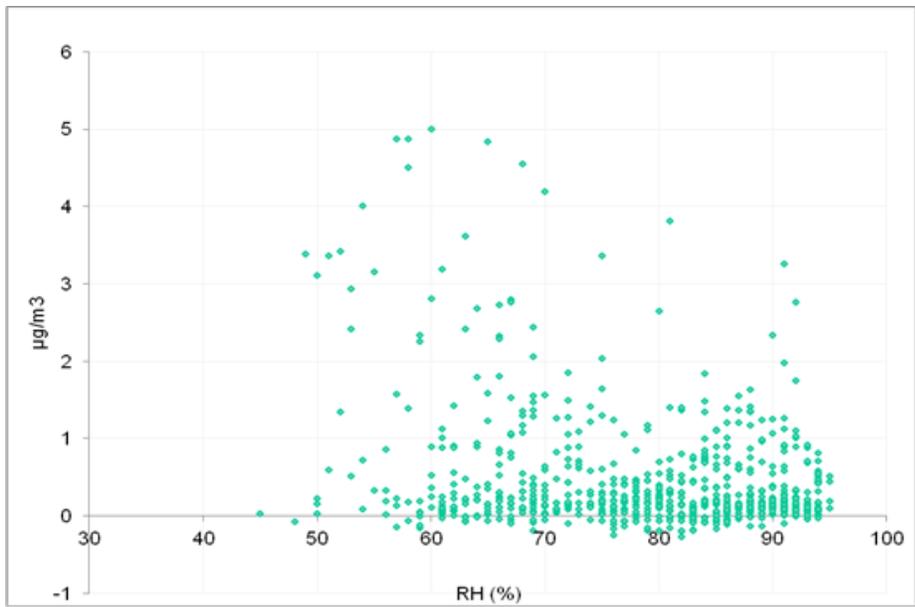


Figure 10 *Difference in the hourly measured HNO_3 concentrations before and after the Leckel filter as function of ambient hourly relative humidity*

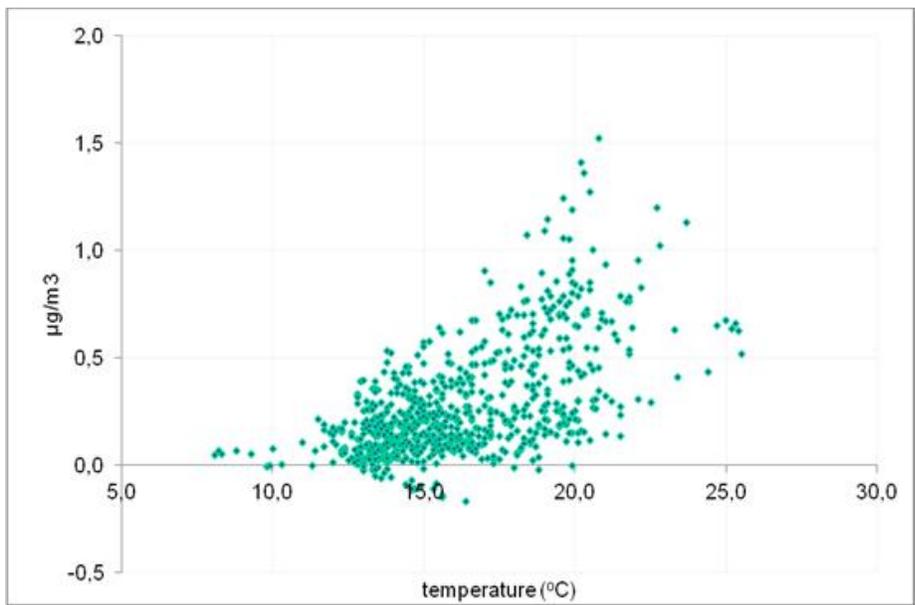


Figure 11 *Difference in the hourly measured HCl concentrations before and after the Leckel filter as function of ambient hourly temperature*

