

Measurements of secondary inorganic aerosols in the Netherlands

This is a publication of the Netherlands Research Program on Particulate Matter II



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Measurements of secondary inorganic aerosols in The Netherlands

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Summary

In this report two studies are presented that were executed within the framework of the second Netherlands Research Programme on Particulate Matter (“BOPII”). The first study (Chapter 2) describes a technical evaluation of the routine measurement methodology (LVS-RIVM) for secondary inorganic components (SIA) as applied in the National Air Quality Monitoring Network (LML) up to 2009. The incentive was an apparent underestimation in SIA concentrations observed when routine LML-results were compared with simultaneous measurements carried out according to the reference methodology (as part of BOPI).

The origin of the underestimation of the LVS-RIVM instrument could be established here. The reason is the technical configuration, in particular the inlet system that causes a large loss of PM. In addition, the analysis revealed that the loading of the filters did not proceed in an optimal manner due to leaking valves. The capturing efficiency seems to vary with different humid atmospheric conditions that changes the particles’ diameters. It is concluded that a correction of the SIA concentrations should be in the range 1.5-1.6 (in agreement with Hafkenschied et al. (2010)). These results implied that the SIA measurements in the LML network from before 2009 will not be used for the calibration of the GCN maps of air quality components.

The second study (Chapter 3) quantifies and interprets artefacts that occur when measuring PM10 with a filter mass collection instrument according to the reference methodology. An example is the evaporation from the filter during sampling of semi-volatile ammonium nitrate, the most dominant form in which nitrate is present in our region. The depletion of chloride is another example investigated here. During two experimental campaigns (in 2010 and 2011) the operation of the reference instrument (“Leckel”) was studied on unintentional loss of mass by using a Marga system, an instrument measuring the on-line chemical composition of PM10 by ion-chromatography.

The statement that no loss of mass occurs when measuring with the reference Leckel system (as claimed by the manufacturer) appeared untrue. Especially during fine weather conditions loss of nitrate and chloride has been measured during the campaigns. It is shown that higher ambient temperatures and low relative humidity favour the loss of PM mass from the filter. Even below 20°C volatilization of nitrate has been measured contrasting earlier reports.

In the long term, effect on PM levels will be negligible. On a daily basis, however, the effect the occurrence of daily exceedences. In the case of nitrate the loss could be as high as 1.8 $\mu\text{g}/\text{m}^3$. Considering the dominant role of nitrate during periods with high concentrations in Northwest Europe, it is anticipated that this evaporation of nitrate might lower the number of exceedences of the PM10 daily limit. However, further research is needed to substantiate this assumption which should include other instruments measuring according to the reference methodology.

Introduction

Secondary inorganic aerosols (sulphate, nitrate, ammonium; SIA) constitute a dominant part of particulate matter (PM) in the Netherlands. They are called secondary because they are not emitted directly into the atmosphere but are the products from chemical reactions concerning sulphur dioxides, nitrogen oxides and ammonia. These gases are emitted by transport, industry and agriculture, all abundantly present in north-western Europe. During the last decades their emissions decreased considerably and this resulted in lower ambient concentrations for SIA. However, from around the years 1999-2000, the rate of decrease weakened or even disappeared (Hoogerbrugge et al., 2010) and in the attainability of EU limit values, the SIA still play an essential role. In particular, this is the case for the nitrate component contributing more than any other component to the number of exceedences of the daily limit for PM10 in the Netherlands.

This report deals with the measuring of SIA aerosols, now and in the past. Today, on-line chemical speciation of PM is technically possible (MARGA, AMS) yielding concentrations every hour. An example is the implementation of such instruments in EPA's Clean Air and Trends Network (CASTNET; 2011). The more traditional approach (and consistent with EU guidelines) is the collection of PM on filters (over at least a day) which are chemically analysed afterwards. Though sounding straightforward, filter sampling techniques are prone to different kinds of artefacts. An example is the evaporation during sampling of semi-volatile ammonium nitrate, the most dominant form in which nitrate is present in our region (e.g., Schaap et al., 2002). This depends on the type of filter and ambient meteorological conditions (Chow, 1995). In the end, the loss of material leads to an underestimation of the true values. Another example is due to the filter type. Cellulose type aerosol filters may adsorb nitric acid which is then assigned to aerosol nitrate resulting in an overestimation (Savoie and Prospero, 1982).

Here, we present two studies that were executed within the framework of the second Netherlands Research Programme on Particulate Matter ("BOPII"). The first study describes the technical evaluation of the measurement method applied in the past in the National Air Quality Monitoring Network (LML). The incentive for this investigation was the mismatch observed in SIA concentrations when measuring with the traditional low-volume sampler (LVS, further denoted by LVS-RIVM) and the reference low volume sampler ("Leckel"). In the BOPI program this discrepancy finally led to the conclusion that the contribution of secondary inorganic aerosol to particulate matter air in the Netherlands was higher (30-50%) than originally thought. More on this can be found in Weijers et al. (2010) and Matthijsen and Koelemeijer (2010).

The second study focuses on possible differences in mass concentrations when measuring with the reference instrument for PM10 measurements as used today ("Leckel") and a Marga system. Measurements by the reference instrument are considered as the actual concentrations to be reported for policy purposes. However, as mentioned above the question remains whether filter measurements correspond with the actual ambient concentrations. The Marga system is an online measurement instrument that does not apply the traditional filter setup and therefore does not suffer from such an artefact. In this respect the latter can be considered as an approximation of the "true" ambient conditions in the atmosphere.

This report starts with a concise introduction of the instruments used in the technical analysis of the LVS-RIVM sampler and the experimental campaigns that were carried out (Chapter 1). The studies are then presented separately in Chapters 2 and 3 (which can be read independently from each other). To summarize, the following goals were defined in advance:

- Study 1: To quantify and interpret the mismatch/correspondence of the experimental results obtained by the 'traditional' LVS-RIVM sampler instrument compared to sampling following EN12341 ("Leckel").
- Study 2: To quantify and interpret the role of volatilization of particulate matter from the filter in the reference Leckel instrument when measuring PM10.

1. Instruments

The LVS-RIVM is shown in Figure 1.1. A volume of air (2500 l per 24 h) is sucked through the PM filters (eight in total) with a constant flow. Concentrations of sulphate, nitrate, ammonium and chloride were analyzed with the aid of ion-chromatography. The instrument has been used in the Dutch National Air Quality Monitoring Network (NAQMN; in Dutch: LML) for the daily determination of SIA and operated over an extended period (1993-2007). A schematic picture of the different parts is given in Figure 2.3.



Figure 1.1 *The Low Volume Sampler as applied in NAQMN (LVS-RIVM)*

The reference sampler considered here is the SEQ47/50 from Leckel GmbH in Germany (Figure 1.2). Its design and operation have been prescribed according to CEN guidelines (CEN EN 12341 and 14907; European Committee for Standardization) for PM10 and PM2.5. The instrument is widely used in national monitoring networks over Europe. Advantages are a relatively simple design and the fact that unattended measurements can take place over a period of 14 days which makes the instrument appropriate for long-term routine measurements. Here, Leckel filters have been chemically analysed for nitrate, sulphate, ammonium and chloride.



Figure 1.2 *The Low Volume Sampler SEQ47/50 (“Leckel”)*

The MARGA system has been developed for the collection of long-term data on the chemical composition of aerosols (Figure 1.3). It is (still) a relatively new technology that not only measures composition of particulate matter but also its precursors and acidifying gasses. The separation between gases and solid material is done by a Wet Rotating Denuder (WRD) and Steam Jet Aerosol Collector (SJAC). The chemistry of the collected samples is determined on-line by an integrated ion chromatograph producing hourly results on concentrations. Quality assurance of the measurement takes place with internal standards. The system shown here is one with one sample box, in the study presented here we used a version with two boxes.

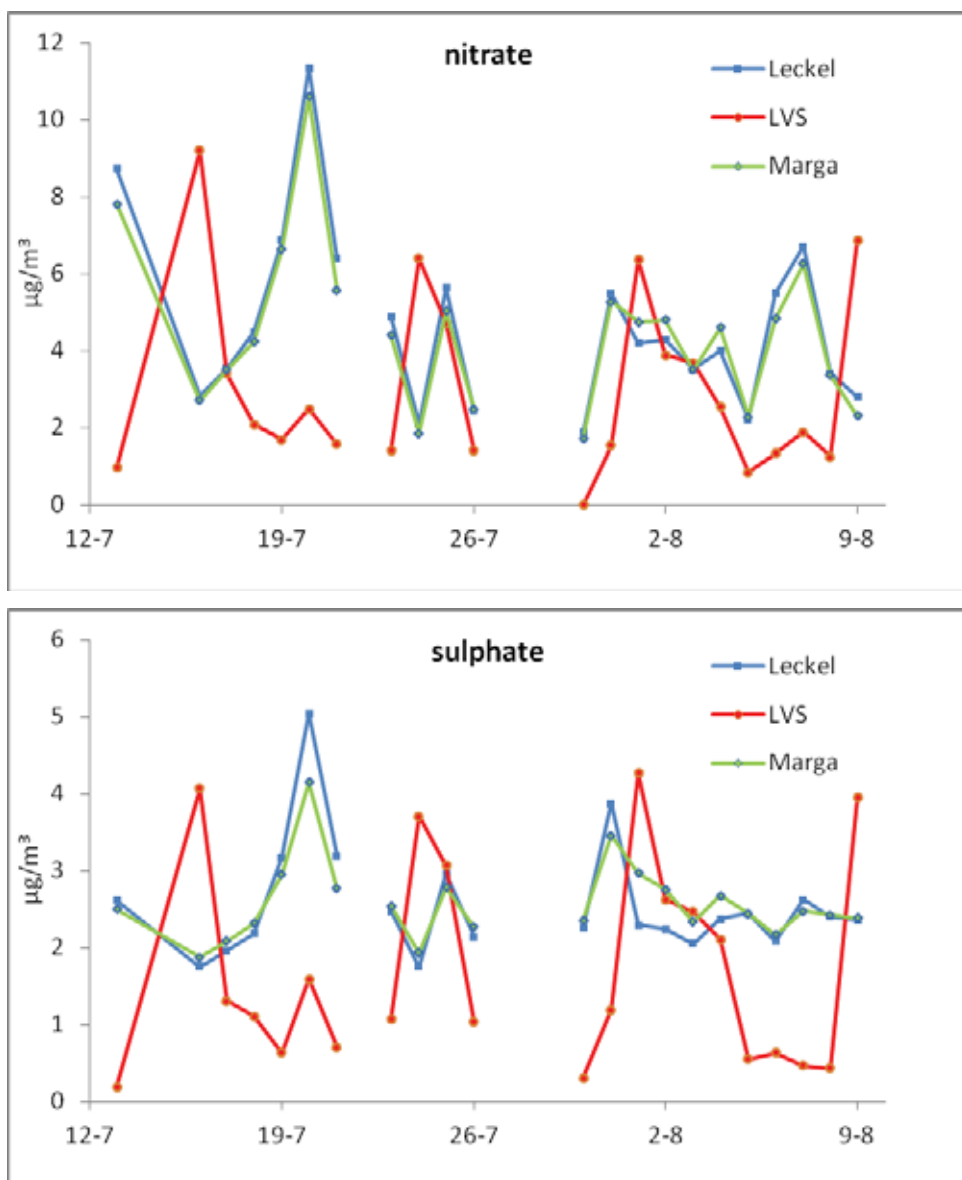


Figure 1.3 *The Marga system*

2. Investigation of the LVS –RIVM instrument

2.1 Time series

The investigation started with a comparison between the three instruments introduced in the previous chapter. The LVS-RIVM, Leckel and MARGA system were installed at the LML site of Wieringerwerf, a rural/marine site in the Northwest of the Netherlands (Province of Noord-Holland). An important reason for selecting this site was of a practical nature: no deviation would occur with the routines and procedures in the continuous SIA measurements within LML. The comparative measurements took place in the summers of 2010 and 2011. The motivation for choosing the summer period is that a maximum in the evaporation of the volatilized matter could be expected. (It was assumed that the LVS-RIVM would also suffer from such an artefact.) Firstly, the similarity in time between these instruments was examined. To this end, the daily values during the measuring campaign of 2010 are illustrated in Figure 2.1 for both the SIA components and chloride. The corresponding average concentrations and component ratios are given in Figure 2.2 and Table 2.1.



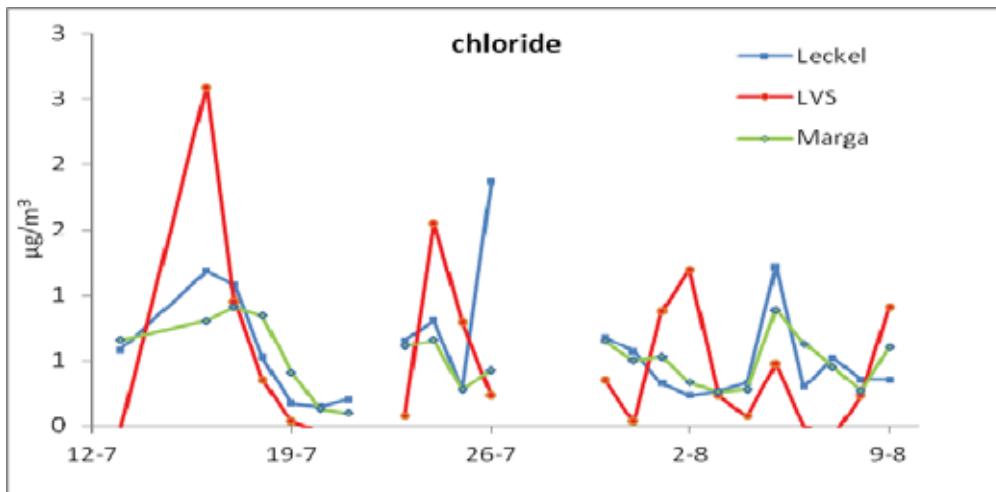
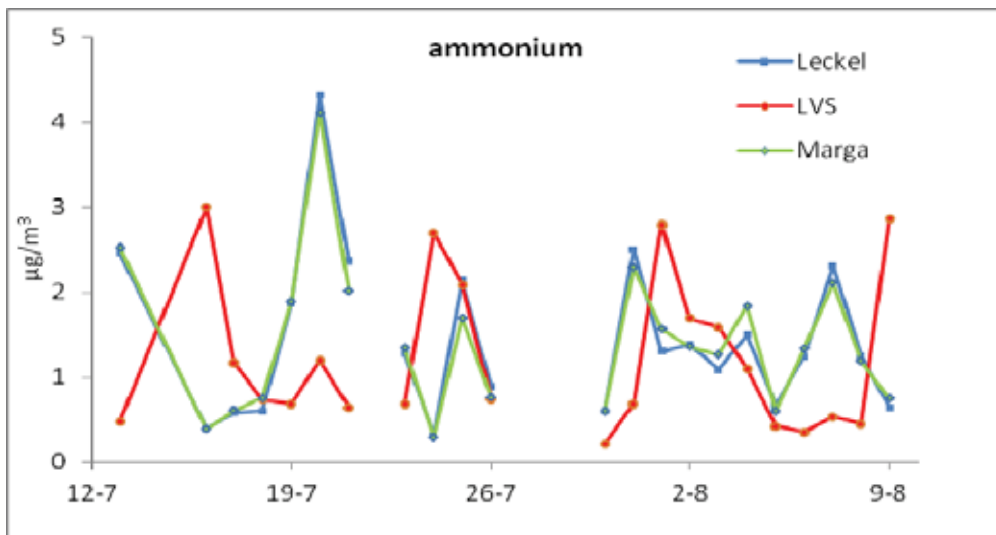


Figure 2.1 Time series of the LVS-RIVM, Leckel and Marga during the 2010 measurement campaign in Wieringerwerf

