

Report Laboratory tests on measurement of IONS in PM_{2.5}

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anions and cations in PM2.5'**

REPORT

LABORATORY TESTS ON

MEASUREMENT OF IONS IN PM2.5

Work Package 2

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ECN	Energy Research Centre of the Netherlands
NILU	Norwegian Institute for Air Research
FMI	Finnish Meteorological Institute
NPL	National Physical Laboratory, , UK
CNR	Institute of Atmospheric Pollution, Italy
JRC	DG Joint Research Centre, Italy
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Summary

This report represents the results acquired under WP2 of the method validation project for anions and cations in PM_{2.5}. WP2 was dedicated to the laboratory tests comprising the ruggedness test and the EMEP equivalence test. The ruggedness tests were focused on the artifact induced by volatile inorganic substances and performance of the various filter analysis methods.

Preloaded quartz filters with mixtures of NH₄NO₃ and (NH₄)₂SO₄ were prepared. Subsequently the filters were exposed to sampling conditions that were expected to lead to evaporation. By measuring on line the extra NH₃ and HNO₃ behind the filter we were able to observe the evaporation velocity characteristics of NH₄NO₃. Apparently two different phases of evaporation exist, a high rate phase followed by a low rate phase. The high velocity rate is in the order of 20 ug/hour and the low rate in the order of 2 ug/hour. It is assumed that the latter represents evaporating NH₄NO₃ with affinity to the quartz filter material. The transition between both phases is dependent on the quantity of NH₄NO₃ on the filter and the relative humidity (approximately 80 ug at 40% rH and 230 ug at 75% rH). The velocity at the high rate phase correlates with the calculated deficit of NH₃ and HNO₃ when compared to the atmospheric equilibrium concentrations. This relationship could not be found for the low velocity phase. The average amount of NH₄NO₃ seen at the WP3 field trial would have been 27% higher when losses were taken into account, assuming that 50% of the time the sampled NH₄NO₃ was exposed to low velocity phase evaporating conditions. Changing atmospheric conditions during sampling can easily lead to this magnitude of losses. Cl also endure evaporation losses though induced by HNO₃.

Consequences for the working range. NO₃: no practical working range can be defined as it is dependent on the input concentrations of NH₃ and HNO₃. NH₄: no practical working range can be defined as the NH₄NO₃ part is dependent on the concentrations of NH₃ and HNO₃. Cl: no practical working range can be defined as Cl is dependent on the concentration HNO₃. SO₄, Na, K, Ca and Mg: working range is not dependent on sampling conditions and determined by the results of the field test study (WP4).

Performance of the various filter analysis methods applied by the participating laboratories were assessed by Round Robin standard solutions (provided by EMEP) and the field validation tests (WP3). The results are not available yet and will be presented in the statistical analysis report of WP4.

Concern was raised with respect to the homogeneous filter loading during the field trials. This was of importance because filter punches were analyzed by the participating laboratories. The homogeneity was tested by having one lab analyzing the total set of punches coming from two different field trial filters. For all components the relative standard deviation was less or equal to the analytical uncertainty. It was therefore concluded that inhomogeneity of filter loadings as applied at the field validation tests was not detectable.

The European standard for PM accepts the variability of the evaporation losses by convention. This rules out the sampling effects and as a consequence lets the working range of the method be dominated by the analysis uncertainties. According to the definition of PM_{2.5} for the purpose of the European Standard working range for the ions follows the working range of EN12341 and be restricted by the analytical results presented in statistical analysis report of WP4. Taking the conclusion of this laboratory tests into account the method will not be suited for the objectives (to support air quality assessment and management) of the standard. Results for NH₄, NO₃ and Cl should be considered as indicative. In order to determine the PM ions quantitatively and meet the objectives of the standard denuder filter pack methods or on line analyzers as MARGA should be applied.

Equivalence with the EMEP method was conducted at the participating EMEP field sites (Ispra, Waldhof and Cabauw). EMEP made a standard EMEP sampler available for these sites. Results are to be presented in the statistical analysis report of WP4 as not all analysis results were available by the time this report was submitted.

1. Introduction

Directive 2008/50/EC on ambient air quality and cleaner air for Europe sets limit values for particulate matter PM₁₀ and fine particulate matter PM_{2.5}. 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.

The Directive also requires the measurement of inorganic components (anion and cations) and elemental and organic carbon (EC/OC) in the PM_{2.5} fraction with the objective to support air quality assessment and management. In order to ensure better data comparability, validated standard methods for these measurements are required. The measurement method for the inorganic components is being developed by TC264/WG34. In the frame of Grand Agreement SA/2012-11 (Ambient Air Quality) the European Commission granted the validation project for this standard. Besides a literature survey, a field test and the statistical evaluation the project contains under Work Package 2 the ruggedness test and EMEP equivalence test as set out in the call for tender launched April 4 2013 in the frame of EC mandate M/503.

This report represents the results acquired under WP2. The ruggedness tests were focused on the volatile inorganic substances and performance of the various filter analysis methods. It is well known and also recognized by the standard for PM measurements (EN12341) that NH₄NO₃ (ammonium nitrate) and Cl (chloride) may evaporate from the filter during sampling and therefore partly being missed as part of PM_{2.5}. The literature survey (WP1) recommended experimental conditions for the ruggedness tests. The volatile behavior of main component NH₄NO₃ of PM_{2.5} was characterized by exposing a preloaded filter to controlled atmospheric sampling conditions while measuring with a high time resolution the air before and behind the filter on the relevant substances HNO₃ (nitric acid) and NH₃ (ammonia). It was expected that this approach would reveal the major mechanisms for evaporation and an outlook on the impact for the concerning ions. The various filter analysis methods were assessed by Round Robin standard solutions (provided by EMEP) and the field validation tests (WP3). The results will be presented in the statistical analysis report of WP4.

The second part of Work Package is the EMEP equivalence test. The EMEP method resembles filter pack PM sampling without size selection. The literature study assessed the complications involved. Yet the results of both methods were compared by operation of both methods simultaneously at the EMEP locations that were also part of the field tests of this validation project Ispra (It), Waldhof (D) and Cabauw (NI). The set up can be found in this report. The analytical results are presented as part of the statistical analysis report of WP4.

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

2. Terms and definitions

For the purposes of the report, 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 velocity of 30 m³/h (2)
- Low Volume Sampling Method, LVS – method for sampling particulate matter with a flow velocity 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

3. Ruggedness test for volatile inorganic substances

3.1 Introduction

During sampling of PM_{2.5} chemical reactions may occur and affect the mass of the already sampled particulate matter by evaporation. Many parameters can influence the reaction rates. The complex PM matrix, 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 have been identified (4) as major drivers.

The main objectives (5) 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.

In order to accommodate these objectives the ruggedness test of standard have been focused on volatilization artifact and the impact on the determination of the PM_{2.5} ion concentrations. The artifact has been observed numerous times and allocated to obvious chemicals reaction (4), but thus far not characterized by measurements. The ruggedness test was focused on the major evaporation artifact for Europe being NH₄NO₃ (4).

3.2 Methodology

The fundamental driver for the evaporation of NH₄NO₃ is the equilibrium with the gasses NH₃ and HNO₃. This process has been described (7) and among others modelled by Isorropia (6). As the process on the filter substrate was not revealed yet the strategy was chosen to set up a standard PM_{2.5} sampling, analyze the input concentration and output concentration of the relevant species with a high time resolution and vary main parameters that are expected to influence the evaporation velocity.

The input and output concentration of PM_{2.5} (NH₄ and NO₃) and the precursor gases NH₃ and HNO₃ before and behind the filter were analyzed by a Marga 2S with a time resolution of 1 hour. The evaporation velocity is the mass of NH₄ and NO₃ evaporated from the filter per time period. As the sampled air already may contain concentrations of NH₃ and HNO₃, the mass of the evaporated NH₄NO₃ is proportional to the mass of NH₃ and HNO₃ behind the filter minus the mass of NH₃ and HNO₃ before the filter.

Parameters that were expected to influence the evaporation velocity were temperature, relative humidity, the input gas concentration of NH₃ and HNO₃, the SO₄ fraction in PM and the NH₄NO₃ supply on the filter. As 5 independent parameters were identified, testing the matrix covering all relevant combinations (ruggedness) was beyond the capacity of this study. Relevant ranges of these parameters for testing were given by the literature review (4) and accordingly applied in this study though the temperature range was limited.

In order to characterize the evaporation velocity series of filters were exposed to artificial internally mixed concentrations of NH₄NO₃ and (NH₄)₂SO₄ for typically 2 hours. The mass collected on the filter resembled quantities typically found under European conditions. Next step was to stop the generation of PM, continue the sampling and expose the filter to various (normal to extreme) conditions in temperature, relative humidity and NH₃ and HNO₃ for several days while measuring the evaporation velocity of NH₄NO₃. The SO₄ fraction in PM was varied for various sets of filters. The exposure experiments exceeded the normal 24 sampling time as elapsed time is not a relevant parameter for the characterization of evaporation. During the course of filter experiments just like under normal operational conditions the filter was exposed to elevated NH₃ and HNO₃ concentrations at daytime

in contrast to nighttime conditions. The same regime was generally applied for temperature. Relative humidity was kept stable most of the time.