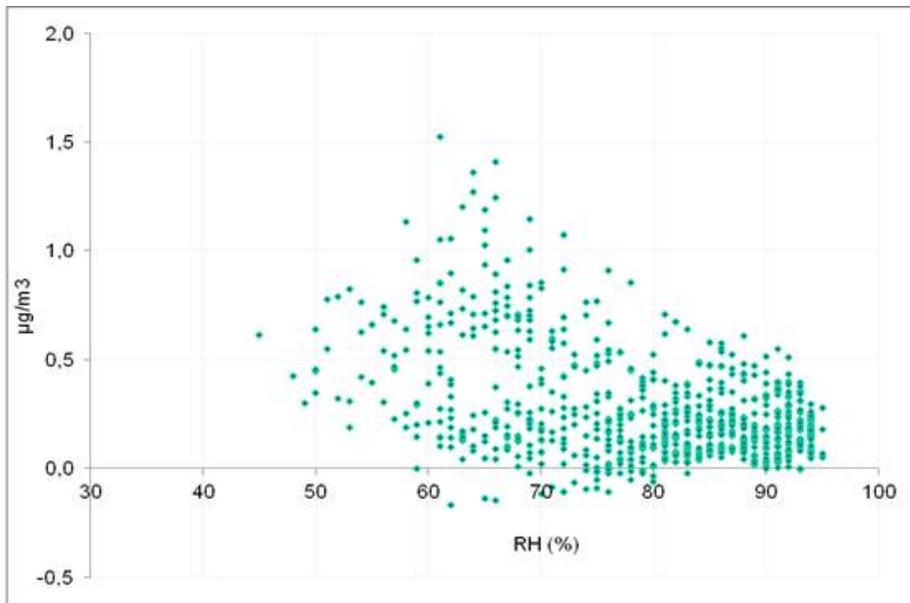
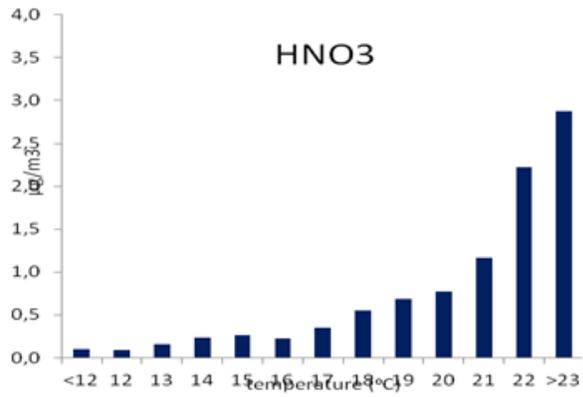


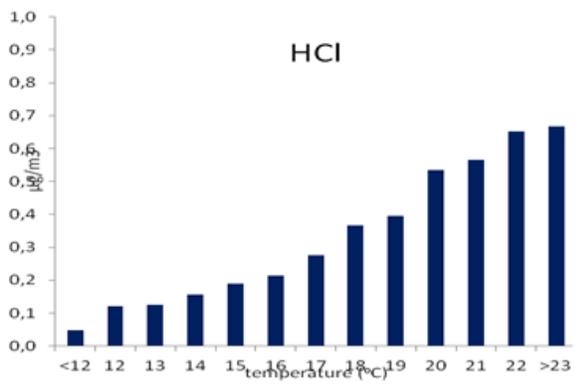
Figure 12 *Difference in the hourly measured HCl concentrations before and after the Leckel filter as function of ambient hourly relative humidity*

The raw (hourly) data shown here further indicate that both the $\text{NH}_4 \text{NO}_3$ partitioning and the depletion reaction take place and that parameters like ambient temperature and relative humidity are important. At this stage it is tempting to estimate the average dependence on temperature and relative humidity (and number of data points). These are given in Figures 13 a-c. Note the exponential behavior for HNO_3 compared to HCl. The number of data points in the lower and higher temperatures ranges are relatively low.

a)



b)



c)