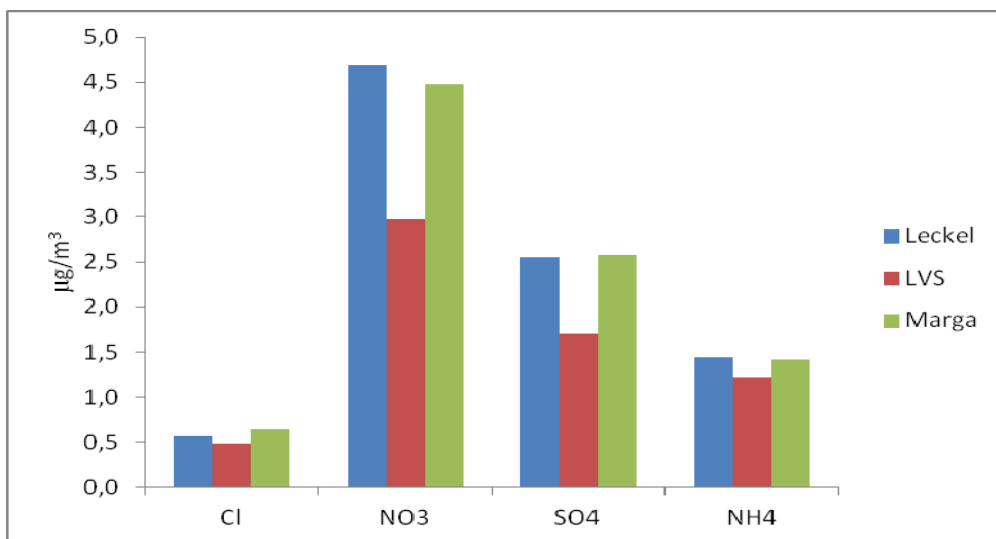


Figure 2.2 Average concentrations during the 2010 measurement campaign

Table 2.1 *Average concentrations and instrument ratios (Wieringerwerf, 2010)*

	Cl	NO3	SO4	NH4
Leckel	0.6	4.7	2.6	1.4
LVS-RIVM	0.5	3.0	1.7	1.2
Marga	0.6	4.5	2.6	1.4
LVS vs. Leckel	0.83	0.64	0.65	0.86

The Leckel and Marga time series show a considerable similarity. In these registrations one observes that the temporal behaviour is very similar for the different SIA components. Chloride performs a deviating almost opposite pattern. This is already well-known, meteorological circumstances and location of sources are responsible. In continental air, i.e. originating in areas east and southeast of the Netherlands, SIA levels are enhanced due to the (industrial) emissions of precursors like sulphur dioxide or ammonia. When the wind direction is Northwest or West, sea salt is abundantly present in the (marine) air while SIA levels are low (due to the absence of sources).

The time series of the LVS-RIVM also has mutual resemblances. Remarkable is that the behaviour of chloride now resembles that of the SIA components. In addition, large deviations exist compared to the Leckel (and Marga) series: correlation coefficients are mediocre to poor (around -0.26 for SIA; 0.32 for Cl). The strong resemblance between Marga and Leckel suggests that the deviating LVS measurements have a technical cause. Next to the deviating daily variation, there is also a systematic difference in collection efficiency. With efficiency is meant here the yield of PM (here: SIA and chloride) as produced by an instrument when compared to the 'ambient conditions'. This can be deduced from Table 2.1 where the ratio LVS-to-Leckel is less than 1 for all ions. This is confirmed by former investigations by Weijers et al. (2010) and Hafkenscheid et al. (2010).

Based on the time series alone, it is not possible to identify a technical cause. Beforehand one wondered whether certain (meteorological) circumstances could have exerted any influence. To find if any relationship exist correlation coefficients with temperature and relative humidity were calculated (see Table 2.2 below). The relation with temperature is reasonably strong for the Leckel and Marga instruments which can be explained by the varying weather conditions, i.e. higher temperatures in periods with offshore wind and lower in case of air transport across the sea. The relation with relative humidity is rather poor. Strikingly, high correlations are estimated for the LVS-RIVM, although not significant. It implies that when lower concentrations are measured this coincides with a higher relative humidity. This may be due to a lower cut-off diameter compared to Leckel instrument when measuring PM10. The binding of water leads to particles growing in diameter. This holds for chloride as well as for ammonium, nitrate and sulphate, although not necessarily to the same extent. A similar conclusion was drawn by Hafkenscheid et al. (2010).

Table 2.2 *Correlation coefficients with temperature and relative humidity. L: Leckel; lvs: LVS-RIVM; M: Marga*

	L_Cl	L_NO3	L_SO4	L_NH4	lvs_Cl	lvs_NO3	lvs_SO4	lvs_NH4	M_Cl	M_NO3	M_SO4	M_NH4
T	-0.43	0.77	0.73	0.74	-0.28	-0.05	-0.09	-0.02	-0.50	0.75	0.65	0.73
RH	0.15	-0.07	-0.04	0.10	-0.29	-0.30	-0.25	-0.31	-0.09	-0.01	0.05	0.11

2.2 Technical aspects

A schematic view of the different parts of the LVS-RIVM is given in Figure 2.3. The technical functioning of the LVS has been examined in detail at ECN. This study entailed the following steps:

1. analysis of the flow rate per filter and operation gas meter
2. determination of the capture efficiency of the instrument.

Based on the results, a correction factor was established for the mass efficiency of the measuring instrument in the case of SIA concentrations.

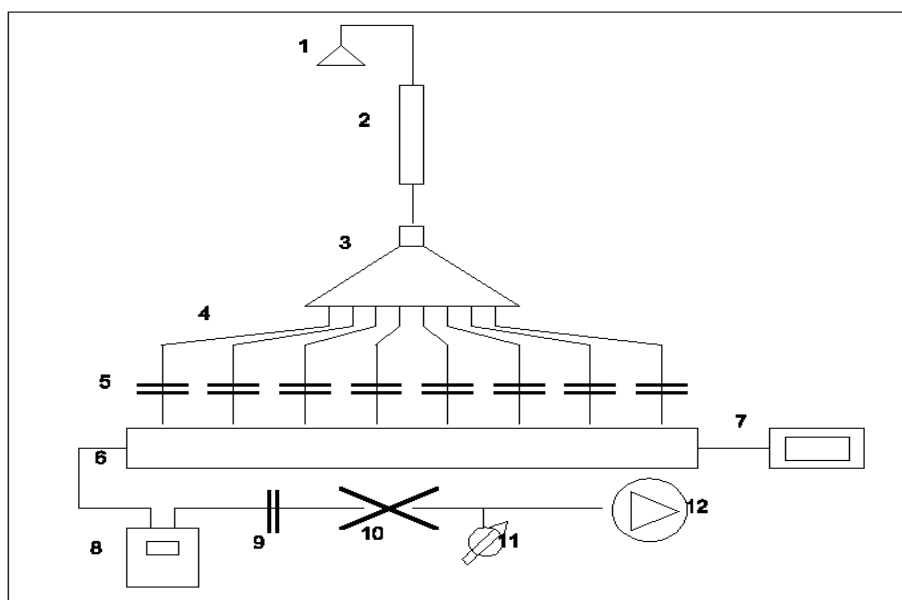


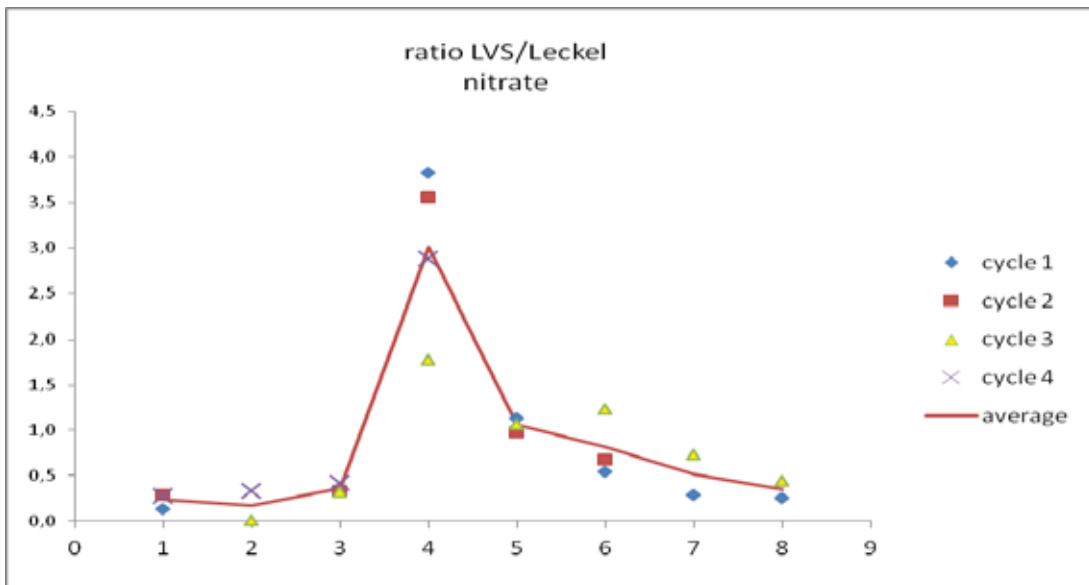
Figure 2.3 Schematic view of the Low Volume Sampler (Visser et al., 2001). 1: sucking funnel; 2: coal denuder; 3: allocation part; 4: sucking hose; 5: filter head; 6: manifold and valve box; 7: electronic steering clock; 8: gas meter; 9: protection filter; 10: critical orifice; 11: indicator underpressure; 12: vacuum pump (Visser et al., 2001)

2.2.1 Flow rate

A closer look of the time series registered with the LVS at the Wieringerwerf site (Figure 2.1) reveals a maximum value being measured once every eight days. Obviously, this applies to both SIA and chloride as a large similarity in time exists when measured with the LVS-RIVM. The fact that the maximum value is measured at such a regular interval suggests a periodical course. The repetition of eight days coincides with the replacement of the filters common in the LVS-RIVM during monitoring: after the eight day all (loaded) filters have to be replaced by empty ones after which the sampling repeats.

The behaviour can be visualised better by scaling the RIVM-LVS daily values with simultaneously measured concentrations by the Leckel instrument. In this way, corrections can be made for the changes in concentrations that occur in the open air under the influence of meteorology and transport. One example is illustrated in Figure 2.4a-b with regards to nitrate and sulphate as measured at Wieringerwerf in 2010. This campaign lasted 24 days, thus containing three cycles of eight days each.

(a)



(b)

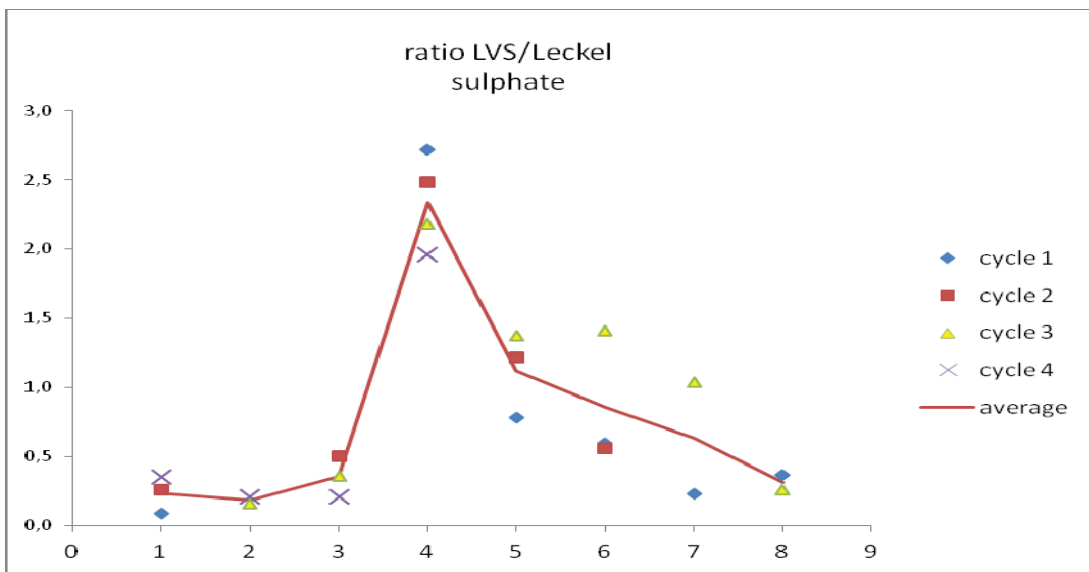


Figure 2.4 Ratios between concentrations measured with the LVS and Leckel during three consecutive cycles of eight days for nitrate (a) and sulphate (b)

What becomes visible is a repetitive pattern with a frequency of eight days. The question that arises is whether such a pattern would also be visible in the measurements of the SIA measuring network. To answer this question, data were used from the comparative measurement that took place in the second half of 2008 (August-December) (Hafkenscheid et al, 2010) at seven background stations in the Netherlands. Two examples of this data set are shown in Figure 2.5, illustrating the relation between the LVS and the Leckel (nitrate) for the Huijbergen and Kollumerwaard stations. This figure shows the daily concentrations for each of the eight filters.

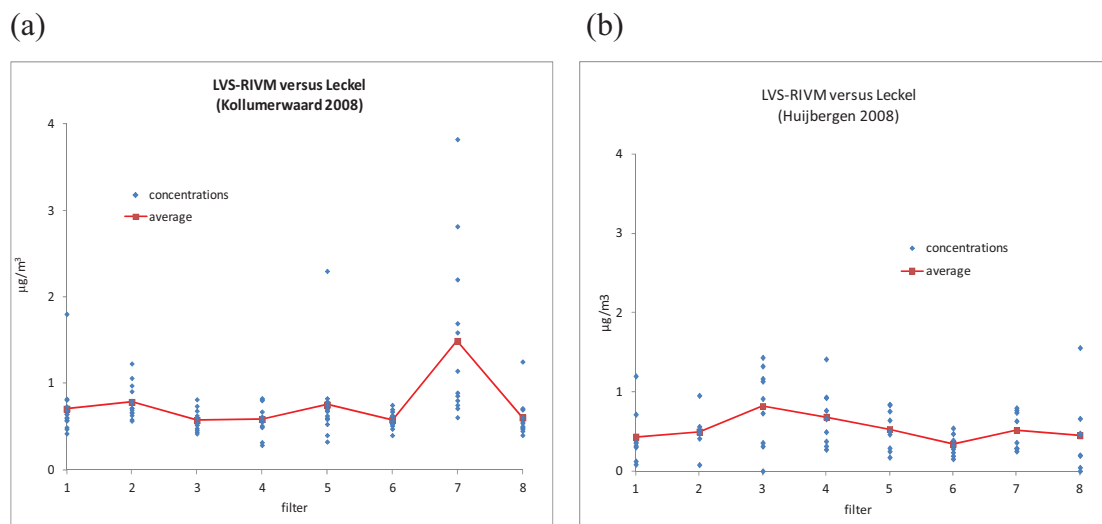


Figure 2.5 Ratios of concentrations of nitrate (raw data and average) measured with LVS and Leckel in Kollumerwaard (a) and Huijbergen (b)

Here, too, a comparable pattern can be seen. Based on the same data set, similar patterns have also been identified at other stations (though not always to the same extent). The above findings yield the conclusion that the system has a measuring artefact that influences the load per filter. An obvious explanation is that when a certain filter is loaded, the sealing valves close insufficiently, hence causing suction through other filters. Possibly one or more filters are also sampled due to a leaking valve. This affects the flow rate of these filter(s). A flow rate measuring per filter confirms this (Figure 2.6; the underlying values can be found in Appendix C). This means that the daily values of the LVS are unreliable. After establishing the amount of mass on each filter, this is subsequently divided by a (fixed) flow rate. In practise, the amount of air suction of this LVS is more or less than this fixed, chosen flow rate value. The result is a concentration value that deviates from the actual concentration in the ambient medium.