Tracer for the measurement quality was the equimolar ratio of NH_3 and HNO_3 evaporating from the filter. The ratio had to be close to 1 unless the NH_3 and HNO_3 concentrations approached the analytical uncertainty of the analyzer.

The evaporation model used for NH_4NO_3 under atmospheric condition Isorropia was applied to predict the evaporation process on the filter. The assumption was that NH_4NO_3 would start to evaporate if the equilibrium concentration of the precursor gasses NH_3 and HNO_3 was not met. This factor of the equilibrium constant is expressed in ppb^2 being the concentration of NH_3 times the concentration of HNO_3 . In other words the deficit of NH_3 and HNO_3 expressed in ppb^2 was used to characterize the evaporation rate.

3.3. Experimental

3.3.1. Set up

Ambient air, see figure 1, was drawn through an air dryer (a) and with an overflow subsequently exposed to an ventilator (b). The dried air was blown into a pipeline (c) with initially inserted a temperature and relative humidity sensor (d1). The air is led through a HEPA filter (e) to cut off particulate matter followed by an acid coated denuder (f) to strip ambient NH_3 . The concentration of HNO_3 is usually quite low in the Netherlands and it was therefore decided that additional scavenging of HNO_3 was not needed. The purified airflow was next led through a controlled air heater (g) in order to be able to apply a temperature set point above the inlet air temperature. Next the humidifier (h) was inserted.

An unit with generators for NH_3 (m), HNO_3 (i) and NH_4 -salts (j) was assembled. HNO_3 and NH_4 salts were generated by spraying devices followed by a dryer (k) to evaporate HNO_3 and dry the aerosols and a neutralizer (l) to condition the particulate matter. The NH_3 is applied by a gas cylinder (m) with a pressure regulator. By means of this unit PM and gas mixtures were added to the purified air flow.

A mixer (n) in the pipeline was introduced to create a homogenous mixture. Next the air flow was introduced into the reference PM sampler (o) with temperature and relative humidity (d2) being measured. The air was sampled on the quartz filter (p) under LVS conditions at $2.3 \text{ m}^3/\text{hr}$, while an extra $1 \text{ m}^3/\text{hr}$ was sampled by the first Marga (q1) sampling unit. At the rear site of the filter $1.3 \text{ m}^3/\text{hr}$ was drawn towards the regular sampler air pump while $1 \text{ m}^3/\text{hr}$ went to the second Marga sampling unit (q2).

Because just the evaporation characteristics from the filter were investigated a PM2.5 cut off nor a standard inlet was obligated making it possible to apply the necessary adaptations.

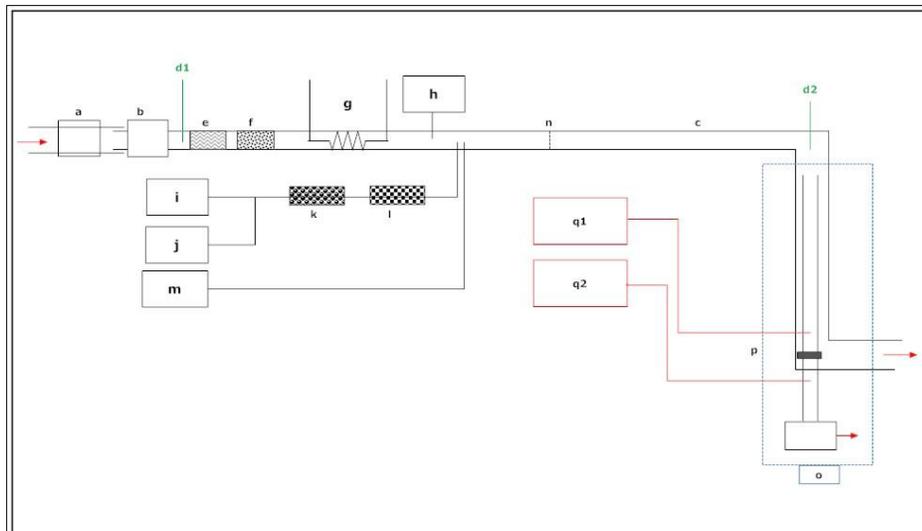


Figure 1 Lay out of Set up

See Annex 1 for a detailed description of the used components.

3.3.2. Applied sampling protocol

The PM sampler was equipped with a pile of filter cassettes arranged in such a way that after each filter cassette an empty cassette was following. When the empty cassette was put in place both MARGA sampling units collected the same air and were analytically normalized in order to perform optimized differential analysis when the PM filter was put in place. This reference measurement without a filter was usually carried out for a period of 6 hours. Initially blank filters were inserted in the sampler and exposed to defined quantities of PM analyzed on line by Marga. Later on preloaded filters with known concentration were used, due to the wall interaction of the PM causing uncontrolled evaporation of NH_3 and HNO_3 . After having a loaded filter in place evaporation tests were conducted typically over a period of 3 days.

3.4 Results

In total 11 runs with 11 filters (F1 to F11) were carried out under various conditions in the period of February 25, 2014 to April 24, 2014. Filters F1 to F6 were loaded with $\text{NH}_4\text{NO}_3/\text{SO}_4$ prior to each experiment during a period of 2 hours. Filters F7 to F11 were preloaded separately. The filter experiments are listed in table 1. The experimental conditions and analytical results are visualized in Annex 2. Analysis of filter numbers 1, 2, 3 and 9 could not be used due to operational problems.

Table 1 Overview Filter runs

Filter number	Loaded mass NH_4NO_3 in ug	Y (SO_4 frac.) * 1 = no SO_4	Remark **
4	354	1	90% rH
5	216	1	10% rH
6	138	0.33	11 °C
7	329	0.28	31 °C
8	355	0.28	Y=0.28
10	312	0.53	0 ppb ²
11	337	0.53	-

* Y (SO_4 fraction) is expressed as $[\text{NH}_4\text{NO}_3] / ([\text{NH}_4\text{NO}_3] + 3*[(\text{NH}_4)_2\text{SO}_4])$ Lit ref (4)

** Generally we were able to follow the recommendations by literature study. Most were met, almost met or even exceeded (min. rH).

3.4.1. The transition

We observed relatively high evaporation rates at the beginning of the filter runs and low to practically zero evaporation at the end of the runs as the initial amount of NH_4NO_3 is almost evaporated. The transition between both phases were characterized by an sudden strong reduction in the evaporation velocity of NH_4NO_3 . The results for each experiment are therefore divided into two experimental conditions. First the zone with excess amount of NH_4NO_3 , secondly the zone with limited NH_4NO_3 on the filter and the transition being marked by a significant reduction of the evaporation rate. The transition becomes visible when the course of mass of NH_4NO_3 on the filter is visualized in time. Although various atmospheric regimes were applied with as a consequence varying evaporation rates (no linear slope), still the phase of transition can be observed. See figure 2, Examples of transitions. Other filter experiments were either rejected or took place at one of the two discriminated phases.

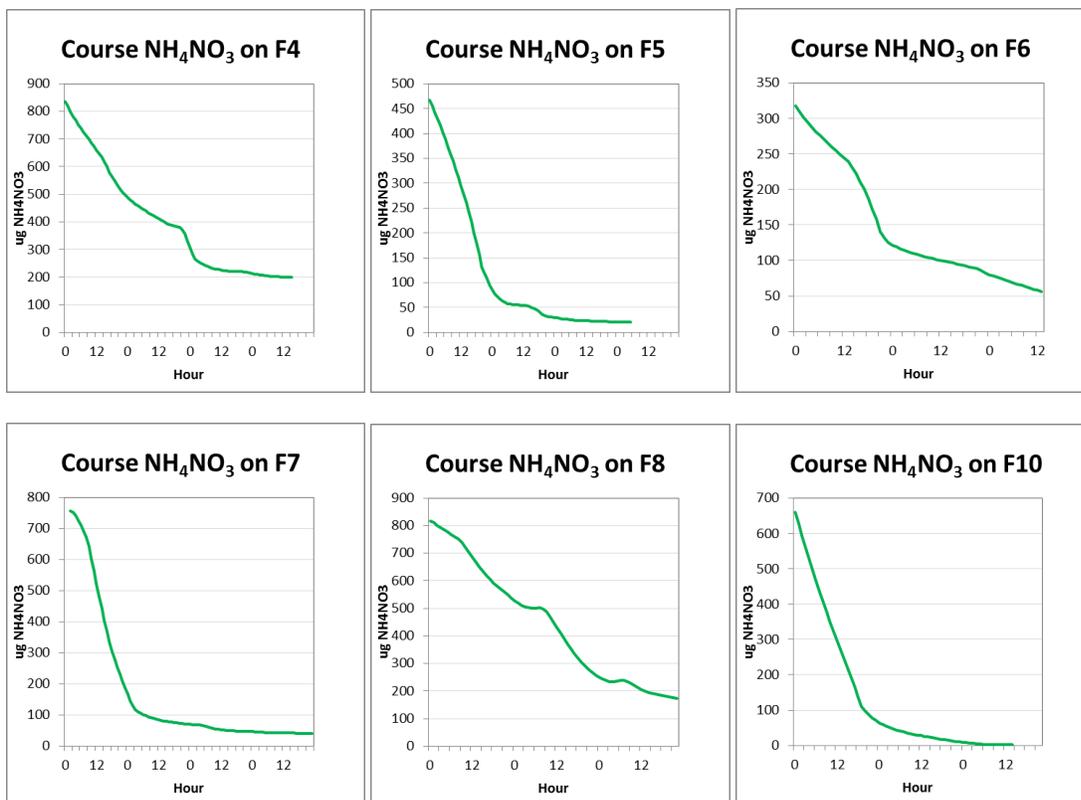


Figure 2 Examples of transitions

Under WP3 field test were conducted at various European sites. During 40 days samples were taken and analyzed. Looking at the results for sites with a relative high NO_3 concentrations (figure 3), the same type of phase pattern shows up when the NH_4NO_3 mass distribution is displayed suggesting phases with high and low evaporation rates.