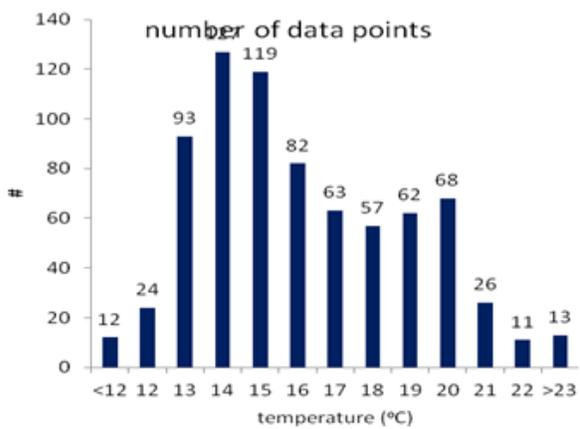
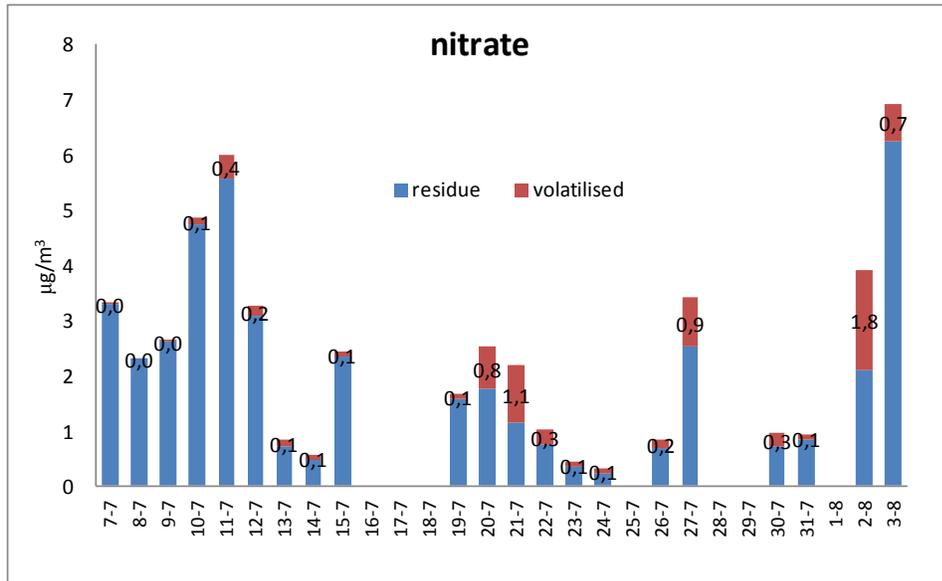


Figure 13 Volatility as function of temperature (a) and relative humidity (b); also given number of data points for each temperature (c)

How will this affect the average concentration of the PM mass as produced by the Leckel sampler? For the entire campaign in 2011 (summer period of 28 days) we have estimated the NO₃ and chloride mass disappearing from the filter per day (Figures 14 a-b and 15 a-b). In the case of NO₃ the loss was 18%, on average, and ranging between 0 and near 50%. As the NO₃ concentration over the entire period was near 2.5 µg/m³, less than 0.5 µg/m³ disappeared per day, on average. However, on a daily basis it may be quite different. For example, on August 2nd nearly half of the average NO₃ mass disappeared that day (1.8 µg/m³).

The chloride depletion occurs every day and the relative mass loss due to this process can be quite substantial (Figures 15 a-b). The mass that disappeared from the filter is, on average, around 48% of the total chloride originally present, and varies between 2 and 88% on a daily basis. Expressed in absolute mass concentrations the effect of the depletion of chloride is smaller than the loss of NO₃ because the amount of chloride in the air is relatively small at days when these processes are strongest (transport of continental air with high temperatures and low relative humidity).

(a)



(b)