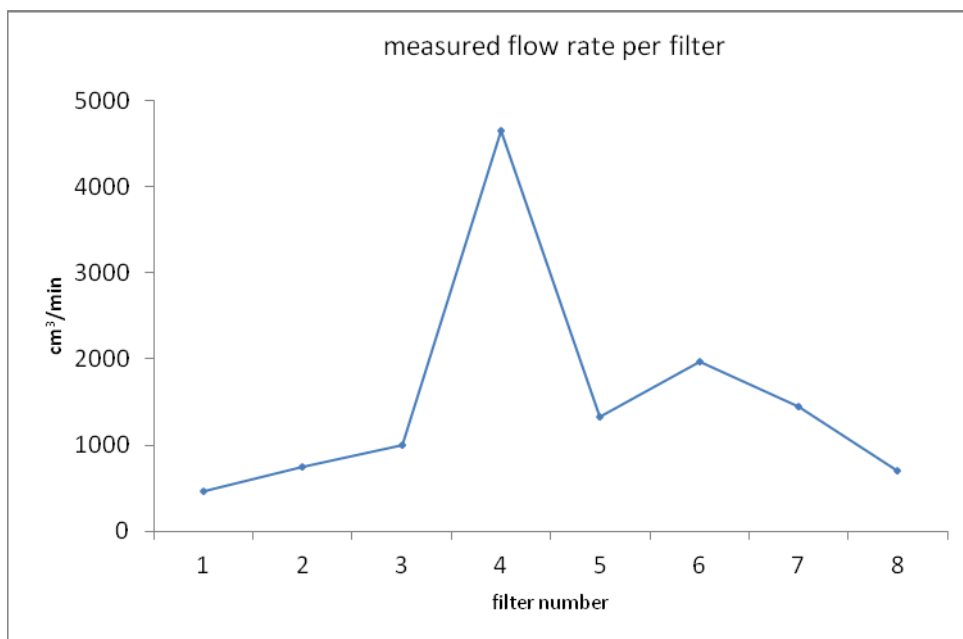


Figure 2.6 Flow rate per filter as measured in the LVS sampler over the measuring period of eight days

Averaging over a longer period (in a small data set at least a multitude of eight days) can still yield useful information (in case of open air concentrations that do not vary too much). After all, the total flow rate of eight days should be correct. However, a comparison between LVS and Leckel data from the 2008 campaign (Hafkenscheid et al., 2010) indicates (considerable) differences in the Leckel-to-LVS ratio (Figure 2.7).

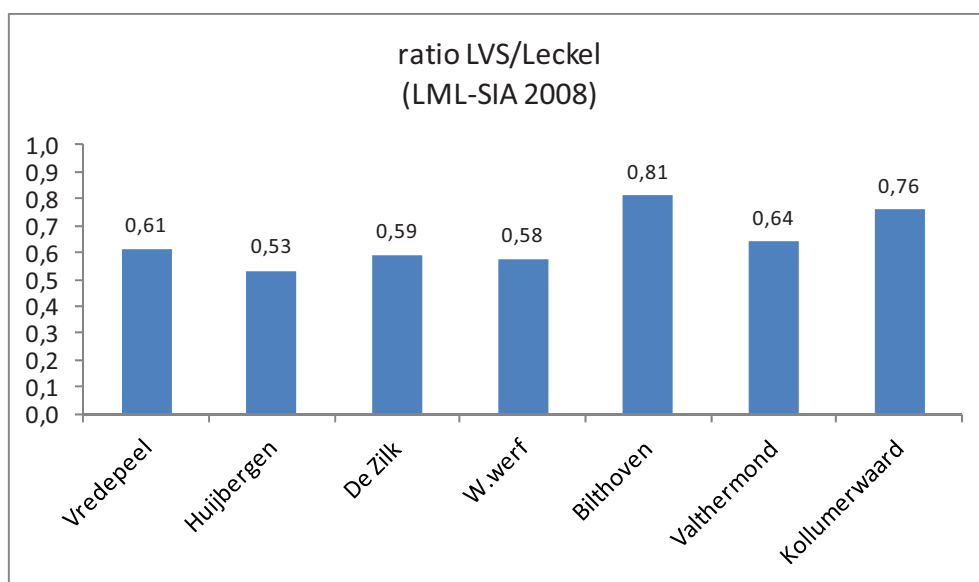


Figure 2.7 Ratio between concentrations for nitrate as measured with LVS and Leckel during a comparative campaign of RIVM in 2008

It is possible that the artefact described here will manifest itself in different ways in different LVS samplers, which makes them unsuitable for mutual comparison. Given that there was only one LVS apparatus, this could not be further studied. A second reason could be that the raw time series show extremes that are determined by the LVS cycle. After cleaning them up

(according to the criteria formulated by Hafkenscheid et al. (2010) these will be removed. However, these higher concentration values should not be left out because they actually compensate for the too low concentrations that have been measured with other filters. This (partly) explains why the concentrations are too low and also introduces differences in the ratio LVS/Leckel per station.

During this study, the flow rate of the critical orifice alone was also examined (location 10 in Figure 2.3) as well as the joint flow rate of the critical orifice tube and the filter. A critical orifice is a tube that is placed in the air inlet of a system to determine the flow rate. It has such a small opening that in case of sufficient low (absolute) pressure (equal to or lower than 0.5 bar) the flow rate is constant. The pressure gauge indicated about 0.4 bar of underpressure between pump and capillary tube (1 bar). This means that there was an absolute pressure of 0.6 bar between pump and orifice: this is not enough to have a constant flow rate when placing a filter, because this also brings along a significant drop in pressure. Eventually, the ratio (capillary tube)/(capillary tube + filter) turned out to lead to a 10% difference in flow rate. This coincided with the deviating volumes of the gas meter that was placed behind the filter as an indicative check for the entire system (location 8 in Figure 2.3). The gas meter was measuring in underpressure as a result of the drop in pressure, which led to the volume being overestimated with a factor 1.1.

2.2.2 Efficiency

To determine the throughput efficiency of the RIVM-LVS, a similar experimental set-up was used as in Wieringerwerf. Before the filter holders in the LVS, the supply was split up and led to an aerosol spectrometer (LasX PMS USA, range of 0.1-10 μm). The connection was made with a switchable ball valve. A similar switchable ball valve was used to make a direct connection from outside to the LasX with a length that was kept as short as possible. The pipes consisted of 1/4-inch, flexible, carbon-filled pipes that are designed specifically for high-efficiency throughput of aerosol. The valves are operated electrically and can be turned simultaneously by means of a time switch. This way consecutive measurements can be made with a LasX to determine the aerosol content in the open air and the amount of aerosol that would have been deposited on the filter (discriminating sufficient turning moments). Hence, a signal pattern evolves as shown in Figure 2.8; it shows the number of particles per cm^3 . The smallest particles are the most numerous and dominate the figure.

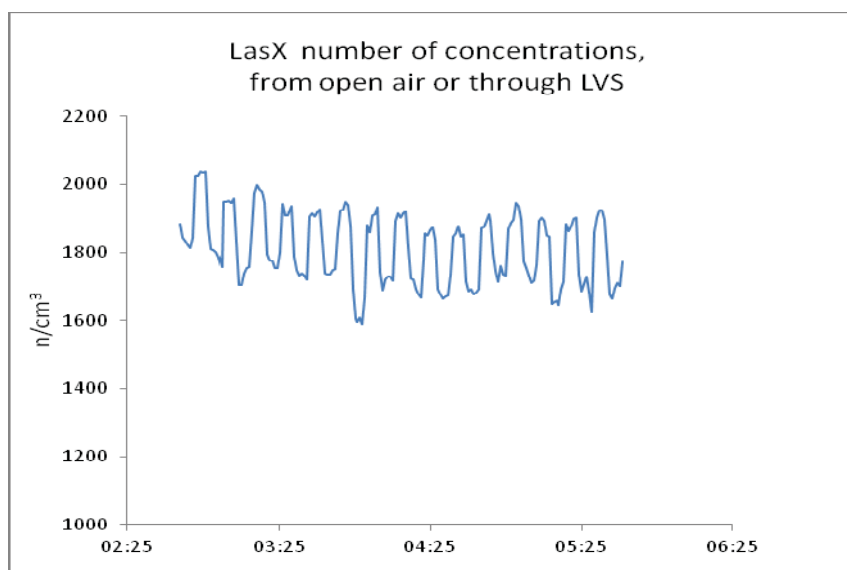


Figure 2.8 *Example of a time series measured with a test set-up, alternately measuring aerosol in open air and through LVS*

The LasX measured with 15 channels that were semi-logarithmically divided across a range of 0.1 to μm . Making series of the numbers of various particle sizes obtained in the open air or indirectly through the inlet system makes it possible to derive an efficiency curve for aerosol as can be present in the open air and what was present in the comparison period. During this period, the aerosol was obtained from the continent for part of the time and from the southwest for another part. The four-day period was averaged and shows a reasonably average picture of the aerosol that can be present in the Netherlands.

The result of this comparison is shown in Figure 2.9. The optical diameter was converted into an aerodynamic diameter. Next, a polynomial function was calculated to obtain an approximation of the decrease in yield. This figure shows a gradual decrease in the sampling efficiency as of about 500 nm. The 50% efficiency point is reached near 2 μm . Thus, for particulate matter in total, the RIVM-LVS appears to have functioned as sample-taking instrument for PM_{2.5} rather than for PM₁₀. Due to the blurred truncated diameter, the chemical compound of the collected particulate matter will also have been influenced by particles larger than 2 μm .

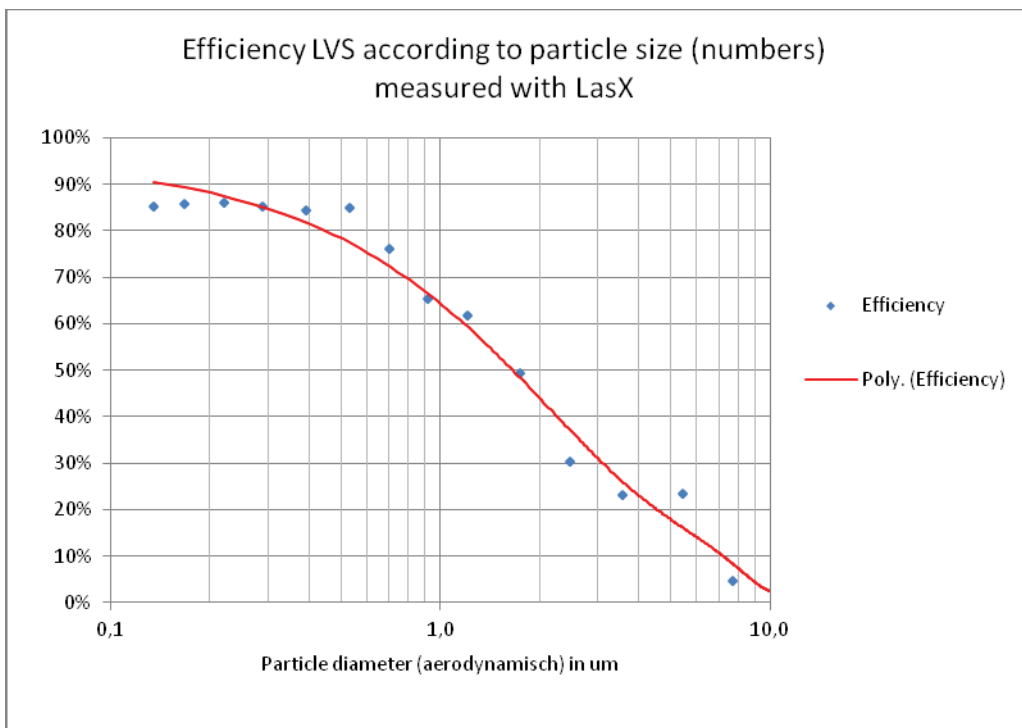


Figure 2.9 *Efficiency of RIVM-LVS (0.14-11.3 μm) and approximation with polynomial function. Each dot in the figure has a certain range in the aerosol spectrum. The last dot covers 7 to 9 μm , thus approaching the PM₁₀ scope sufficiently*

This function has now been used to calculate the volumes that have passed per particle size of the identified aerosol spectrum. The result is given in Figure 2.10. It can be derived that 70% of the aerosol mass present in the open air is below about 4 μm . The composition of the fraction larger than 4 μm is different: this is mostly sea salt and windblown dust. Below 4 μm , the particles mostly consist of secondary inorganics, EC and OC.

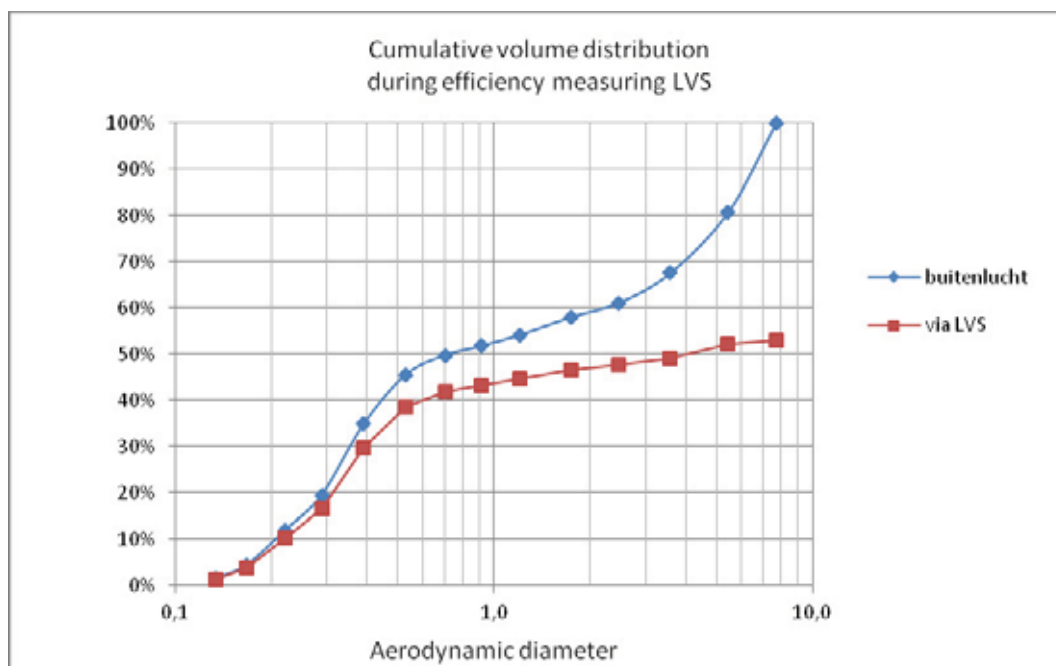


Figure 2.10 *Volume distribution of particles during test measuring: immediately in the open air and through the RIVM-LVS*

The spectrum of aerosol in the open air is variable and depends on the source (maritime and/or continental) and hence also the percentage of aerosol volume per particle size. The variation in the volume of the aerosol per particle size area also determines the efficiency of the sample taker as in the case of the tested RIVM-LVS. That is why the outcome of this test, containing a mixture of continental and marine aerosol, provides a good indication. By averaging the volume distributions of the ambient aerosol in the open air and the amount of aerosol in the LVS across a long time series, and subsequently dividing them by each other, you can establish the average efficiency of the RIVM-LVS.

If we compare the volume spectra found behind the inlet system and in the open air, the loss factor for PM₁₀ amounts to 1.9 (=100%/53%) based on Figure 2.10. SIA has a loss factor of 1.4 (=70%/50%). In the latter case, it is assumed that the fraction larger than 4 μm is negligible as this consists mainly of sea salt and windblown dust, hence no secondary inorganic aerosol.

2.2.3 Conclusions

Based on the comparative measurements from the BOP-I campaign (Weijers et al., 2010) and an RIVM campaign from 2008 (Hafkenscheid et al., 2010) the conclusion is drawn that the LVS delivers lower SIA concentrations compared to other particulate matter equipment (such as Leckel and Marga). To find out what causes this, the performances of the 'old' LVS sampler (used in the LML measuring network for SIA) were examined more closely in the framework of BOP-II. A new comparison measurement with Leckel equipment that was made during an intensive campaign in Wieringerwerf from July till August 2010 confirms the above-mentioned view. Both for sulphate and nitrate, the concentrations measured with the LVS were 35% lower. For ammonium, this amounted to 15%.