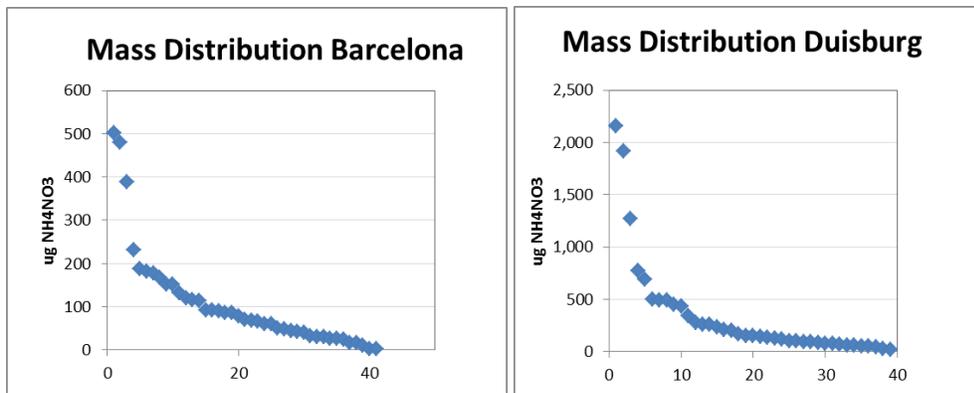


Figure 3 NH4NO3 mass distribution at some field sites

Both findings led to the assumption that the evaporation velocity of NH_4NO_3 may be effected by affinity with quartz filter material. With excess amount of NH_4NO_3 the evaporation velocity appears to be dominated by NH_4NO_3 not attached to the quartz filter material. As the “free” NH_4NO_3 is evaporated the velocity slows down and becomes dominated part of NH_4NO_3 attached to the filter material. Moreover, we noticed the transition phase to be sensitive for relative humidity. Under relatively dry conditions (40%) the transition took place at approximately 80 ug NH_4NO_3 . Under more wet conditions (75%) the transition shifted towards 230 ug NH_4NO_3 and will probably increase even more towards 100% rH.

3.4.2. The high evaporation velocity phase

Under conditions with a relatively high load of NH_4NO_3 (before the transition zone) high evaporation rates up to 41 ug NH_4NO_3 per hour were observed. The filters were exposed to various settings of parameters that were expected to influence the evaporation rate, temperature, relative humidity and the input gas concentration of NH_3 and HNO_3 . With the model Isorropia the equilibrium concentrations of NH_3 and HNO_3 were derived. By subtraction of the input concentration the deficit in ppb^2 was obtained. On an hourly basis a delayed effect of the applied deficit was seen. Short term deficits of NH_3 and HNO_3 led to peak rates of evaporation 1 or 2 hours later. In steady state situations fairly stable evaporation velocity rates were obtained (figure 4). The highest evaporation velocity was induced at filter experiment F7. With a temperature of 31 °C, rH 40% and a deficit of 211 ppb^2 NH_4NO_3 evaporated with velocity of 41 ug/hour.

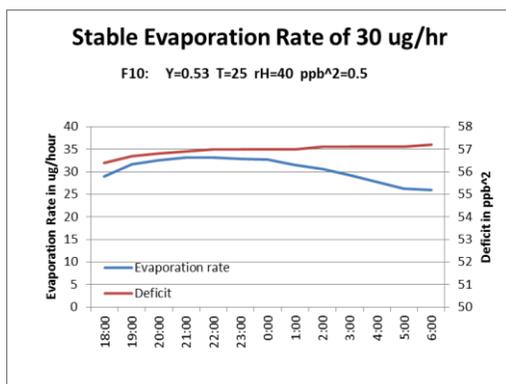


Figure 4 Stable evaporation velocity

The averaged deficit of NH₃ and HNO₃ before the transition phase of each filter experiment was compared to the observed averaged evaporation velocity of NH₄NO₃ in order to assess the relationship. Six filter experiments could be used for this purpose. See figure 5 for the correlation plot. With a moderate $r^2 = 0.64$ the retrieved relationship was:

$$EV_{NH_4NO_3} = 0.23 \times Def_{NH_3 \times HNO_3} + 8$$

$$Def_{NH_3 \times HNO_3} = C_e - C_{in}$$

With $EV_{NH_4NO_3}$ being the Evaporation velocity of NH₄NO₃ in ug/hour and $Def_{NH_3 \times HNO_3}$ being the Deficit of NH₃ and HNO₃ in ppb². C_e being the product of the equilibrium concentrations of NH₃ and HNO₃ in ppb² according to Isorropia and C_{in} being the product of the input concentrations of NH₃ and HNO₃ in ppb².

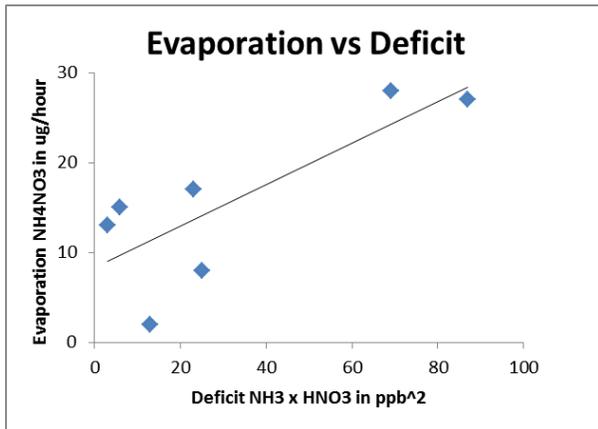


Figure 5 Relationship between deficit and evaporation velocity

3.4.3. The low evaporation velocity phase

While the high evaporation velocity phase was characterized for the averaged period before the transition phase, we characterized the low evaporation velocity phase over the 24 hour period after the transition. Six filter experiments could be used for this purpose. See table 2 for the results. The observed averaged evaporation velocity varied between 1.6 and 3 ug NH₄NO₃/hour with an averaged velocity of 2 ug/hour. None of the parameters effecting the NH₄NO₃ equilibrium showed significant correlation with the measured evaporation rate.

Table 2 Low evaporation phase

Filter Experiment	Temp oC	rH %	NH4NO3 ug	SO4 Y	deficit ppb ²	Evaporation ug/hr
5	25	60	80	1	58	1.6
4	19	50	220	1	18	1.7
7	18	40	113	0.28	13	1.8
6	16	40	127	0.33	8	1.8
10	25	40	86	0.53	59	2.8
8	21	80	245	0.28	5	3

4. Ruggedness test for filter analysis methods

The participating laboratories applied various methods for the analysis of the filters punches coming from the field validation campaigns. Applied analysis methods comprise ion chromatography (anions and cations), inductively coupled plasma (cations) and spectrometry or conductometry for NH_4^+ conform Decision 69 of WG34. The anions concerned are the water soluble fraction of SO_4^{2-} , NO_3^- , Cl^- and the cations the water soluble fraction of NH_4^+ , Na^+ , K^+ , Mg^{2+} and Ca^{2+} . See table 3 for an overview of participating laboratories and their certified methods. The methods were tested on applicability both by the analytical results of the field validations and by participating twice in the yearly EMEP Round Robin test for artificial made solutions. Results of both tests will be presented by NPL in statistical analysis report of WP4 as the results are of the field validation and the Round Robin were not complete at the moment this report was submitted.

Table 3 Analysis methods participating labs

	Cl, NO_3 , SO_4 ,	Na, K, Ca, Mg	NH_4
CNR	Anion IC	Cation IC	Cation IC
UBA (Aut)	Anion IC	Cation IC	Cation IC
ECN	Anion IC	ICP	Conductivity
ISCI	Anion IC	AAS	Spectrometry
TNO	Anion IC	ICP	Spectrometry
FMI	Anion IC	Cation IC	Cation IC

5. Assessment of working range of the method

The assessment was divided into two fields of concern, the sampling and the analysis. The sampling and an introduction to the analysis part are presented here. Final assessment of the working range is presented in the statistical assessment report (deliverable of wp4).