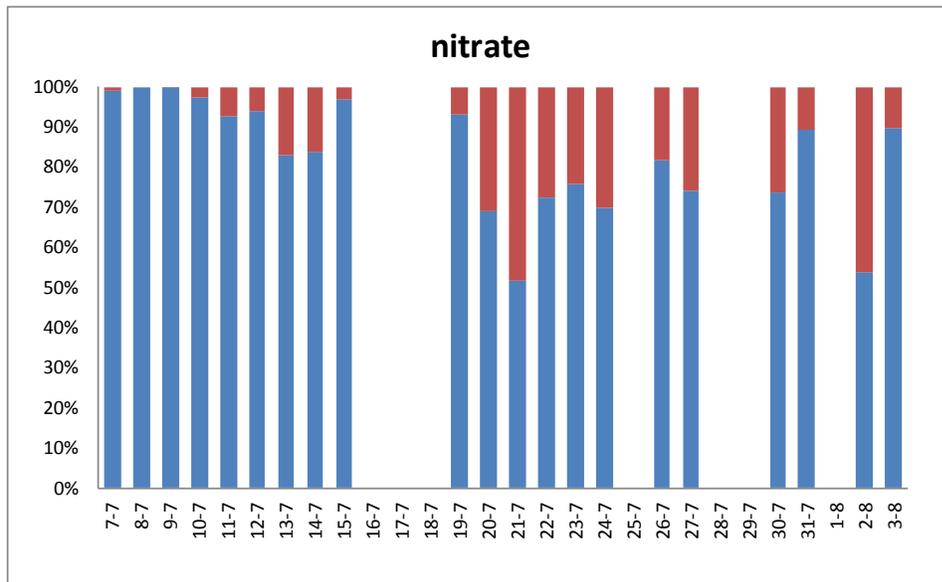
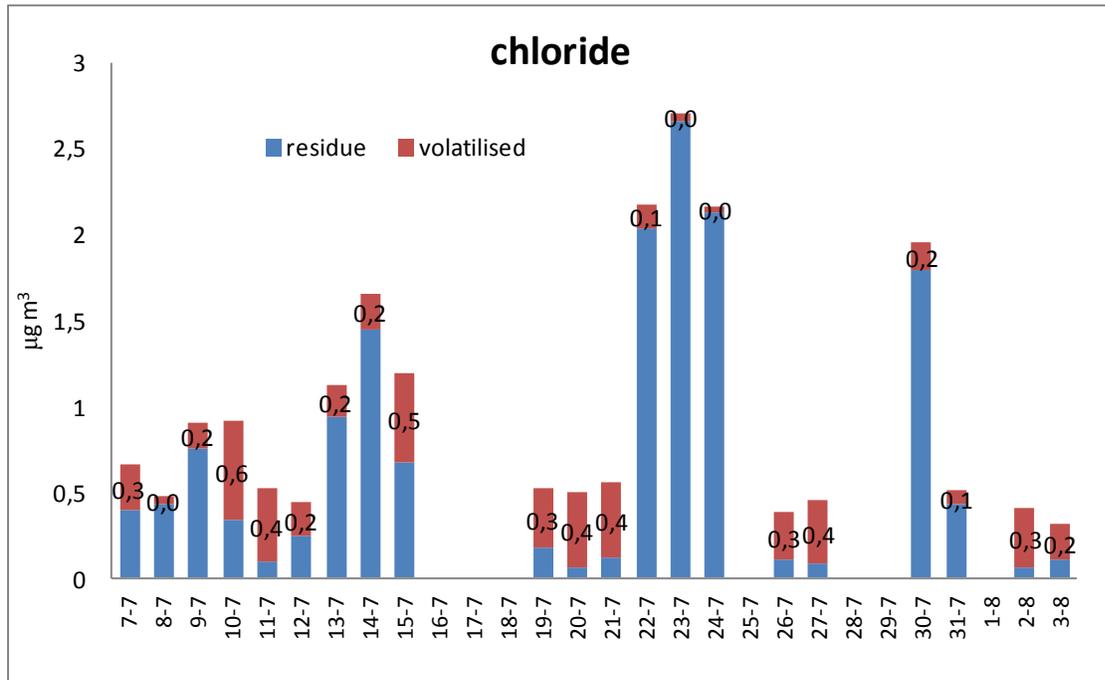


Figure 14 Volatilisation of NO₃ mass from Leckel in absolute (a) and relative (b) values

(a)



(b)