A check of the flow rate in the laboratory of ECN showed that not all eight filters in the LVS were taking in the air in the same way. Because a fixed flow rate was used in calculating the concentrations, this either meant that the concentration was too low (if the actual flow rate was lower than assumed) or too high (in case of a higher flow rate). As a consequence, the day concentrations of the LVS are less reliable. This explains the limited correlation with day values

of the other instruments. If the deviations were constant during previous periods, corrections can still be made if it is also known on which day the eight filters were sampled. Given the long duration of the sampling (1994-2008) this will probably not be the case. It is also possible that the sampling per filter has shifted in time due to failure.

The average values of the concentrations over a longer period of time will hardly be influenced by this effect although the standard deviation will remain significant. After all, the flow rate across longer periods of time will approach the actual flow rate. However, the data set of 2008, in which a period of four months was averaged, shows significant differences in the relation between LVS-Leckel per station. These may be the result of differences between the LSVs that were used. A possible correction would have to be established per measuring station. The comparative study that RIVM conducted in 2008 could be used for this purpose. However, this study is based on a comparative period of four months in 2008. Moreover, the LSVs should always have been location related and the failure should have remained unchanged. This is not very likely though.

During these checking measurements, the flow rate of the critical capillary tube was also examined. If the flow rate of the critical capillary tube was taken as real flow rate of the set-up and no correction was made for the pressure drop that was caused by the filter and led to a lower flow rate, this means that a correction needs to be made afterwards. The factor of this correction is about 1.1 (1.1 times lower flow rate and therefore 1.1 times higher concentration, the loss factor increases accordingly).

A second check measurement with the Las-X was done to establish the efficiency curve. This curve shows a gradual decrease in the sampling efficiency as of about 0.5 μm . The diameter used to capture 50% of the total mass is almost 2 μm . Thus, for particulate matter in total, the LVS appears to have functioned as sample-taking instrument for PM_{2.5}- rather than for PM₁₀. If we compare the volume spectra found behind the LVS-RIVM and in the open air, the loss factor for PM₁₀ amounts to 1.9 and SIA has a loss factor of 1.4.

In summary, the assumption that the LVS-RIVM underestimates the mass has been confirmed by this study. This is caused by the configuration of the instrument, and particularly the inlet system which causes a large share of the mass to be missed. This factor could vary under the influence of meteorology (particularly humidity). The previous idea was to calculate the factor variation as a function of meteorological parameters. This way, condensation on the particle depends on temperature and relative humidity, thus changing the size and hence also the capturing. However, the experiment showed that the loading of the filters of the set-up does not proceed in an optimal manner due to leaking valves. The filter is loaded to a higher or lower extent and this cycle is repeated every eight days (when the set-up remains unaltered). This means that the day concentrations are no longer representative and it is impossible to determine a relation with the daily meteorology. Based on this study, it is concluded that a (possible) correction of the SIA concentrations (as measured in the LML network with the LVS-RIVM) lies in the range of 1.5 to 1.6 (in agreement with the relation factor 1.58, as found by Hafkenschied et al. (2010)).

The outcome of the results from this study have been reported to the team at RIVM responsible for the production of large-scale concentration maps (GCN, see Velders et al. 2012). The GCN team uses the SIA measurements from the LML network to calibrate the particulate matter (PM) maps. The most important results from this study for GCN purposes, imply that the SIA measurements from the LML network from before 2009 (with the LVS-RIVM) can not be used for the calibration of the GCN maps of air quality components. Therefore, for the new GCN-maps only data from the Leckel measurements will be used for the SIA components.

2.3 Implications for trends in PM and SIA

As already mentioned, in the first BOP program it was found that the modelled and measured concentrations for SIA have previously been underestimated by 50 per cent. The new method applied by the Dutch national air quality monitoring network (LML) confirmed these findings. In this study and in Hafkenscheid et al. (2010) it was investigated whether the measurements of SIAs with the original LVS method over the period 1992-2008 can be corrected in order to estimate more realistic values over this period. This is especially important for the determination of long-term trends of the SIA components. Below we apply correction factors as found for all the SIA components in order to construct a new time series for SIAs over the period 1992-2010. First, we visually check for artificial trends in the time series, subsequently a trend analysis is performed for the SIA data. A trend analysis of SIA is especially useful when a trend analysis of PM₁₀ can also be performed at the same site, in order to determine how much SIA components are contributing to the actual decrease in PM₁₀ levels.

SIA components are currently measured at seven locations in the Dutch national air quality monitoring network (LML). However, *simultaneous long-term* measurements of SIA components *and* PM₁₀ are only available at four locations in the Netherlands. These four locations are Vredepeel (131), De Zilk (444), Wieringerwerf (538) and Valthermond/Witteveen (928/929). The last station is in fact a combination of two stations: Valthermond (929) replaced Witteveen (928) in 2000, Valthermond is located 19 kilometres northeast of Witteveen.

For all four locations trends are calculated of the concentrations of the sum of the SIA components and the PM₁₀ concentrations. The long-term measurements of the SIA components are obtained by using correction factors for the SIA components as measured by the original LVS monitoring method during the period 1992-2008. These correction factors are respectively 1.74 (nitrate), 1.74 (sulphate) and 1.13 (ammonium) as discussed in this work and earlier work by Hafkenscheid et al. (2010). For the years 2009 and 2010 measurements were taken based on the reference sampling (Leckel) of the PM₁₀ fraction of the SIA components. The years before 2009 have been based on samples collected with the original LVS method (as discussed earlier in this report).

Time series of the concentrations of PM₁₀ and SIA over the period 1992-2010 are presented in the Figures 2.11-2.14. No apparent breaks in the time series are observed due to the switch in 2009 to a new monitoring system. Furthermore, one can see that on average roughly half of the PM concentrations come from the contribution of SIA components. Subsequently, a trend analysis is performed: an overall trend analysis is performed for the period 1992-2010, after which this period is split up in two parts: 1992-2000 and 2001-2010. The results of the trend analysis are shown in Tables 2.3-2.6, which are further discussed below.

The decrease in PM over the period 1992-2010 is on average, 0.90 µg/m³ per year of which the SIA components contribute more than half, i.e. on the average of 0.55 µg/m³ per year (both numbers estimated over the four stations). The results in the Tables 2.3-2.6 also seem to indicate that the decrease in concentration in both PM₁₀ and SIA are larger over the period 1992-2000 than in the period 2001-2010. A statistical analysis is performed to test whether these change in trends are significant. The analysis follows the method which was also used in an earlier BOP-report (Hoogerbrugge et al. 2010). The results of this statistical analysis show that the change in trends between the first (1992-2000) and second period (2001-2010) is only significant for SIAs and not for PM₁₀. The stagnating trends in the last decade could be explained by increased emissions of gaseous precursors on the European continent during this period (e.g., see Weijers et al., 2010).

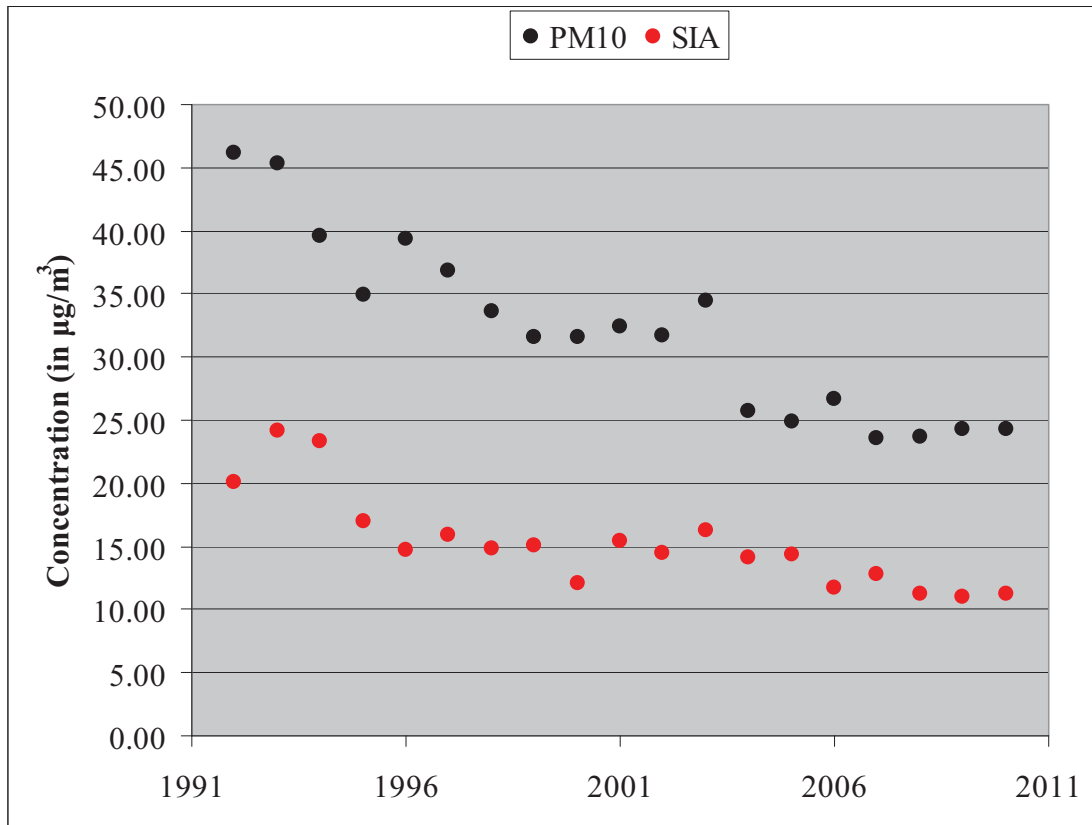


Figure 2.11 The concentration of SIA (red dots) and PM₁₀ (black dots) in units of µg/m³ over the period 1992-2010 at the location of Vredepeel (131)

Table 2.3 Trend analysis for the SIA and PM₁₀ components at the location of Vredepeel

	Reduction	Interception	P-value
Trend PM10 1992-2010	-1.18	42.8	<0.01
Trend SIA 1992-2010	-0.55	20.2	<0.01
Trend PM10 1992-2000	-1.82	45.0	<0.01
Trend SIA 1992-2000	-1.29	22.6	<0.01
Trend PM10 2001-2010	-1.11	32.2	<0.01
Trend SIA 2001-2010	-0.57	15.8	<0.01

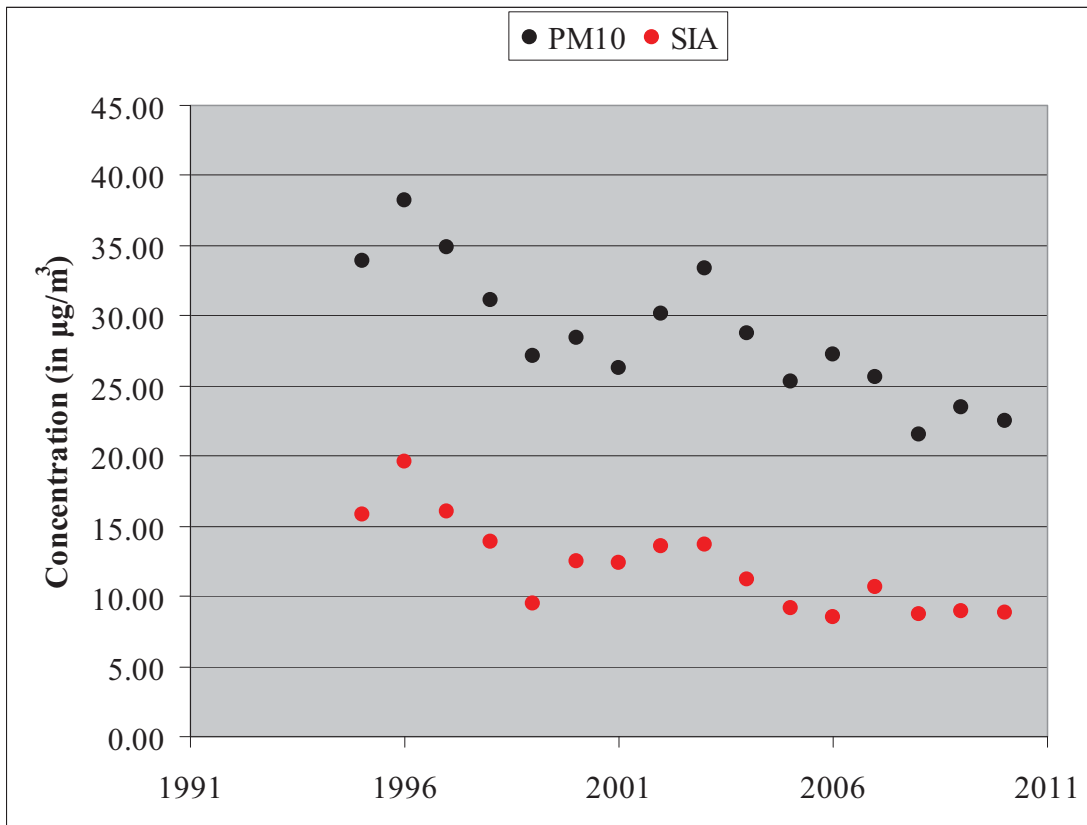


Figure 2.12 The concentration of SIA (red dots) and PM₁₀ (black dots) in units of µg/m³ over the period 1995-2010 at the location of De Zilk (444)

Table 2.4 Trend analysis for the SIA and PM₁₀ components at the location of De Zilk

	Reduction	Interception	P-value
Trend PM10 1995-2010	-0.83	34.8	<0.01
Trend SIA 1995-2010	-0.56	16.2	<0.01
Trend PM10 1995-2000	-1.84	36.9	0.04
Trend SIA 1995-2000	-1.42	18.1	0.08
Trend PM10 2001-2010	-0.88	30.4	0.01
Trend SIA 2001-2010	-0.56	13.0	<0.01

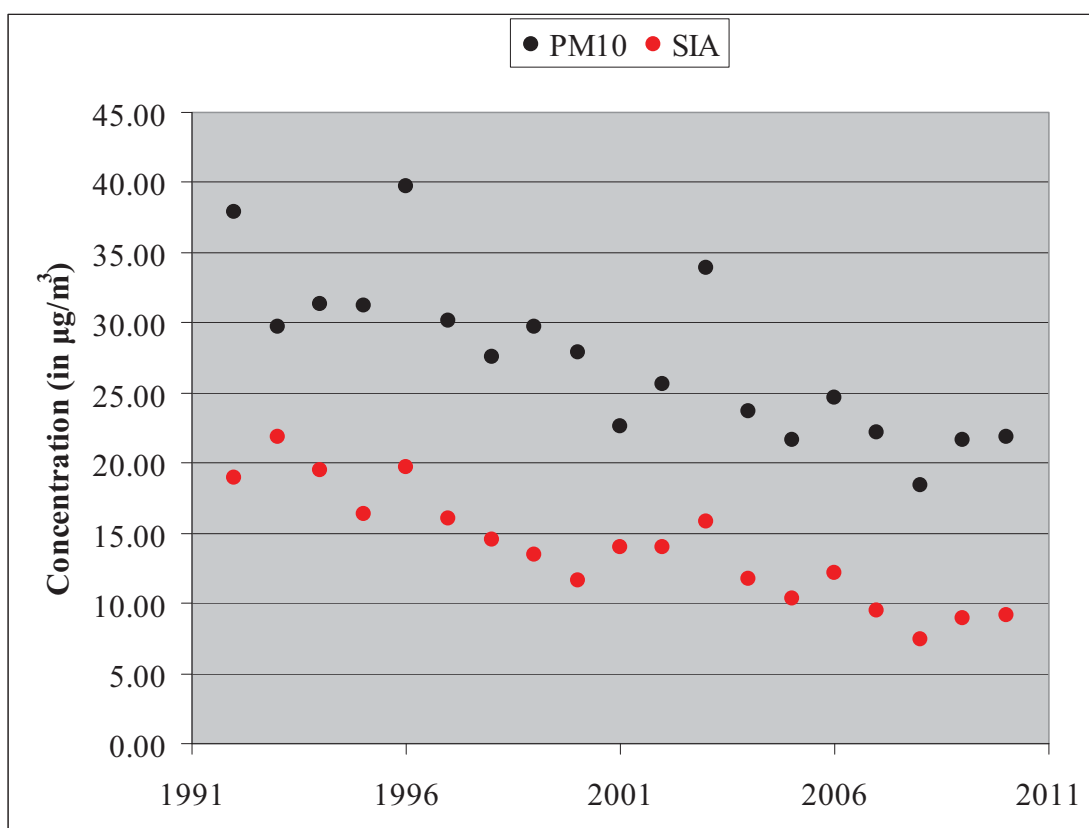


Figure 2.13 The concentration of SIA (red dots) and PM_{10} (black dots) in units of $\mu\text{g}/\text{m}^3$ over the period 1992-2010 at the location of Wieringerwerf (538)