The ruggedness tests focused on the volatile inorganic substances. It is well known and also recognized by the standard for PM measurements (EN12341) that NH_4NO_3 and Cl may evaporate from the filter during sampling and therefore partly being missed as part of $\text{PM}_{2.5}$.

The results of the described laboratory tests confirm EN12341 statements. The test results show that the method is not reliable for the measurement of NH_4 and NO_3 in the form of NH_4NO_3 . The uncertainty is the highest when 80 μg NH_4NO_3 or more is collected on the filter. This quantity marks the lower limit of the transition phase between free and filter attached NH_4NO_3 under low RH conditions. Above this quantity NH_4NO_3 may rapidly evaporate with an averaged velocity of 20 $\mu\text{g}/\text{hour}$. Quantities of NH_4NO_3 below 80 μg remain more stable on the quartz filter though evaporation velocities of 2 $\mu\text{g}/\text{hour}$ may still take place, still leading to significant underestimation. The high evaporation velocity of 20 $\mu\text{g}/\text{hour}$ corresponds to 9 $\mu\text{g}/\text{m}^3$ at 2.3 m^3/hr sampling and the low velocity to 0.9 $\mu\text{g}/\text{m}^3$. Losses vary with sampling conditions from 0 to 41 $\mu\text{g}/\text{hour}$.

During the field tests conducted in Duisburg, Waldhof (D), Barcelona, Ispra and Amsterdam the average residue of NH_4NO_3 on the filter was 145 μg . If the filter was exposed evaporating conditions for 50% of the sampling time, losses of 4.6 μg per hour and 55 μg in total are to be expected. Correct mass was in that case 200 μg . Hence 55 μg was lost, 27% of the initial mass.

It is in general concluded that the working range of the method is valid under the sampling conditions representing equilibrium concentrations of NH_3 and HNO_3 or higher. This is not a practical working range as normally these concentrations on the relevant time scale in hours remain unknown.

If no NH_4NO_3 and NH_4Cl was sampled, all sampled NH_4 was likely to be associated with SO_4 . $(\text{NH}_4)_n\text{SO}_4$ salts are stable on the filter, but in Europe NH_4NO_3 free sampling cannot be assumed beforehand.

Cl, according to the literature survey, is present in $\text{PM}_{2.5}$ as NaCl or occasionally as NH_4Cl under very cold conditions. Cl may evaporate from the filter as HCl dominantly and significantly in the presence of HNO_3 . Laboratory tests on this phenomenon were beyond the capacity of the laboratory tests and conclusions are therefore based on the literature survey findings.

In conclusion:

- NO_3 : no practical working range can be defined as it is dependent on the concentrations of NH_3 and HNO_3 .
- NH_4 : no practical working range can be defined as the NH_4NO_3 part is dependent on the concentrations of NH_3 and HNO_3 .
- Cl: no practical working range can be defined as Cl is dependent on the concentration HNO_3 .
- SO_4 , Na, K, Ca and Mg: working range is not dependent on sampling conditions and as a consequence determined by the results of the field test study.

5.1 Relationship with PM standards

The standard EN12341 for PM 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 velocity predominantly determined by the temperature in the system. Losses of semi-volatile material is expected when the European Standard is followed and the loss may differ between the different location, day and PM values. 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 (5) for the determination of ions in PM_{2.5} however 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.

The European standard for PM accepts the variability of the losses by convention. This rules out the sampling effects and as a consequence lets the working range of the method be dominated by the analysis uncertainties. According to the definition of PM_{2.5} for the purpose of the European Standard working range for the ions follows the working range of EN12341 and be restricted by the analytical results presented in statistical analysis report of WP4.

Taking the conclusion of this laboratory tests into account the method will not be suited for the objectives of the standard. Results for NH₄, NO₃ and Cl should be considered as indicative. In order to determine the PM ions quantitatively and meet the objectives of the standard denuder filterpack methods (EMEP) or on line analyzers as MARGA should be applied.

6. Laboratory Tests supporting the field tests (WP3)

6.1 Inhomogeneity of filter loading

6.1.1 Introduction

Inhomogeneous loading of particulate matter on filters may occur by preferred flow patterns through the filter body. This is usually not an important issue as the filter is handled for further analysis as a whole. It becomes an issue when parts of the filters are taken for various analytic reasons like inter laboratory comparisons or for multicomponent analysis. If inhomogeneous loading occurs during the field validation tests it may lead to incorrect deviations for the uncertainty determination of the method. The literature review (4) mentioned researchers reporting both homogeneous and inhomogeneous loading. Therefore it was of importance to test spatial inhomogeneity of the filter loadings in the setting being applied at the field validation tests.

6.1.2 Test setup

In order to assess the inhomogeneity of the filter loading sets of all six filters punches were analyzed by one laboratory. This way additional variation introduced by analysis by separate laboratories were omitted. The laboratory of ECN, also a participating in the field validation test, analyzed all 6 punches of a filter sampled at the Duisburg site and of a filter sampled at the Barcelona site. This way the inhomogeneity test was performed for two European sites with different characteristics (geographically and by composition). The filters were locally punched in the regular way as part of the field test filter series acquired at the Duisburg and Barcelona site. The punches were also treated equally as the standard punches in terms of transportation and analysis procedures. The anions were analyzed by ion chromatography, NH₄ by conductometry after membrane diffusion and the other cations by ICP.

6.1.3 Results

The Duisburg filter was sampled on April 9, 2014 and carried the code *DUI-PM2.5-A12x-9-4-2014-Lab-1*. The Barcelona filter was sampled on April 4, 2014 and carried the code *BCN-PM2.5-D09-04apr-Lx0*. The analysis results are given in table 4.

Table 4 Analysis of punches inhomogeneity test

	NH4	Cl	NO3	SO4	Ca	K	Mg	Na
DL	<0.2	<0.2	<0.2	<0.2	<0.37	<0.38	<0.055	<0.31
An. Unc. %	12	4	3	3	10	15	9	13
BCN-PM2.5-D09-04apr-L10	7.1	1.1	8.5	24	2.6	2.7	0.4	2.6
BCN-PM2.5-D09-04apr-L20	6.6	1.1	8.0	23	2.5	2.5	0.4	2.1
BCN-PM2.5-D09-04apr-L30	7.0	1.1	8.1	24	2.7	2.5	0.4	2.1
BCN-PM2.5-D09-04apr-L40	6.9	1.1	8.3	24	2.6	3.6	0.4	3.4
BCN-PM2.5-D09-04apr-L50	7.0	1.1	8.2	24	2.3	2.5	0.4	2.2
BCN-PM2.5-D09-04apr-L60	6.8	1.1	7.7	23	2.3	2.4	0.4	2.1
DUI-PM2.5-A12a-9-4-2014-Lab-1	55	4.2	139	71	2.1	3.7	1.4	10.9
DUI-PM2.5-A12b-9-4-2014-Lab-1	51	3.9	131	65	1.9	3.3	1.3	10.0
DUI-PM2.5-A12c-9-4-2014-Lab-1	54	4.3	137	70	2.2	2.9	1.4	10.0
DUI-PM2.5-A12d-9-4-2014-Lab-1	53	4.0	134	67	1.9	3.1	1.3	10.5
DUI-PM2.5-A12e-9-4-2014-Lab-1	53	4.0	135	69	2.0	2.7	1.4	9.7
DUI-PM2.5-A12f-9-4-2014-Lab-1	56	4.2	138	71	2.0	3.2	1.4	10.4

In order to assess the degree of inhomogeneity the relative standard deviation (RSD) per component per filter was calculated. The RSD is a function of the concentration of the specific component. In the vicinity of the detection limit RSD will be much higher than at higher concentration levels. Therefore also the averaged concentration divided by the detection limit is introduced as parameter (Val/DI). Table 5 shows the results for both filters. In figure 6 the results of both filters are combined. Finally the RSD is per component compared to the analytical uncertainty of the analysis (table 6).