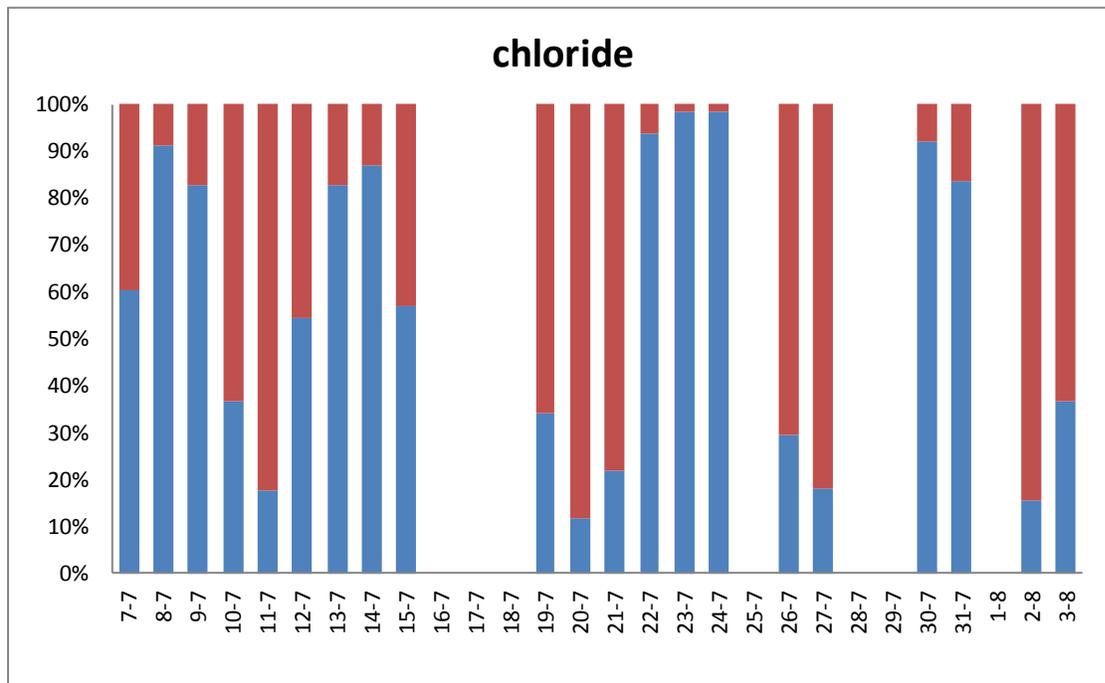


Figure 15 Volatilisation of chloride mass from Leckel in absolute and relative values

B.6. Final conclusions

- The assertion that no volatilization of mass occurs while measuring with the reference Leckel instrument, as claimed by the manufacturer, is untrue. During fine weather conditions with a high temperature and low relative humidity, losses of the NO_3 and chloride components have been established.
- In the long term (i.e., for a yearly average) the effect on PM mass appears limited. For the measurement period presented here the average loss due to the equilibrium reaction of NH_4NO_3 was less than $0.5 \mu\text{g}/\text{m}^3$. The chloride depletion implies that some NO_3 is 'produced' (in the coarse fraction). The NO_3 mass 1.8 times the original chloride mass (due to their different molecular masses). In the long run, this effect is modest because the absolute chloride concentrations are relatively small.
- On a daily basis, however, the loss of mass can be more substantial. It was found that the evaporation of NO_3 could be between 0.8 and $1.8 \mu\text{g}/\text{m}^3$ even on days with moderate temperatures (Figure 16), i.e. 20°C (contrasting earlier reports). Such a decrease might affect the number of PM_{10} -exceedences (in summer). To what extent this prevails deserves further research including a determination in other seasons as well as the performance of other (equivalent) instruments allowed for measurements of PM.