Table 2.5 Trend analysis for the SIA and PM_{10} components at the location of Wieringerwerf

	Reduction	Interception	P-value
Trend PM_{10} 1992-2010	-0.82	34.8	<0.01
Trend SIA 1992-2010	-0.66	19.9	<0.01
Trend PM_{10} 1992-2000	-0.81	34.9	0.15
Trend SIA 1992-2000	-1.08	21.2	<0.01
Trend PM_{10} 2001-2010	-0.69	33.0	0.13
Trend SIA 2001-2010	-0.76	21.6	<0.01

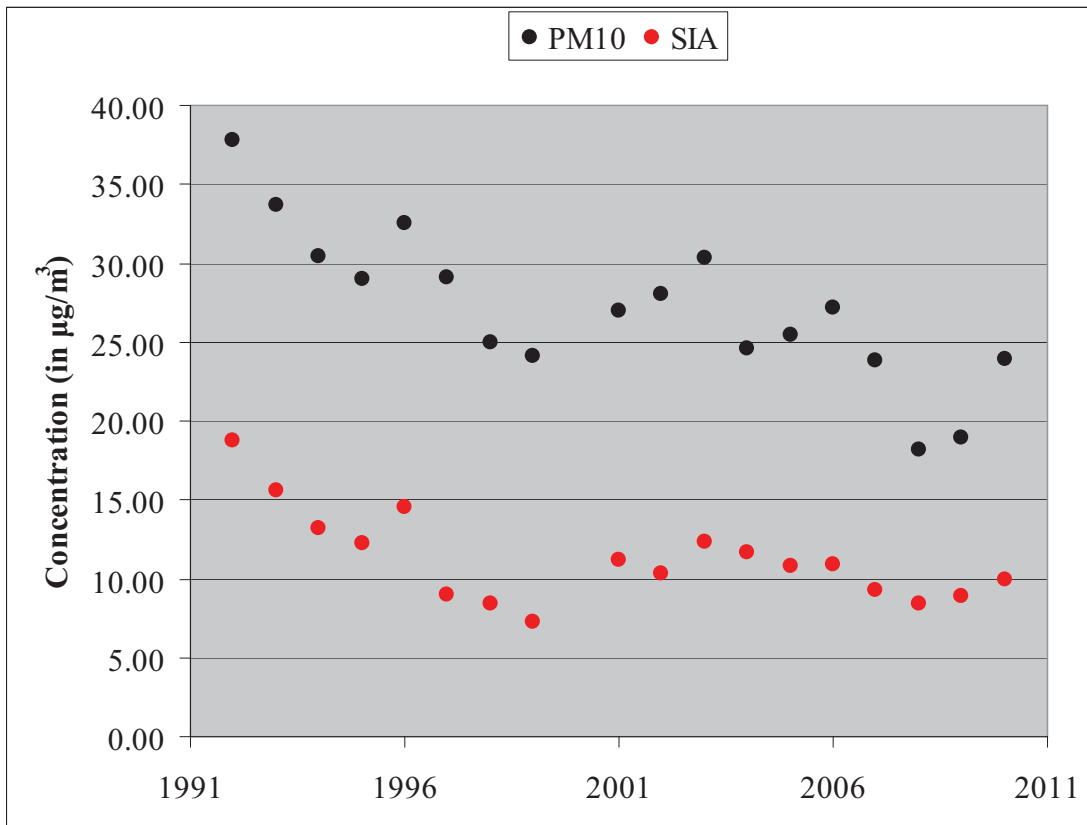


Figure 2.14 The concentration of SIA (red dots) and PM₁₀ (black dots) in units of µg/m³ over the period 1992-2010 at the location of Valthermond and Witteveen (928/929)

Table 2.6 Trend analysis for the SIA and PM₁₀ components at the location of Valthermond/Witteveen

	Reduction	Interception	P-value
Trend PM10 1992-2010	-0.68	33.4	<0.01
Trend SIA 1992-2010	-0.31	14.1	<0.01
Trend PM10 1992-2000	-1.66	36.0	<0.01
Trend SIA 1992-2000	-1.50	17.6	<0.01
Trend PM10 2001-2010	-0.93	28.9	0.02
Trend SIA 2001-2010	-0.30	11.7	0.02

3. Loss of particulate matter in filter measurements

3.1 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 nitrate 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 nitrate and chloride) 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.

3.2 Experimental setup

A (very) schematic setup is given in Figure 3.1. 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.

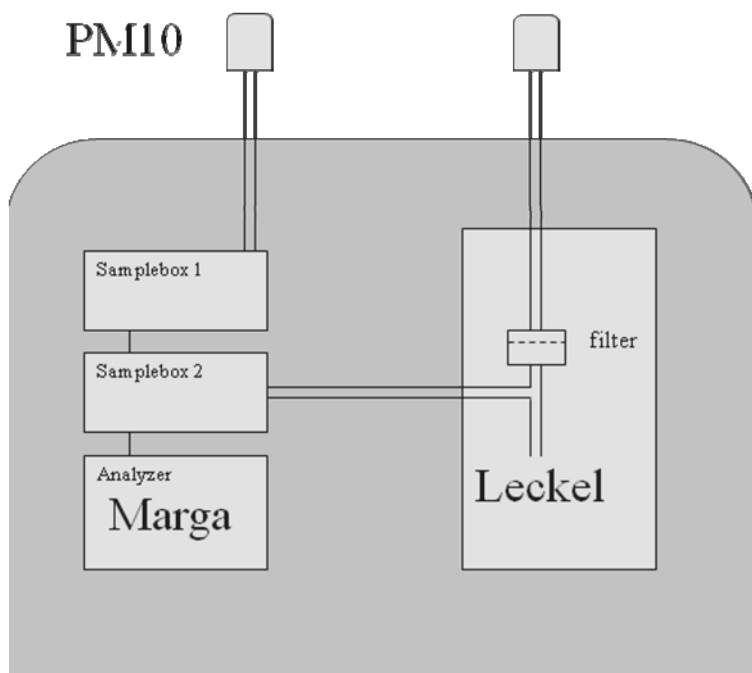


Figure 3.1 *Schematic experimental setup*

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, ammonia 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 nitrate, sulphate, ammonium and chloride. 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.

3.3 Marga time series

An illustration of a time series collected with the Marga instrument has been shown in Figure 3.2. This is a registration of SIA components (chloride, nitrate, sulphate and ammonium) during the 2nd campaign at Wieringerwerf (July-August 2011). Clearly discernible are the periods with rather elevated concentrations for nitrate. At least 10 times the concentration value is larger than 5 $\mu\text{g}/\text{m}^3$; twice its level rises well above 15 $\mu\text{g}/\text{m}^3$ (4-7 August). It is further observed that during these days ammonium and sulphate concentrations are high as well indicating the presence of ammonium nitrate and ammonium sulphate salts. For the periods in between chloride 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.

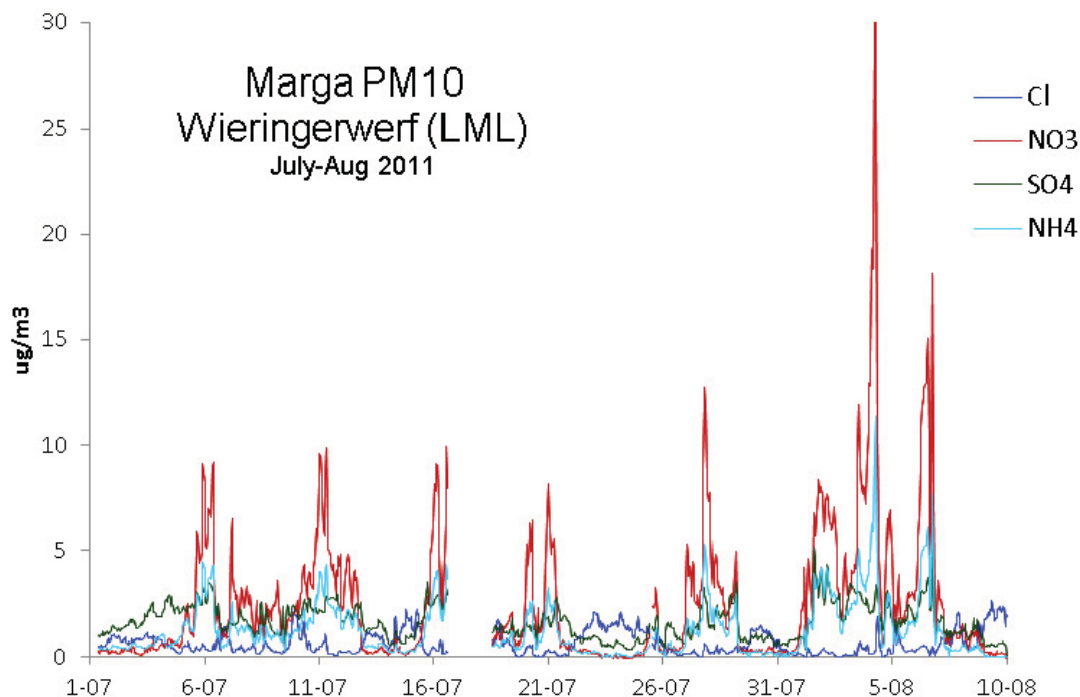
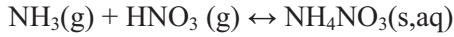


Figure 3.2 *Time series of SIA components during the second BOP campaign at Wieringerwerf*

3.4 Chemistry

3.4.1 Formation of ammonium nitrate

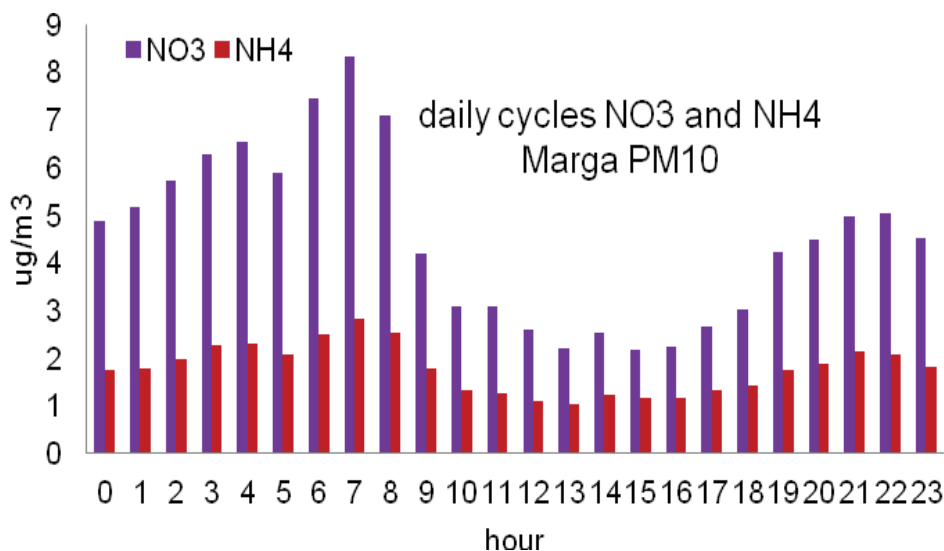
Gas-aerosol partitioning of ammonium nitrate (NH_4NO_3) in the atmosphere takes place between the gases ammonia (NH_3) and nitric acid (HNO_3) according to



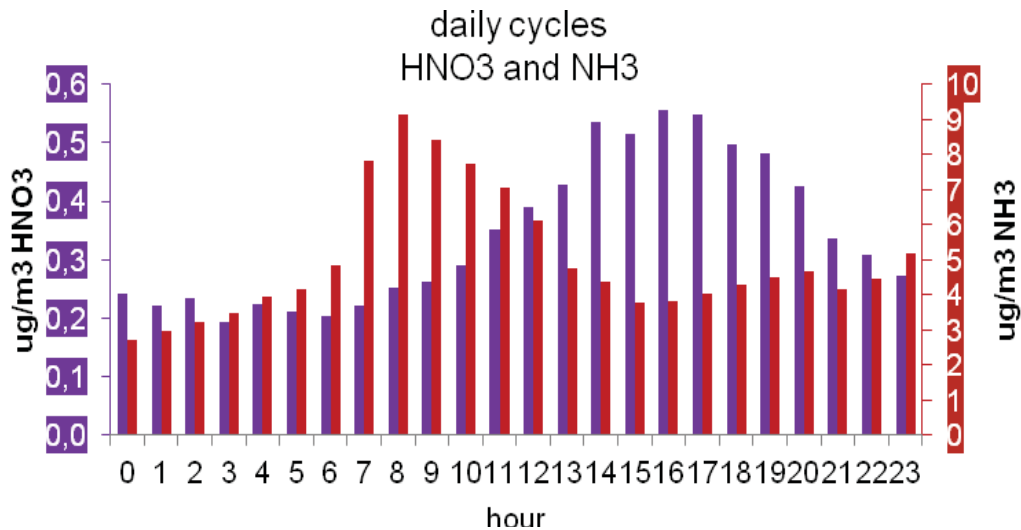
where 'g', 's' and 'aq' stands for gas, solid and aqueous (physical state), respectively. Due to intensified agriculture and large traffic volumes, ammonia and nitrogen oxide are abundantly present in the ambient air in the Netherlands. An important role is played by nitric acid which is a product of 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 ammonium nitrate will be formed or evaporated. For example, when temperature rises the gas-phase precursors will be released from the aerosol (decreasing the nitrate and ammonium 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 ammonium nitrate aerosol.

The influence of temperature can be observed in the daily cycles of aerosol nitrate and ammonium as well as nitric acid (see Figure 3.3a-b). During the day the concentrations of NO_3 and NH_4 are considerable 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 ammonia the pattern differs from HNO_3 for two reasons. The maximum level occurs in the early morning which is due to ammonia deposited during the night (trapped in moisture) as temperatures rises. In addition, the absolute contribution from the aerosol partitioning reaction during the day is relatively small compared to ambient levels of ammonia in the daytime.

(a)



(b)



(c)

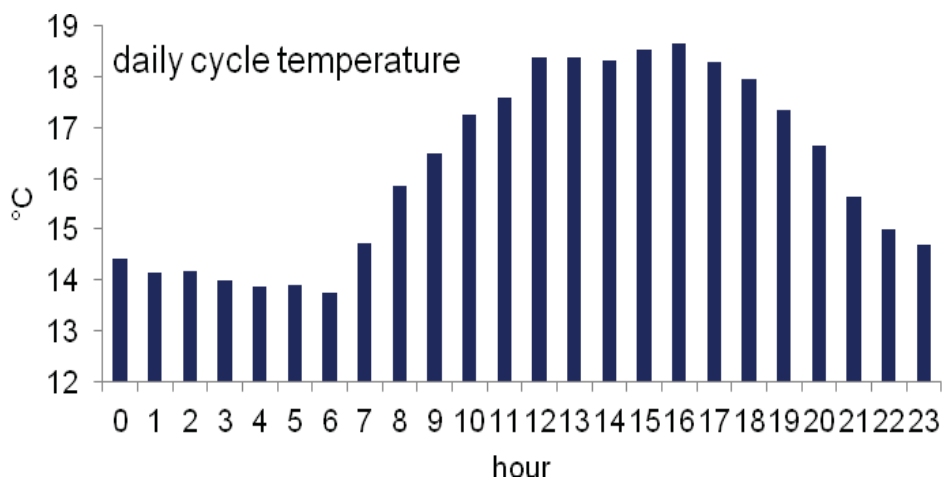
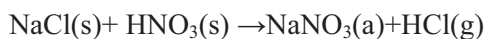


Figure 3.3 Daily cycles of (a) nitrate and ammonium salts, (b) gaseous precursors (nitric acid and ammonia) and (c) temperature as derived from Marga measurements during the second Wieringerwerf experimental campaign

3.4.2 Depletion of chloride

The ‘depletion of chloride’ is another reaction of interest here. Again, HNO₃ plays an important role here. Coarse sea salt particles act as a reactive sink for nitric acid. At first, HNO₃ adsorbs on sea salt aerosol. The chloride present is then removed from the aerosol under the formation of sodium nitrate and the release of gas-phase HCl (hydrogen chloride) according to



producing stable sodium nitrate. Part if not all of the solid chloride is lost while ‘some’ nitrate is gained. Taking into account the molecular masses of chloride (35) and nitrate (62), respectively,

the reaction results in some additional solid (nitrate) mass that will arrive in the coarse fraction due to the binding with sodium.