Table 5 Relative Standard deviation per filter per component

Barcelona		RSD	val/dl	Duisburg		RSD	val/dl
NH4		2.6%	34.5	NH4		3.3%	268.3
Cl		0.0%	5.5	Cl		3.8%	20.5
NO3		3.4%	40.7	NO3		2.2%	678.3
SO4		2.2%	118.3	SO4		3.5%	344.2
Ca		7.1%	6.7	Ca		5.7%	5.5
K		17%	7.1	K		11%	8.3
Mg		4.4%	7.3	Mg		5.1%	25.0
Na		22%	7.8	Na		4.3%	33.1

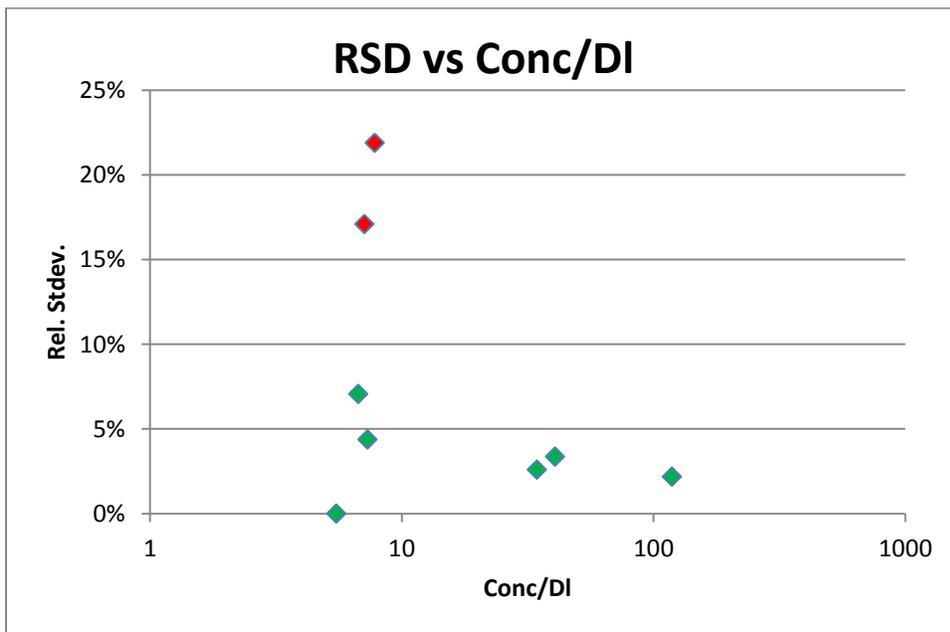


Figure 6 Graph Concentration dependency of RSD

Table 6 RSD and analytical uncertainty per component

	RSD	Ana. Unc.
Cl	1.9%	3
NO ₃	2.8%	4
SO ₄	2.8%	3
NH ₄	2.9%	12
Mg	4.7%	9
Ca	6.4%	10
Na	13.1%	13
K	14.1%	15

6.1.4. Conclusions

For all components the relative standard deviation was less or equal to the analytical uncertainty. It was therefore concluded that spatial inhomogeneity of filter loadings as applied at the field validation tests was not detectable. At higher concentration levels (> 100 * detection limit) the relative standard deviation drops below 4%. This was observed for NH₄⁺, NO₃⁻ and SO₄²⁻.

6.2 Punching

In order to validate the method field test were executed at 6 different sites throughout Europe. With high volume samplers filters were loaded with PM_{2.5} particulate matter. From each the filters 6 punches were taken according to the SOP (3). The total set of punches were transport to the associated laboratories for analysis.

The punching process represents a potential risk in terms of contamination by the puncher itself. This phenomenon has been assessed by testing the puncher on blank filters. The tested puncher was a KS-Tool 40 mm Handle Punch as suggested by the SOP. Actually the tested puncher was later on used by JRC and CSIC at their field tests to punch their filters. In order to exclude variation from blank ion concentration from the filter itself Teflon were used, as according to the literature review, these filters exhibit the lowest blank values and offered the best setting to test the contamination introduced by the puncher itself. The 40 mm punches were taken from 47 mm blank filters. The contamination by the puncher was determined by subtracting the analytical results of the blank filters from the punched filters while correcting for the filter surface difference (40 mm = 12.56 mm² and 47 mm = 17.34 mm²). See table 7 for the results.

Table 7 Contribution of ions by the puncher

	Cl	NO ₃	SO ₄	NH ₄	Na	K	Mg	Ca
In ug/filter	0.25	0.5	0.5	<0.3	<0.4	<0.5	<0.1	<0.5
In ng/m ³ (LVS)	5	9	9	<5	<7	<9	<2	<9

In conclusion contamination by cations was not observed and contamination found by anions was small but detectable. Compared to one of the lowest concentration levels observed in the EU (Hyytiälä, Fin) (4) the contamination remains negligible.

7. Equivalence with EMEP

Second part of Work Package is the EMEP equivalence test. The EMEP method resembles filter pack PM sampling without size selection and not the EMEP denuder filter pack method. The literature study (4) assessed the complications involved. Yet the results of both methods were compared by operation of both methods simultaneously at the EMEP locations that were also part of the field tests of this validation project Ispra (It), Waldhof (D) and Cabauw (NI). EMEP made available a standard EMEP sampler for this purpose. This sampler was used at the Ispra and Cabauw site. Due to carnet issues the sampler had to be returned before the end of the Cabauw campaign. All EMEP filters were analyzed by the laboratory of FMI.

The results are presented as part of the statistical analysis report of WP4 as the Cabauw campaign was still conducted by the time this report was submitted.