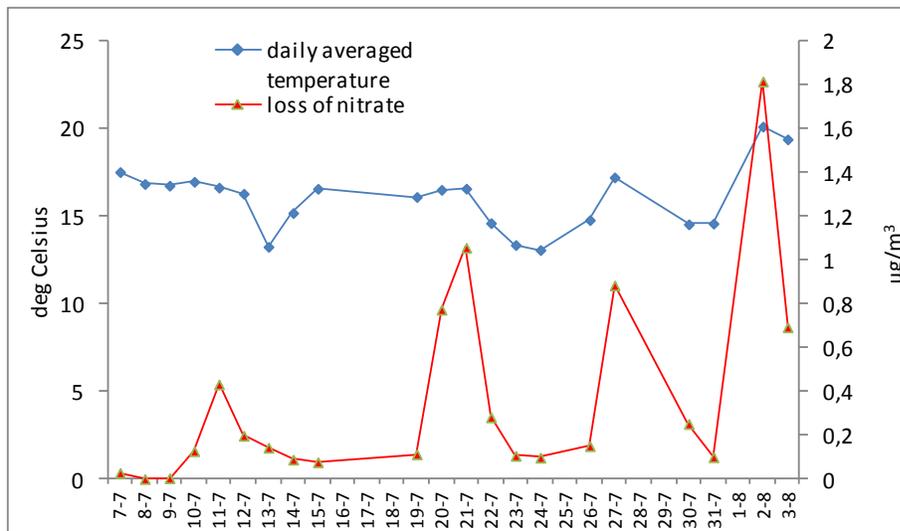
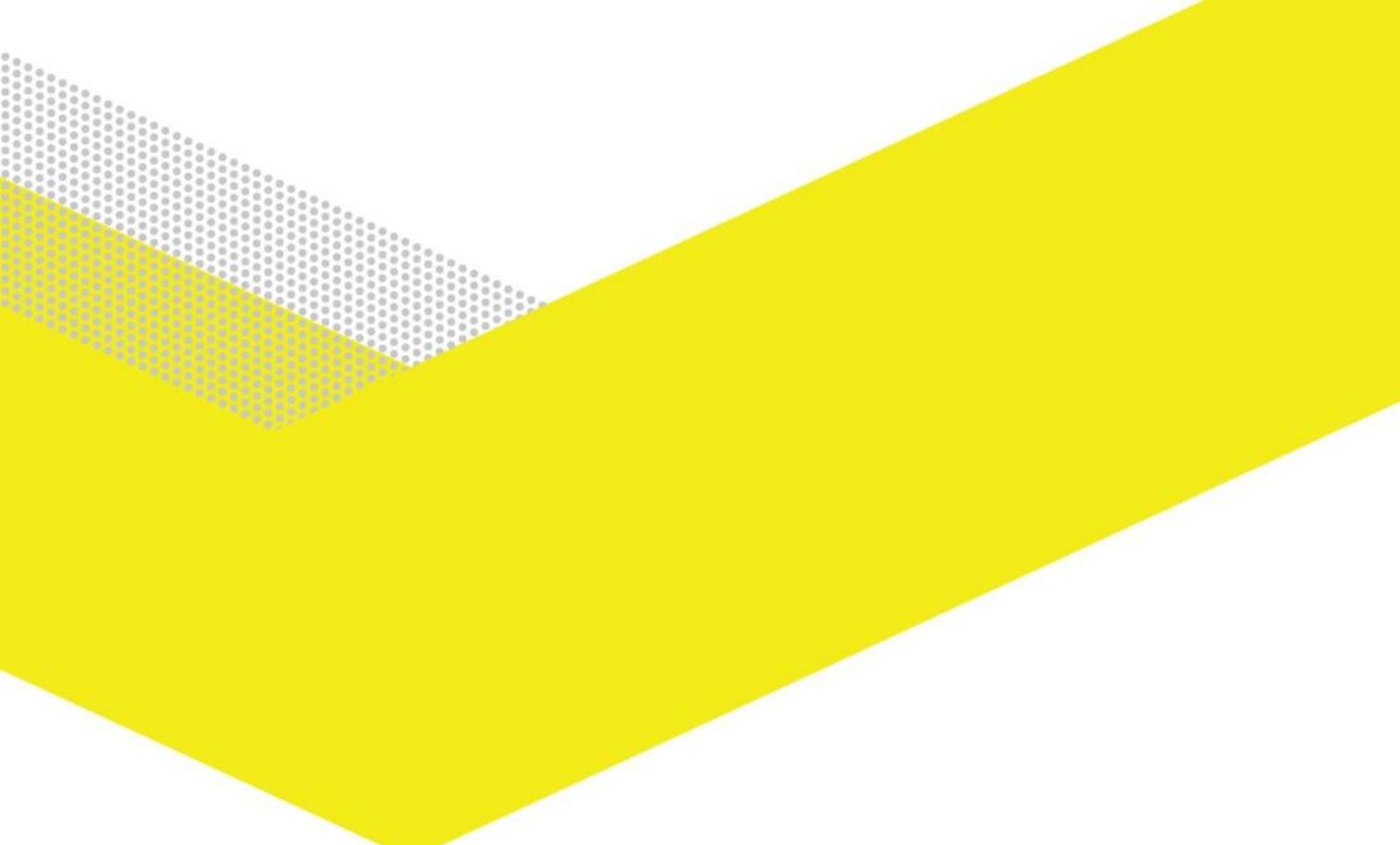


Figure 16 Loss of NO_3 mass and average temperature per day

A near-complete loss of chloride (i.e., more than 70%) occurred on six days (out of 21). It confirms that due to the depletion effect chloride is not an appropriate tracer for the estimation of the sea-salt contribution as discussed in Hoogerbrugge et al (2012).

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