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 3.4 shows the average daily cycles of the chloride deficit and gaseous HCl at the Schiedam site in the BOP campaign. In seawater, the chloride-to-sodium 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.

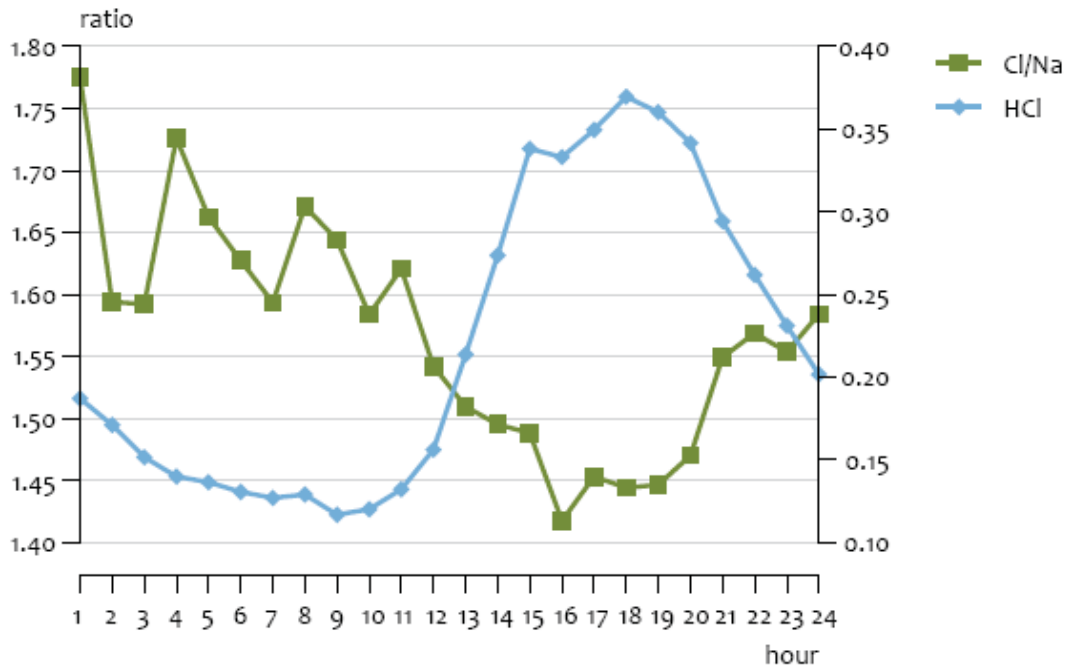


Figure 3.4 Daily cycles of Cl/Na and HCl, as measured with the MARGA system at Schiedam during the BOPI campaign

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.

3.5 Results

That evaporation of gases from the filter indeed takes place can be seen in Figure 3.5, 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 HNO₃ 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.

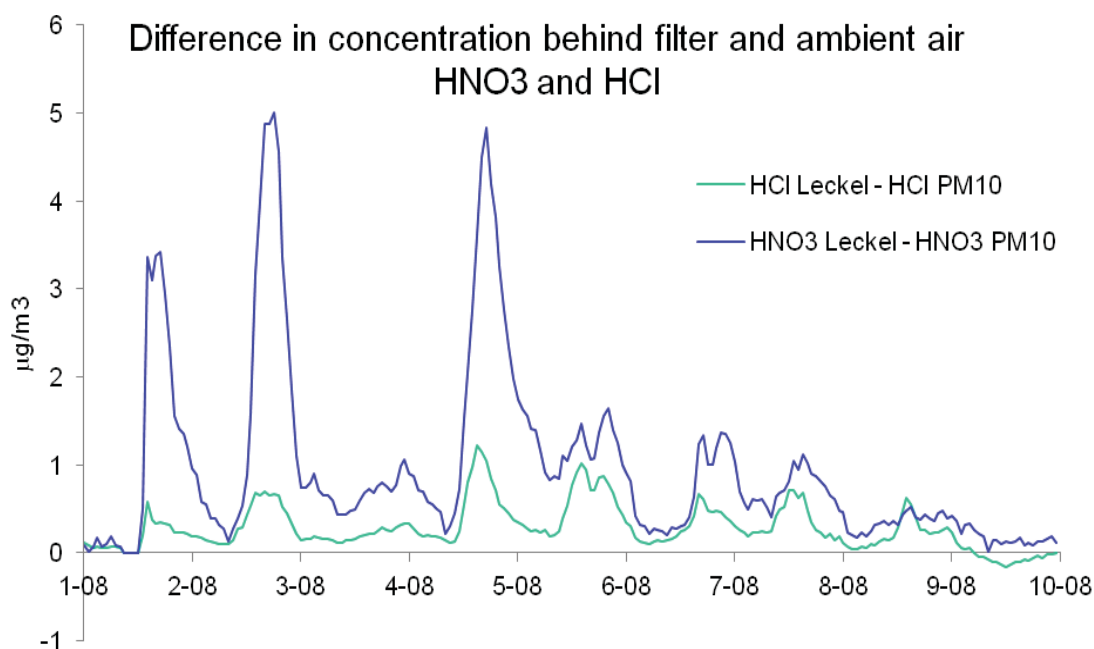


Figure 3.5 *Registration of HNO₃ and HCl evaporated from the filter as measured in the Leckel instrument*

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 3.6a-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 ammonia and nitric acid disappears from the filter. Because the ammonia 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 nitric acid the concentration difference over the filter is well above the levels in ambient air (compare Figure 3.6a with Figure 3.3b). 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 3.3b), inside the Leckel instrument condensation might take place when warmer and moist ambient air enters the instrument. This will capture part of the ammonia 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 chloride depletion process which might explain the occurrence of a maximum value of gaseous HCl preceding the maximum seen in the HNO₃ series.

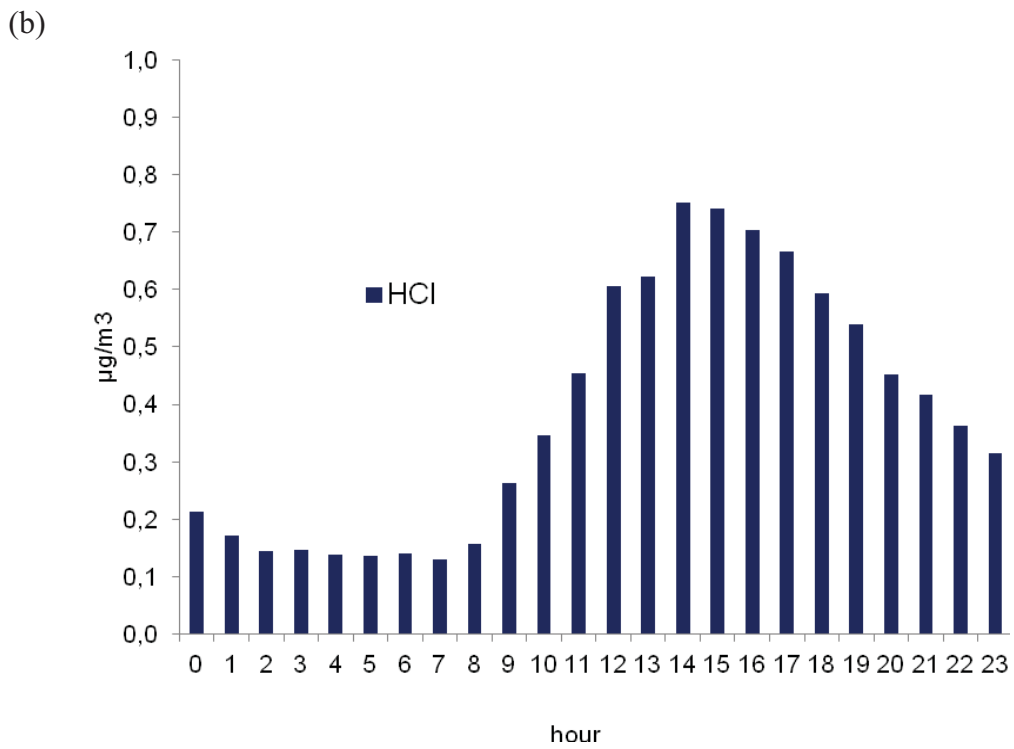
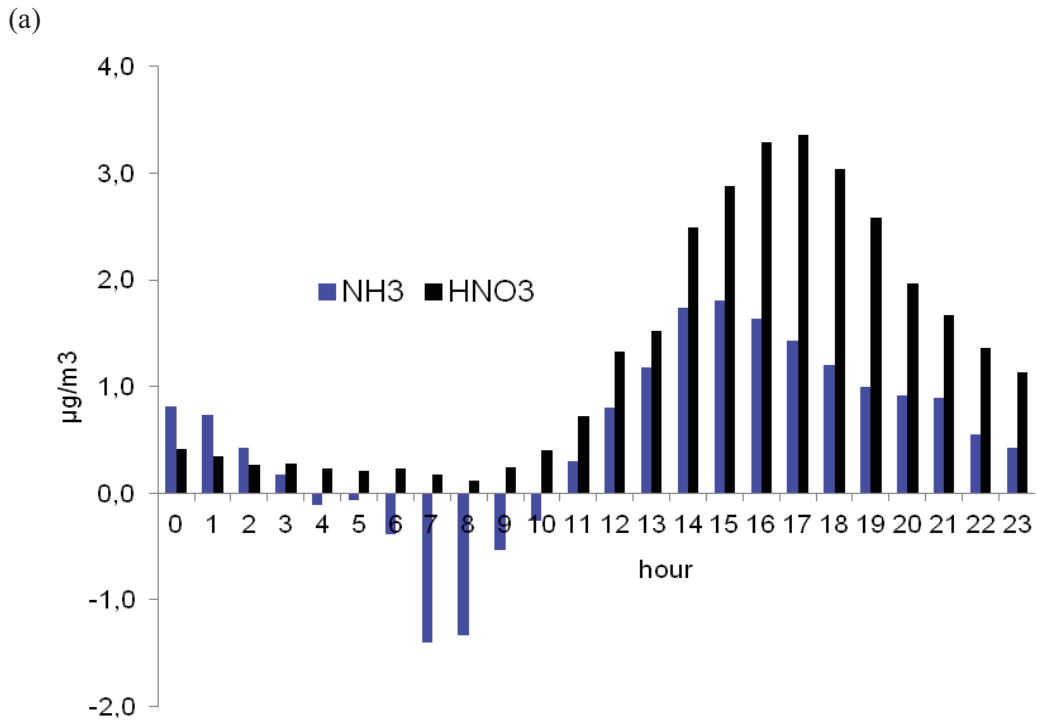


Figure 3.6 Daily cycle of the concentration differences before and after the Leckel filter for HNO and NH₃ (a), and HCl (b); averages over six events

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 3.7 where all available data regarding the differences in HNO₃ concentrations as function of temperature are shown. For the 2010 data set a similar pattern has been observed. Clearly, the chance on evaporation of HNO₃ 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 3.8. 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 3.9 and 3.10) indicate, like in the case of HNO₃, the dependence on temperature and relative humidity is evident.

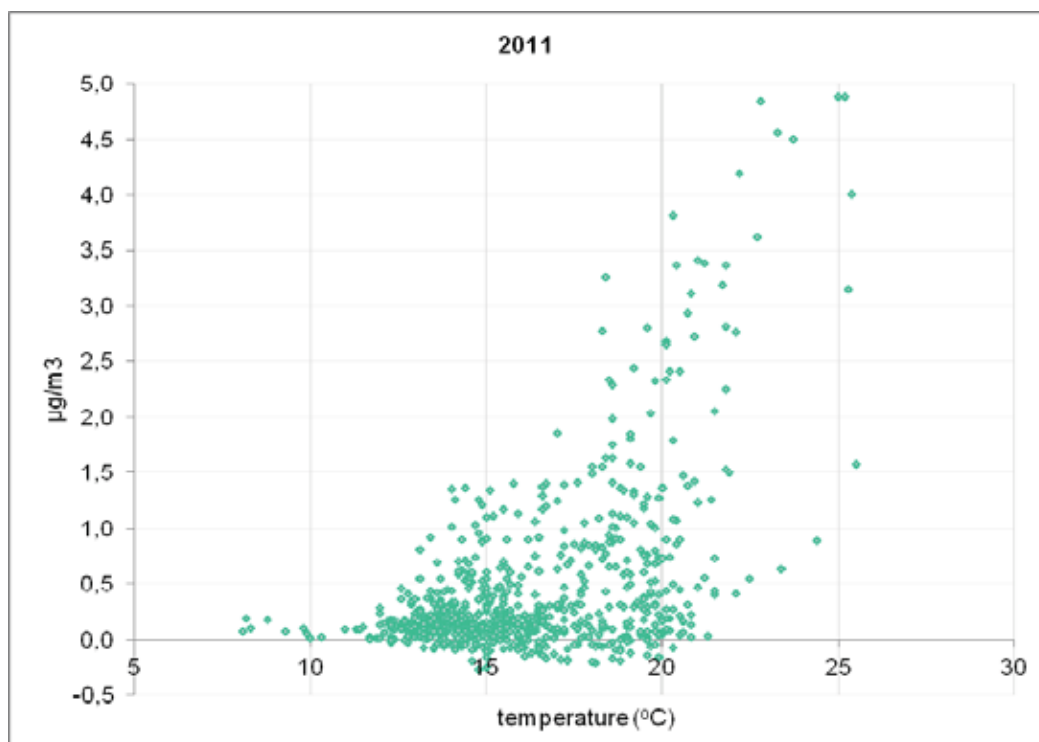


Figure 3.7 *Difference in the hourly measured HNO₃ concentrations before and after the Leckel filter as function of ambient hourly temperature*