8. Acknowledgement

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Annex 1

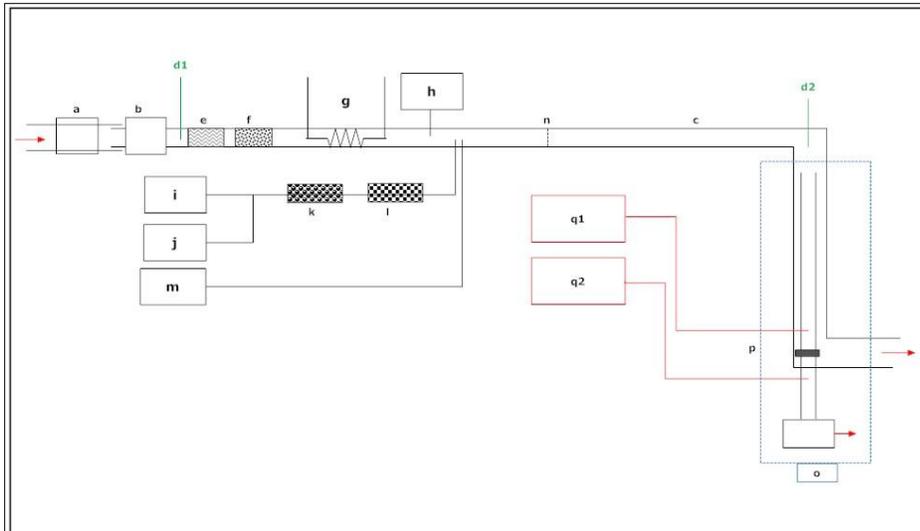
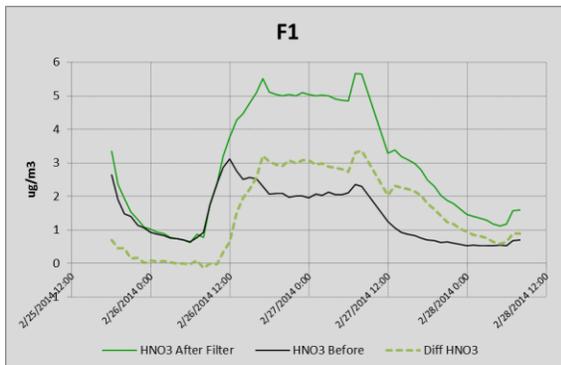
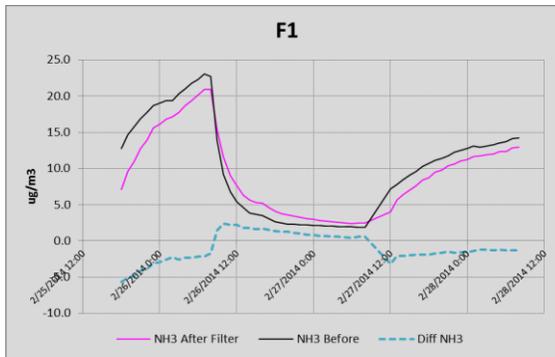
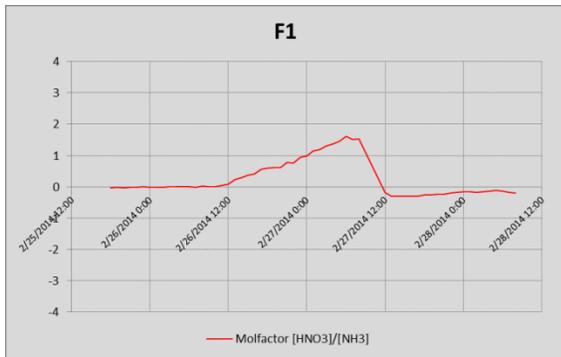
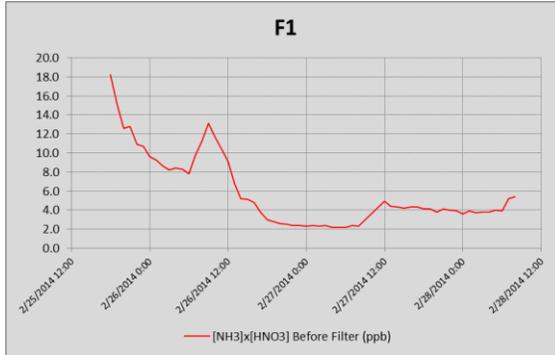
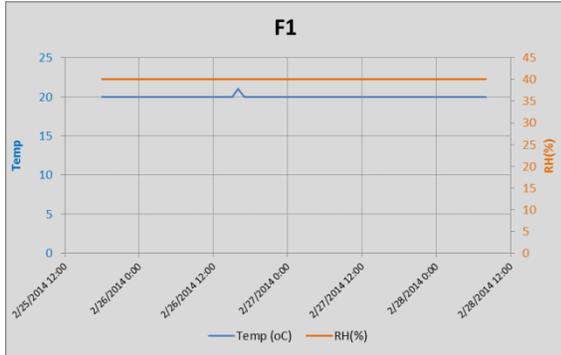
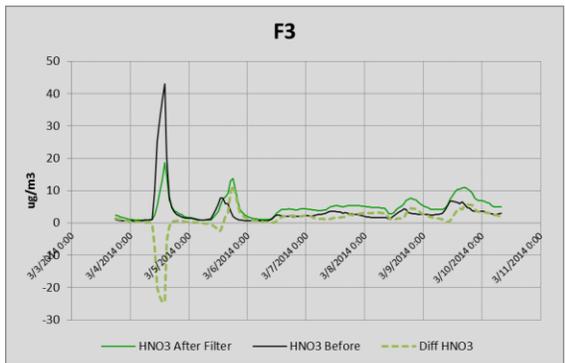
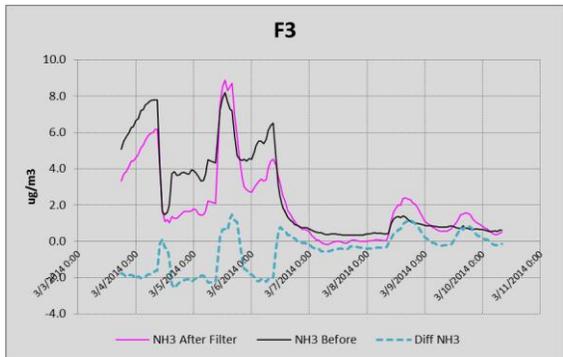
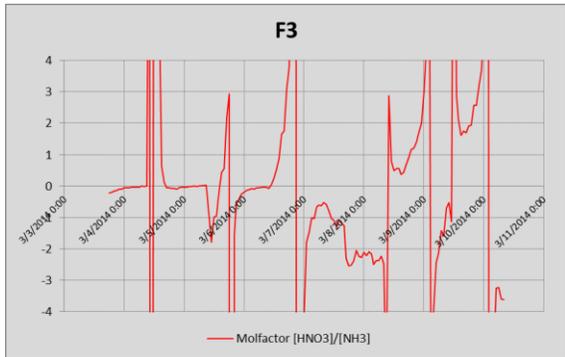
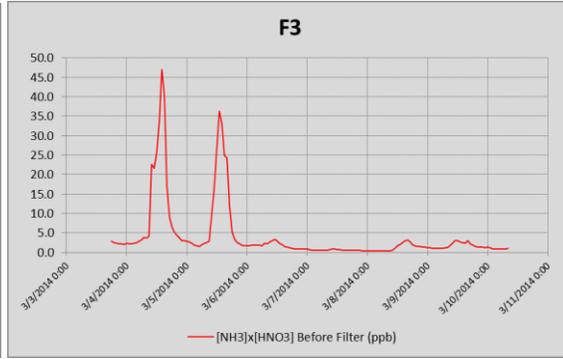
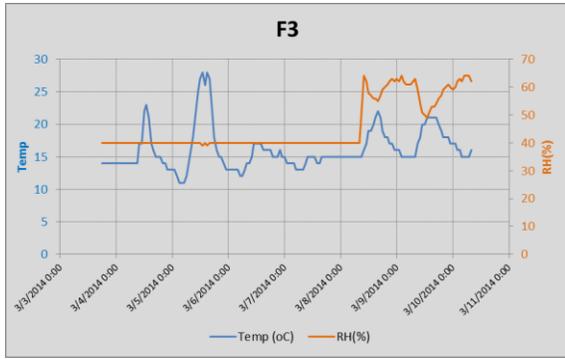


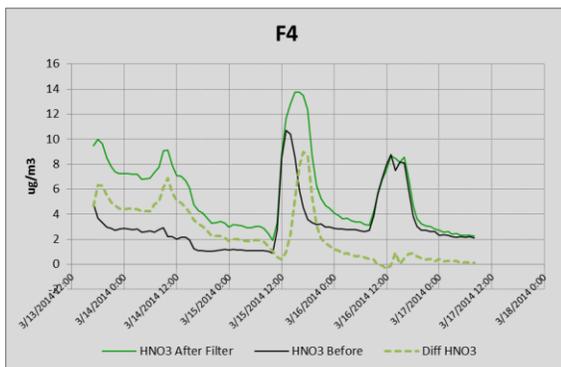
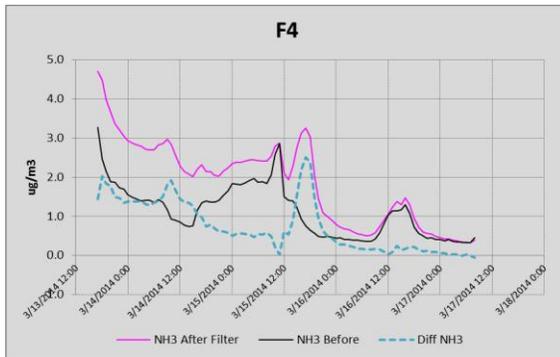
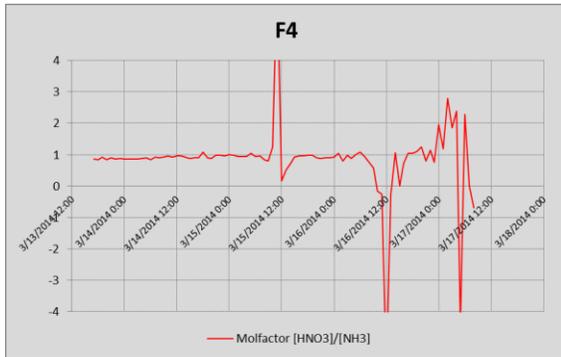
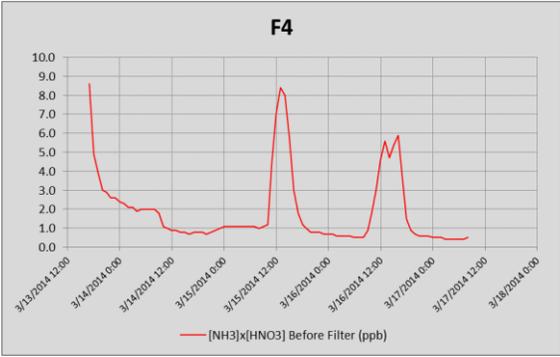
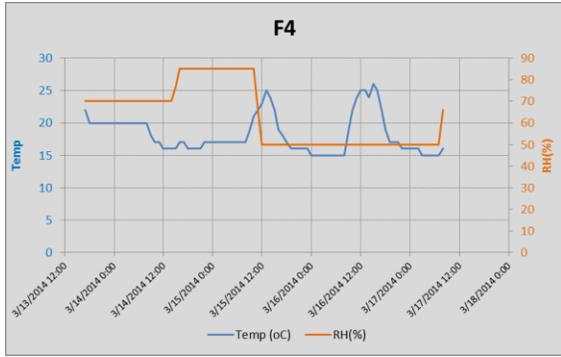
Figure 7 Measurement set up