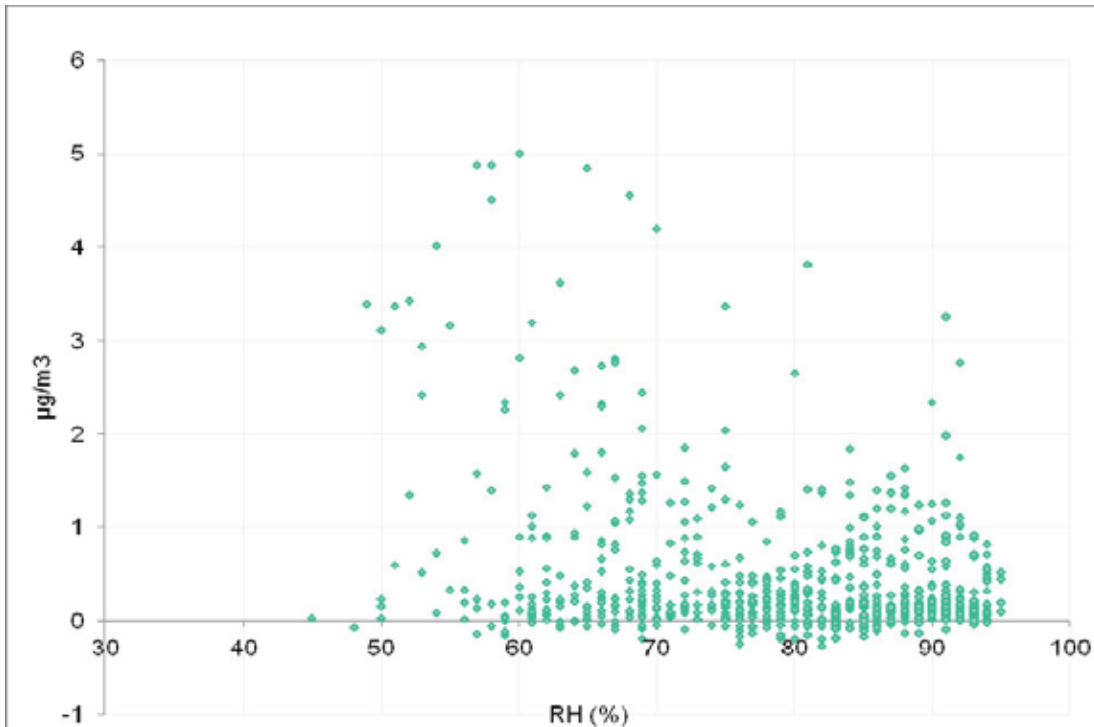


Figure 3.8 *Difference in the hourly measured HNO_3 concentrations before and after the Leckel filter as function of ambient hourly relative humidity*

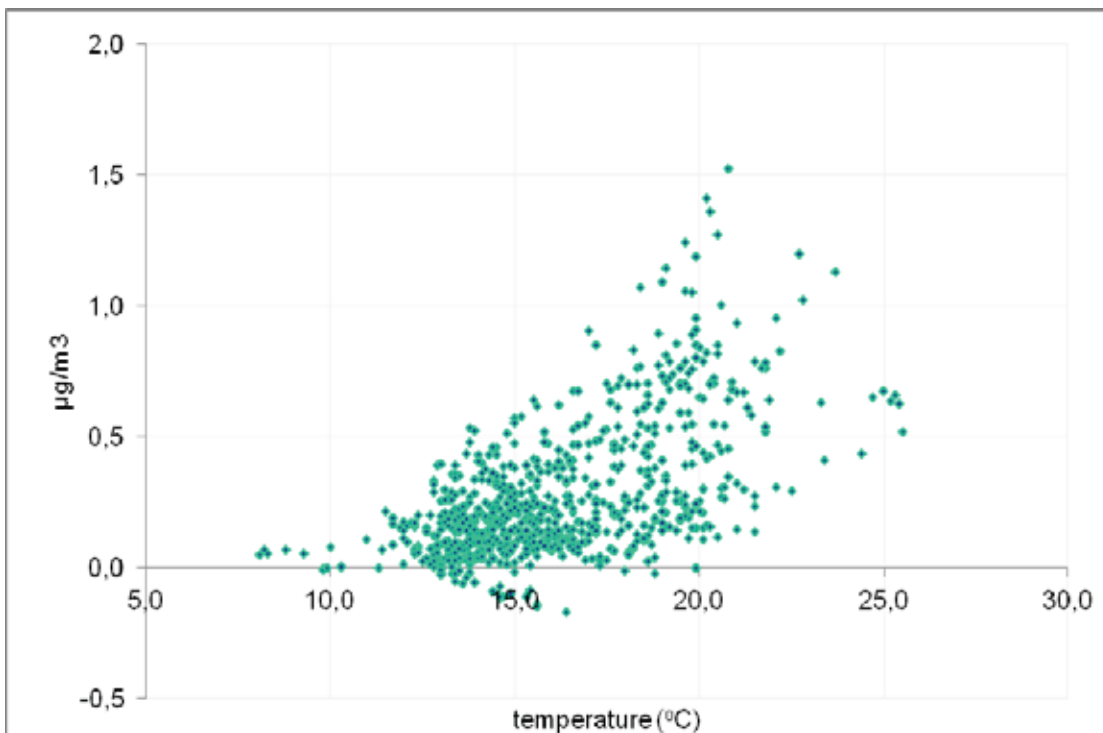


Figure 3.9 *Difference in the hourly measured HCl concentrations before and after the Leckel filter as function of ambient hourly temperature*

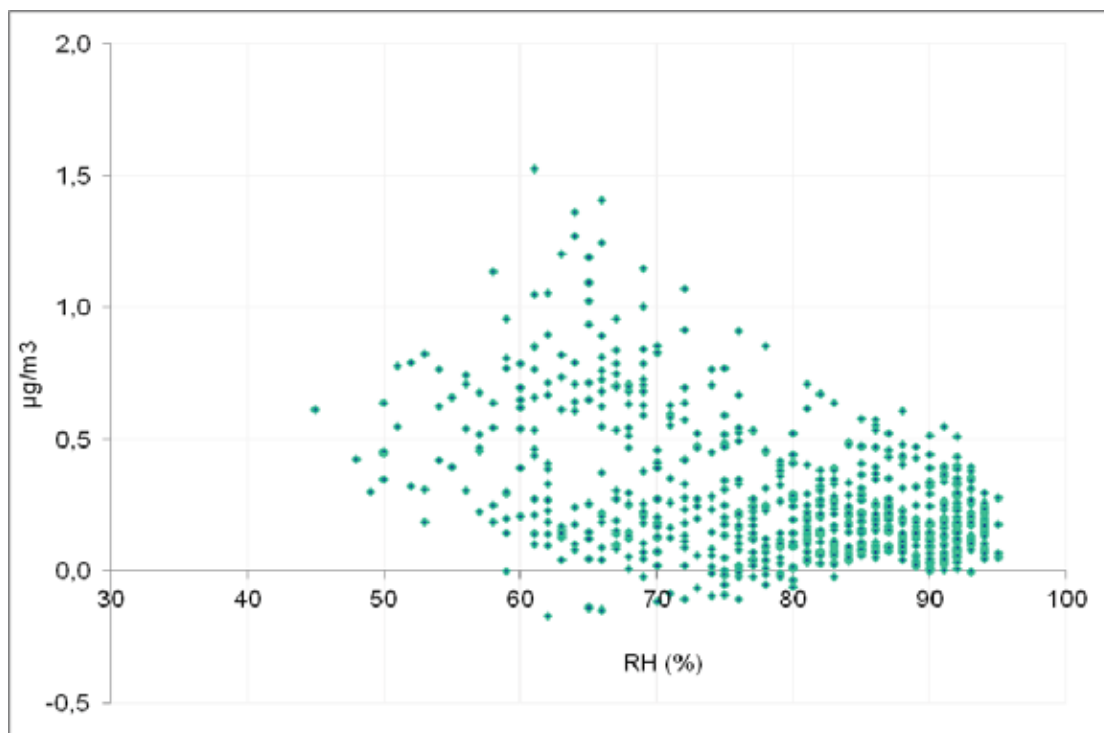


Figure 3.10 *Difference in the hourly measured HCl concentrations before and after the Leckel filter as function of ambient hourly relative humidity*

The raw (hourly) data shown here further indicate that both the ammonium nitrate 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 3.11 a-c. Note the exponential behaviour for HNO₃ compared to HCl. The number of data points in the lower and higher temperatures ranges are relatively low.

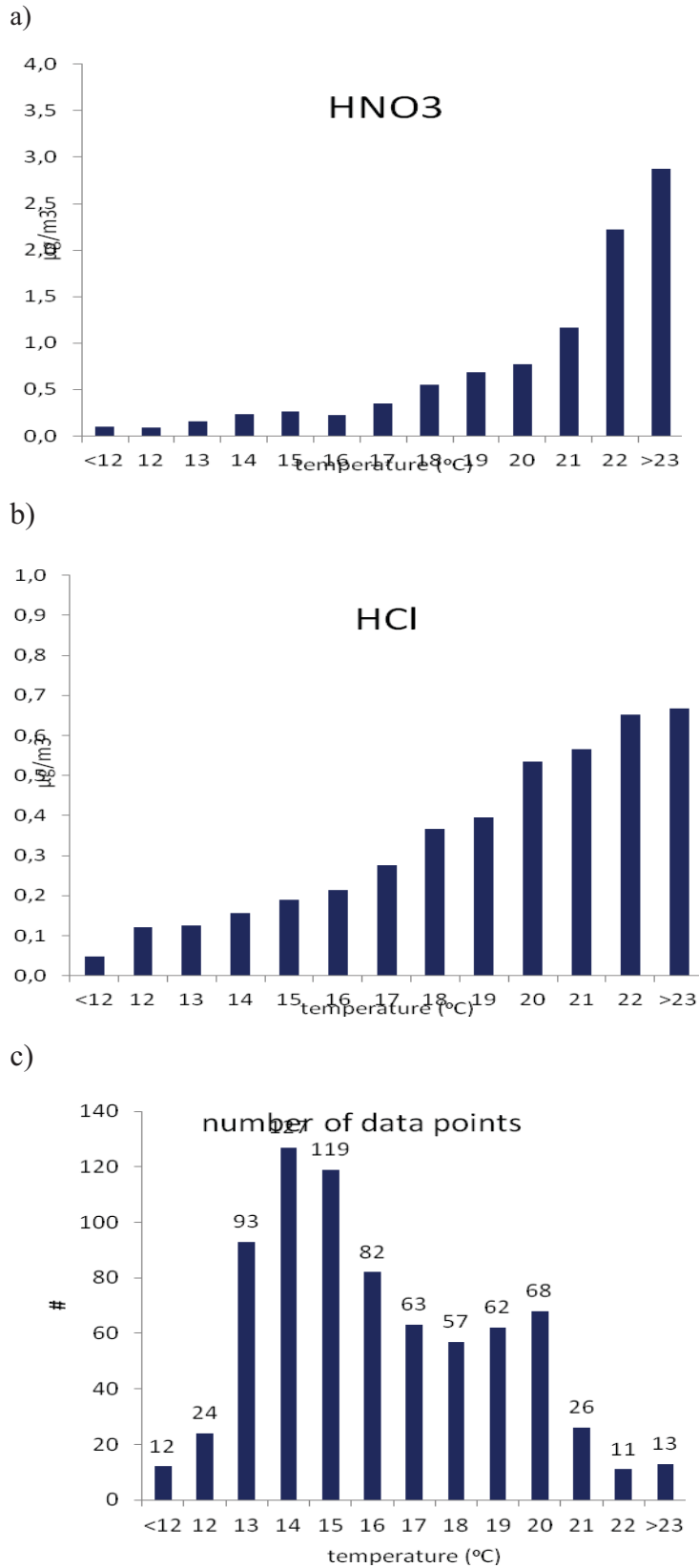
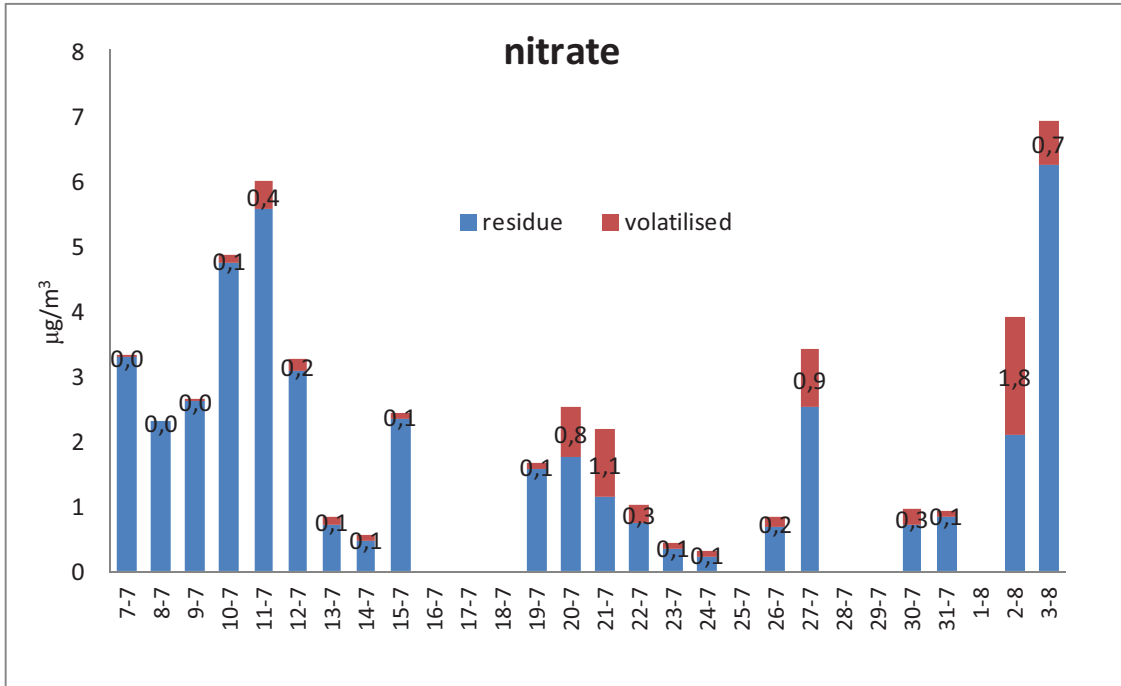


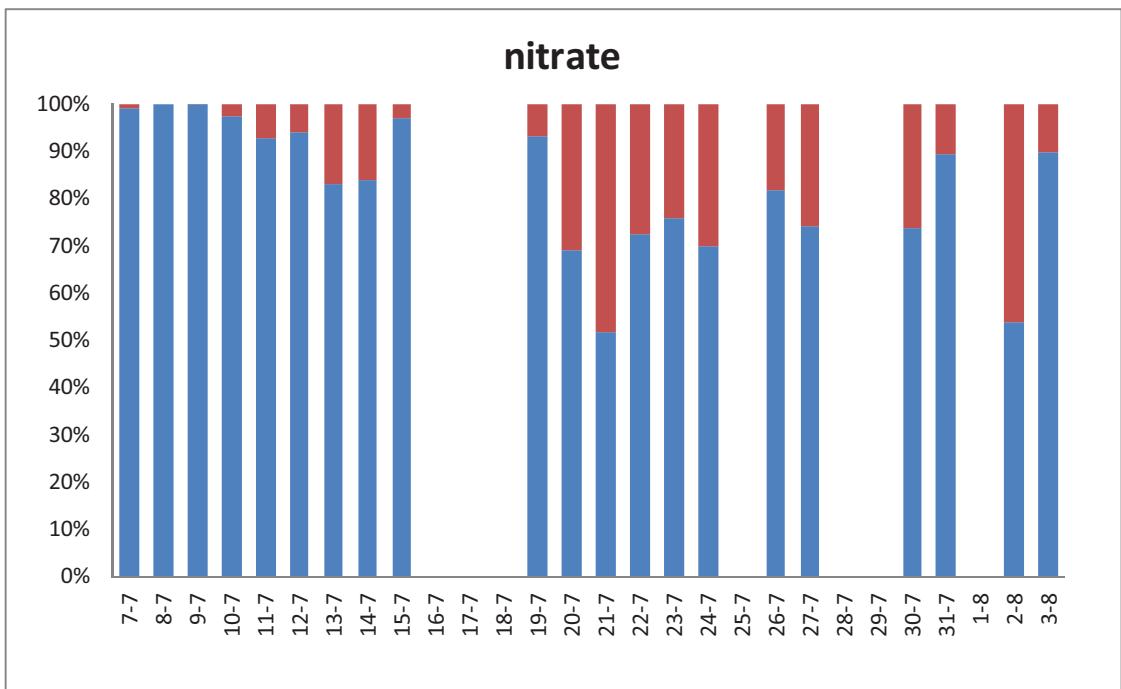
Figure 3.11 Volatility as function of temperature (a) and relative humidity (b); also given number of data points for each temperature (c)

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 nitrate and chloride mass disappearing from the filter per day (Figures 3.12a-b and 3.13a-b). In the case of nitrate the loss was 18%, on average, and ranging between 0 and near 50%. As the nitrate concentration over the entire period was near $2.5 \mu\text{g}/\text{m}^3$, less than $0.5 \mu\text{g}/\text{m}^3$ 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 nitrate mass disappeared that day ($1.8 \mu\text{g}/\text{m}^3$).

The chloride depletion occurs every day and the relative mass loss due to this process can be quite substantial (Figures 3.13a-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 nitrate 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).

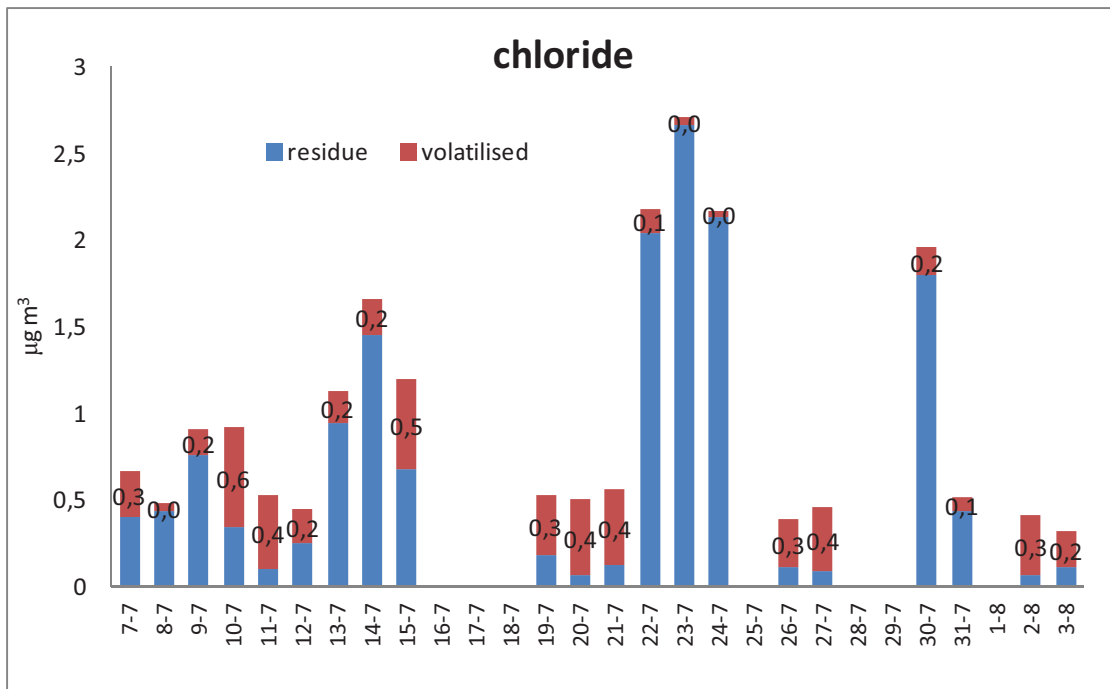


(a)

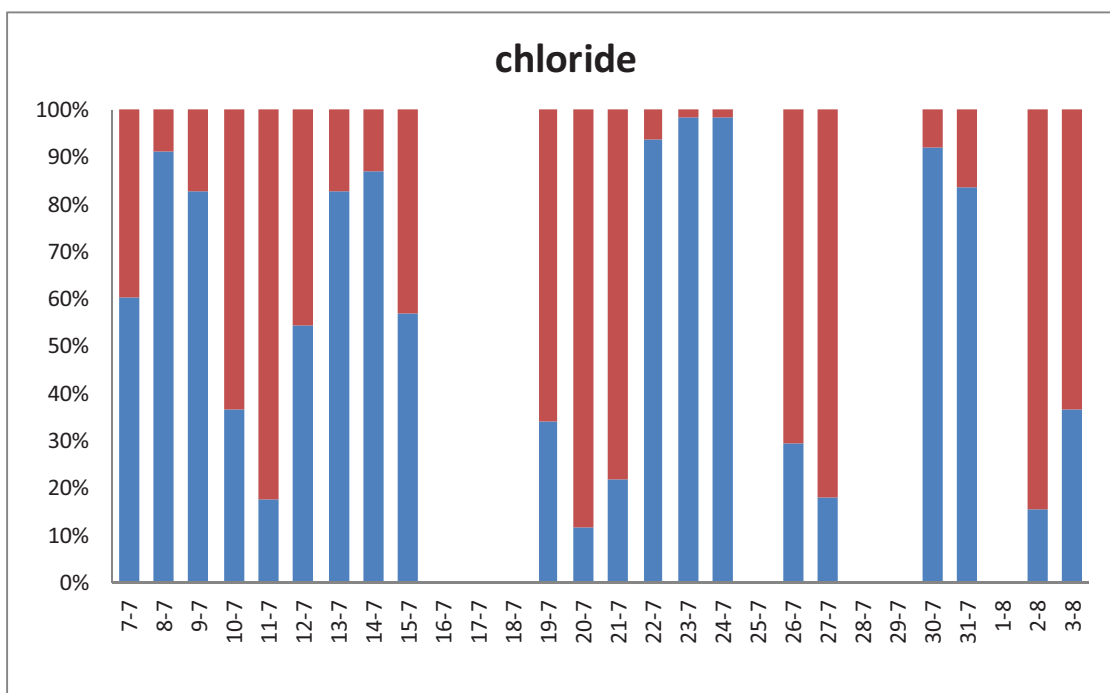


(b)

Figure 3.12 Volatilisation of nitrate mass from Leckel in absolute (a) and relative (b) values



(a)



(b)

Figure 3.13 Volatilisation of chloride mass from Leckel in absolute and relative values

3.6 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 nitrate 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 ammonium nitrate was less than $0.5 \mu\text{g}/\text{m}^3$. The chloride depletion implies that some nitrate is ‘produced’ (in the coarse fraction). The nitrate 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 nitrate could be between 0.8 and $1.8 \mu\text{g}/\text{m}^3$ even on days with moderate temperatures (Figure 3.14), i.e. 20°C (contrasting earlier reports). Such a decrease might affect the number of PM10-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.

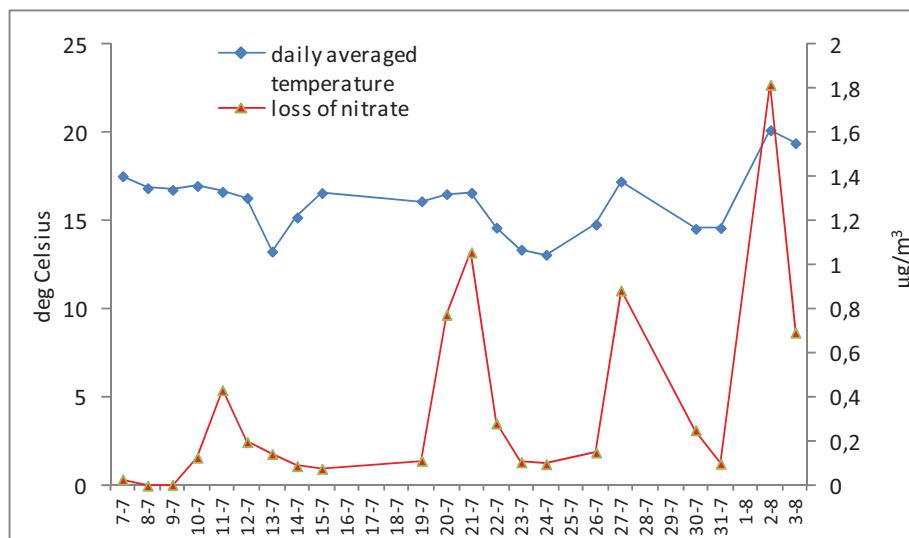


Figure 3.14 Loss of nitrate mass and average temperature per day

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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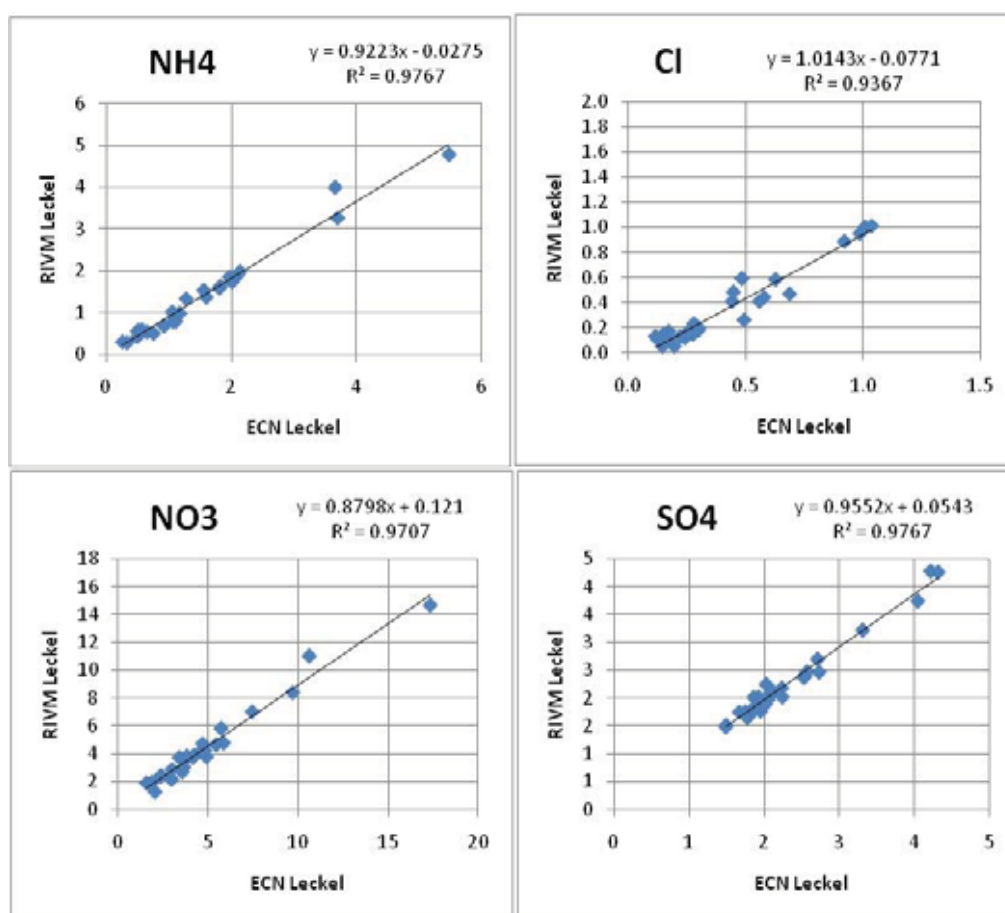
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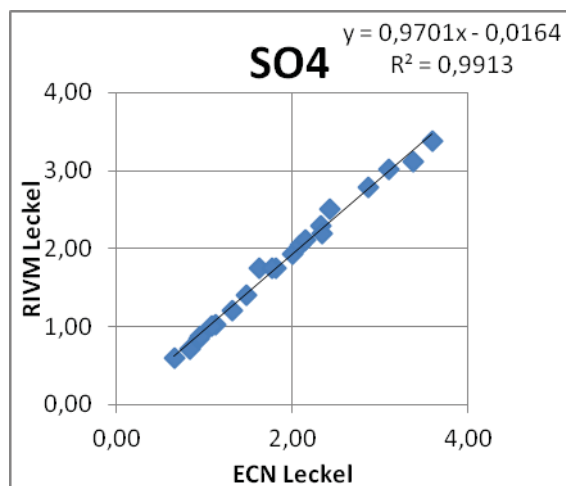
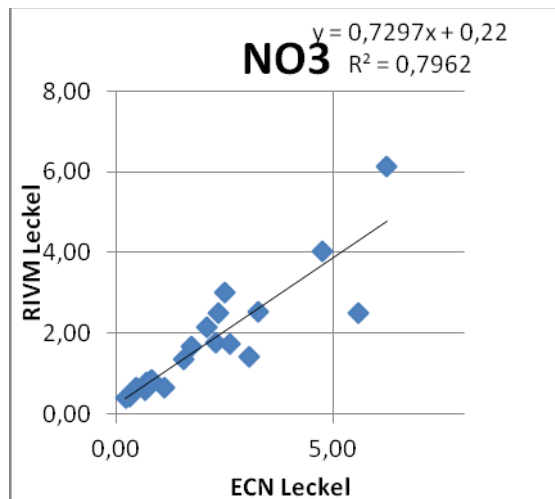
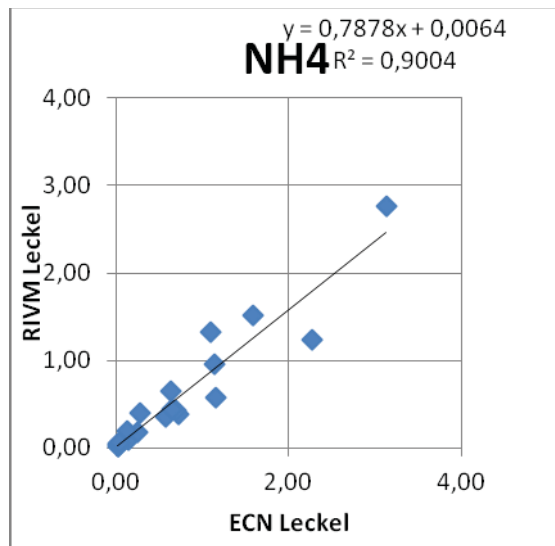
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Appendix A Comparison Leckels RIVM – ECN 2010

At the Wieringerwerf site RIVM operates a standard Leckel instrument as part of the LML network. In the figures below the various components measured have been compared. The results agree reasonably for both the 2010 and 2011 campaign. In particular, this the agreement is very high in the case of sulphate and it is therefore concluded that the experimental set up did not affect the operation of the ECN Leckel. Notable however is a systematic difference between the RIVM Leckel and the ECN Leckel for both nitrate and ammonium. In 2010 this was some 10% (with the RIVM Leckel producing the lower values) but in 2011 the difference was even more than 20%. There is no sound explanation for this phenomenon.



Appendix B Comparison Leckels RIVM – ECN 2011



Appendix C Flow rate measurement LVS

	Valve 1	Valve 2	Valve 3	Valve 4	Valve 5	Valve 6	Valve 7	Valve 8
open	1	2	3	4	5	6	7	8
Valve 1	462	0	30	517	40	145	30	30
Valve 2	0	753	30	510	38	142	30	40
Valve 3	0	0	770	520	40	143	30	40
Valve 4	0	0	40	915	326	213	0	42
Valve 5	0	0	30	524	775	182	30	33
Valve 6	0	0	37	585	49	878	30	30
Valve 7	0	0	30	543	42	162	805	0
Valve 8	0	0	30	539	26	99	490	490
sum	462	753	997	4653	1336	1964	1445	705
	Valve 1	Valve 2	Valve 3	Valve 4	Valve 5	Valve 6	Valve 7	Valve 8
Flow rate per week in cm ³ /min	462	753	997	4653	1336	1964	1445	705

Measurements of secondary inorganic aerosols in the Netherlands

In this report two studies are presented that were carried out within the framework of the second Netherlands Research Programme on Particulate Matter. The first study is a technical evaluation of the monitoring of secondary inorganic components (SIA) in the National Air Quality Monitoring Network (LML) up to 2009. Its incentive was a mismatch between SIA levels when the old routine LML-data were compared with measurements following the current reference methodology. The origin of the apparent difference could be established and is described here in detail. This result assures the comparability between the old and new data and therefore enables long term policy evaluations.

The second study quantifies and interprets measurement losses that occur in a mass collection instrument following the reference method for PM_{10} . Loss of mass from the filter takes place in two ways. Evaporation from the filter during sampling of semi-volatile ammonium nitrate, - the most dominant form in which nitrate is present in our region - was revealed leading to lower levels for nitrate, possibly influencing PM-exceedences on certain days. Also, the depletion of chloride was observed on the filter.

The Netherlands Research Program on Particulate Matter II (BOP II) is a national program on $PM_{2.5}$ and PM_{10} . It is a framework of cooperation involving the Energy research Centre of the Netherlands (ECN), the Environment and Safety Division of the National Institute for Public Health and the Environment (RIVM) and TNO.

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