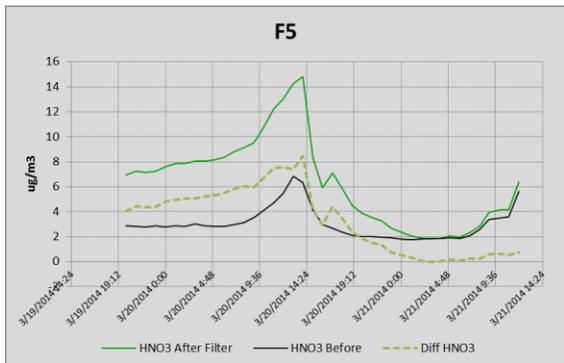
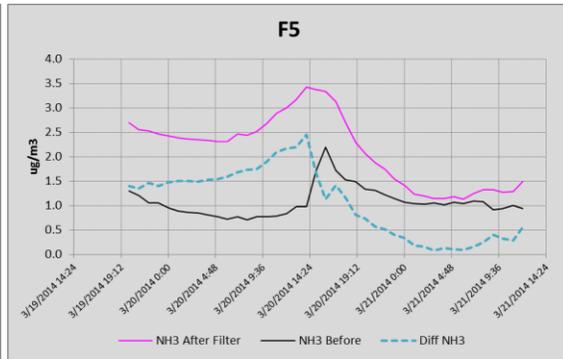
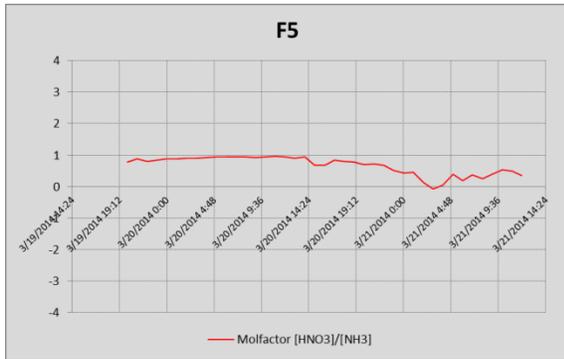
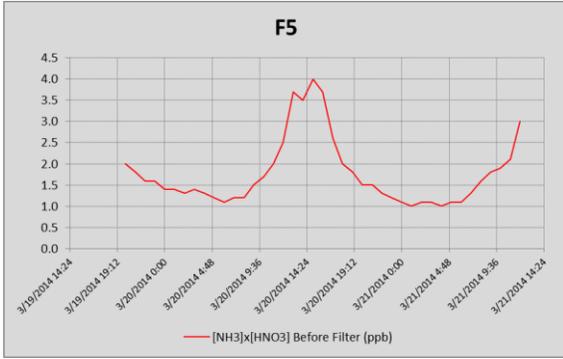
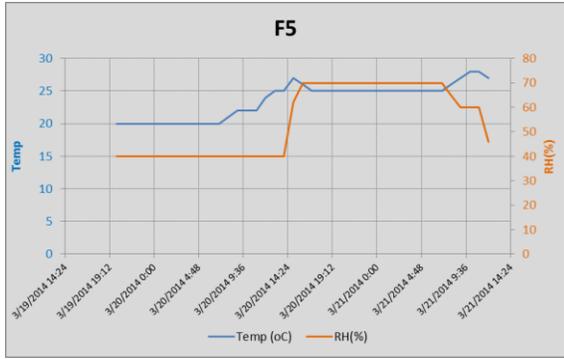
- a Munters MG50 Desiccant Dehumidifier. Air is dried to approximately 10% RH in recirculation mode with a flow of $\sim 50 \text{ m}^3/\text{h}$
- b A ventilator with adjustable control. The airflow could be adjusted between 10 and $70 \text{ m}^3/\text{h}$
- c SS316-tube with an inner diameter of 100mm isolated with 5cm thick Rockwool
- d A calibrated humidity transmitter with an uncertainty of 0.5% rH. The humidity could be regulated from 10 to $95 \text{ }^\circ\text{C} \pm 2\%$. The calibrated temperature transmitter had an uncertainty of 0.1°C . The temperature is regulated from 12 to $32 \text{ }^\circ\text{C} \pm 0.3^\circ\text{C}$
- e HEPA filter (JK-S 15/15, Class H13)
- f Raschig-ring filled denuder, coated with phosphoric acid
- g In-line heater, which is controlled upstream with an E+E Humidity/Temperature transmitter, just in front of the Leckel.
- h Bronkhorst CEM-unit (controlled Evaporator Mixer), also with the measuring/controlling point just in front of the Leckel. Deionized water is used for the humidification.
- i TSI- Constant Output Atomizers (COA) with HNO_3
- j TSI- Constant Output Atomizers (COA) with NH_4 salt mixture
- k Silica gel aerosol dryer
- l TSI Kr-85 Aerosol neutralizer
- m cylinder with homemade concentration of ammonia
- n mixing plate for homogenizing the air/aerosol mixture
- o Leckel SEQ 47/50
- p Filter – Pall Tissuquartz 2500 QAT-UP Diameter 47mm (Sigma Aldrich)
- q Marga 2S

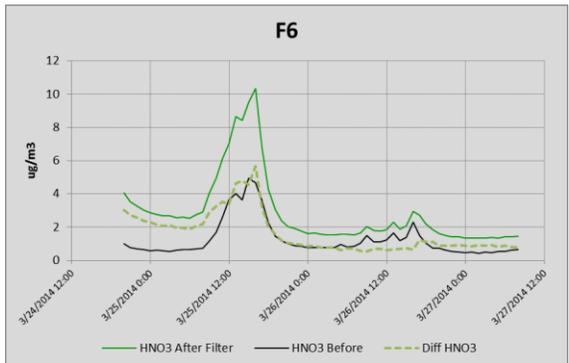
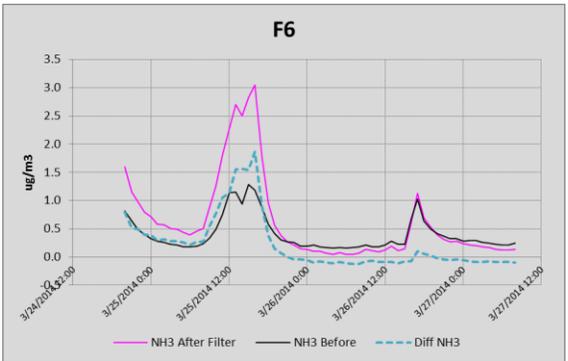
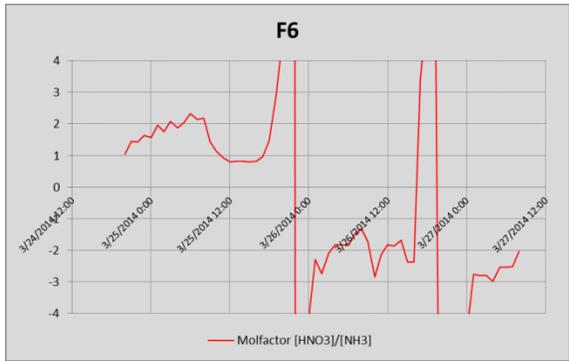
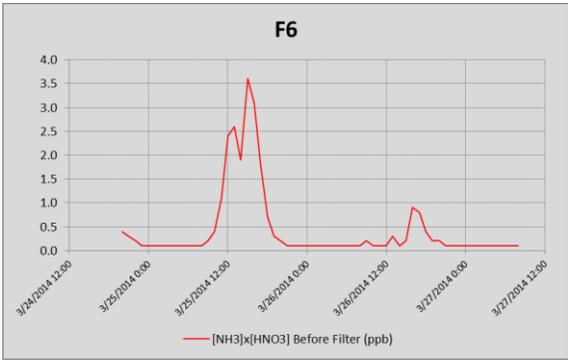
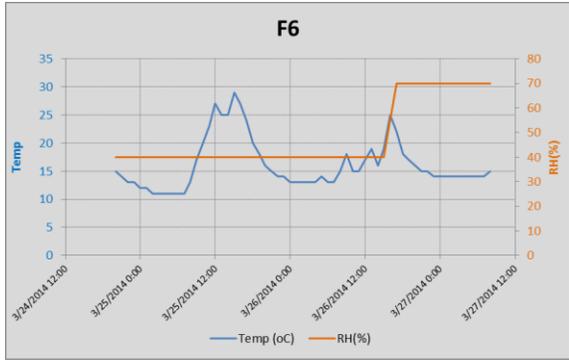
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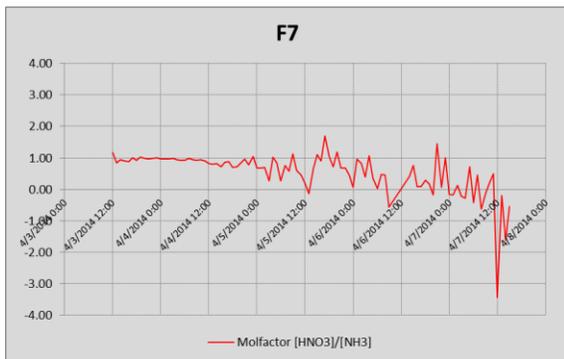
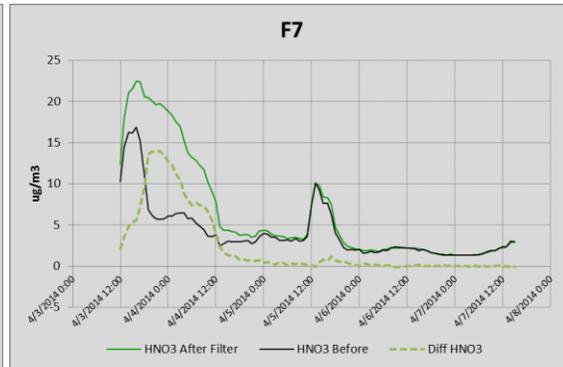
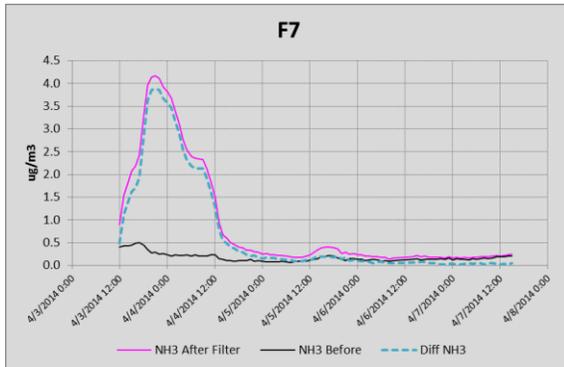
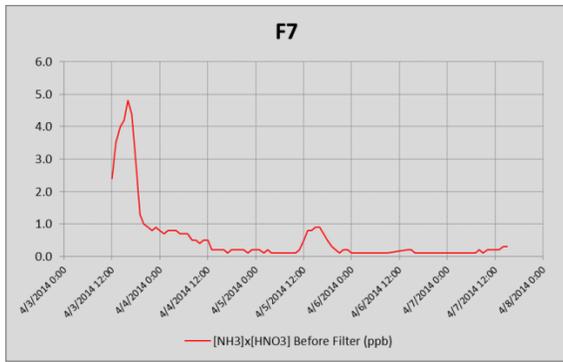
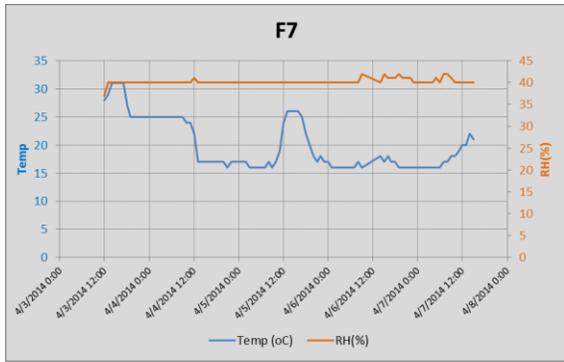


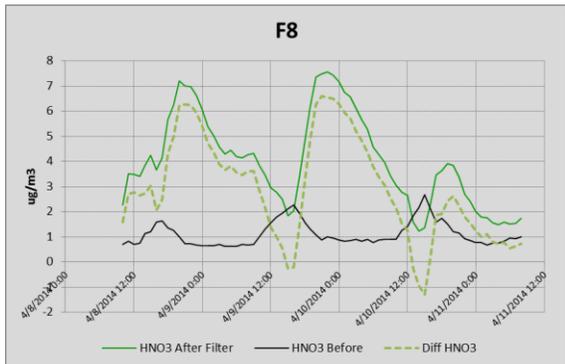
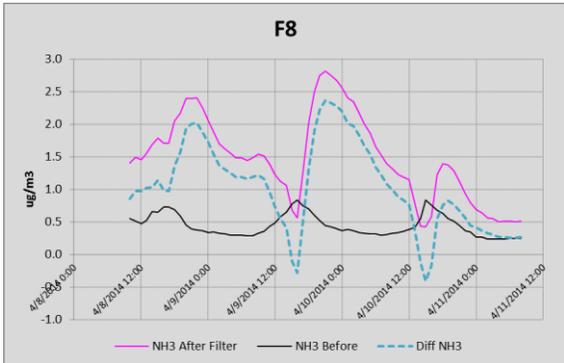
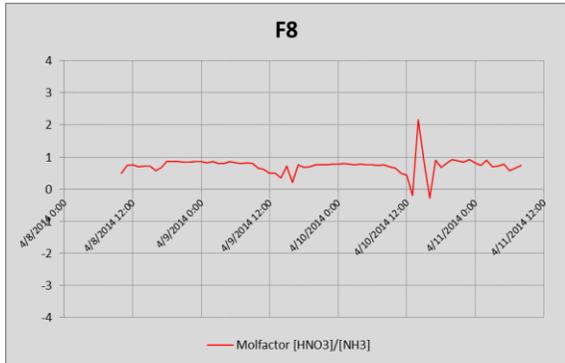
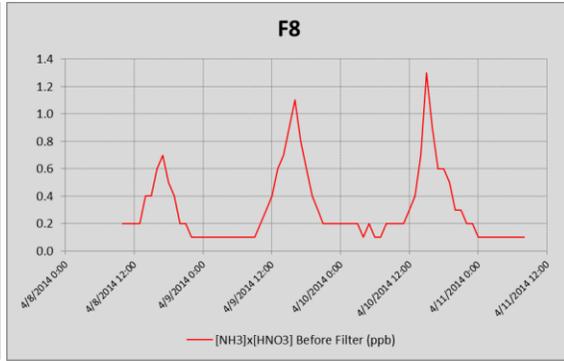
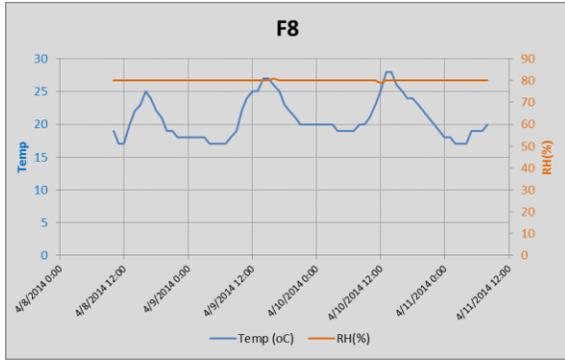


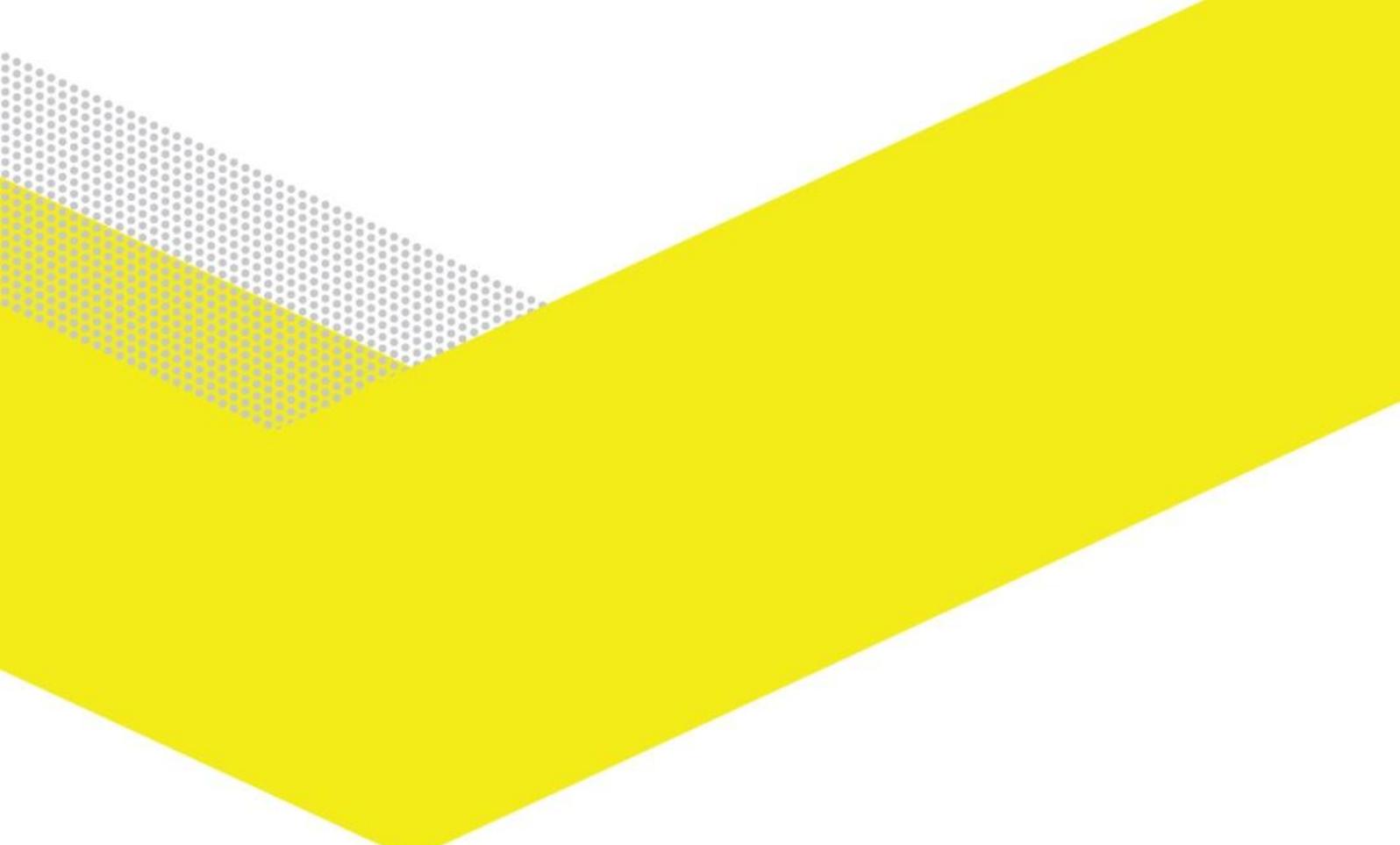












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