

## PM gravimetric measurements and blank filters

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Keywords: PM10/PM2.5, Measurements, Particulate matter, Filters, EN 14907

A significant weight increase of the quartz (Whatman QMA 47mm) field blank filters (FB) of around 140 µg has been found during gravimetric PM10 measurements in 2006. Two types of samplers (single without- and sequential samplers with a temperature controlled storage) showed about the same results (table 1). Since the weight increase of the FB filters did not comply with EN 14907 demands, further research has been done. The manufacturer (Whatman) heats the quartz filters to 500°C in order to obtain the required purity. Short after the heating process the filters are packed and hermetically sealed. Our hypothesis is that adsorption of water vapour from ambient air could be the root cause of a significant mass increase. Also seasonal effects on the weight increase of FB filters have been observed. Possibly adsorption of volatile organic compounds also plays a part in the mass increase of quartz filters.

Table 1. Weight increase of 47mm quartz fibre filters

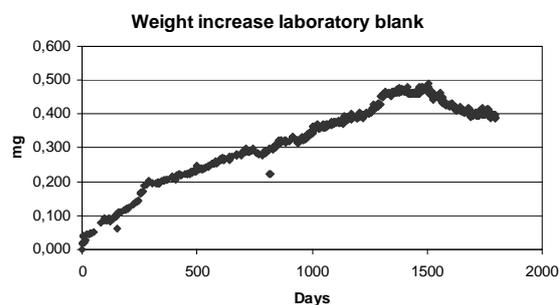
Device	Average weight increase FB (n, sd) µg
Derenda single filter holder	133 (32, 15µg)
Derenda sequential sampler	146 (32, 17µg)

In the Netherlands all air quality laboratories agreed to use one type and brand quartz fibre filters for PM2.5 measurements according to the EN 14907. EN 14907 is the European gravimetric reference method on determination of the PM2.5 mass fraction of suspended particulate matter. This standard prescribes the use of FB filters and laboratory reference blank filters (RB). The mass change of a RB filter between two consecutive weighing sessions as well as the mass change of a FB filter should be less than 40 µg. One of the RB filters in the weighing room of Municipal Health Service Amsterdam has been in use for approximately 1800 days. This specific filter has always complied to the EN 14907 demand of 40 µg mass change at most over two consecutive weighing sessions. However the filter showed a slowly increasing mass of almost 500 µg over the first 1500 days (0,3 µg/day). We believe a mass increase of filters could be caused by adsorption of water vapour. Estimated, from these

observations, Whatman QMA 47 mm quartz fibre filters kept at 20°C and 50% RH will be completely saturated with water after about 1500 days. (figure 1).

Additional to the EN 14907 weighing procedures, a pre treatment of the dry quartz filters has been added to our standard operational procedures. From January 2007 all filters have been stored for at least a month in opened packages in a with water vapour saturated environment at 20°C. The weight increase of three of these filters has been measured over 80 days. The weight increase was 5,1 µg/day, probably due to water adsorption. Compared to the RB filters the saturation process became almost 7 times faster, so complete saturation should be reached after about 3 months.

Figure 1. Weight increase of a RB



Before implementation of this procedure (2006) FB filters gained 140µg (n=64, sd=11 µg) on average. Whereas after implementation in 2007 FB filters gained only 55µg (n=384, sd=3 µg) on average.

EN 14907 (2005). *Standard gravimetric measurement method for the determination of the PM2,5 mass fraction of suspended particulate matter.* CEN/TC 264.

## Semivolatile behaviour of dicarboxylic acids during summer campaigns at K-puszt

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Keywords: carbonaceous particles, filter sampling artifacts, dicarboxylic acids, PM2.5.

It is well-known that the collection of carbonaceous aerosols on quartz fibre filters is prone to both positive and negative artifacts (e.g., Turpin *et al.*, 2000). In studies on these artifacts, one normally concentrates on organic carbon (OC) as a whole or occasionally on water-soluble OC (WSOC). It is rare that studies are carried on individual organic species. One example of the latter type of study is that by Limbeck *et al.* (2001), who used a tandem filter set-up at a rural background site in South Africa and measured dicarboxylic acids (DCAs) and other polar organic species on the front and back filters. Substantial amounts were found on the back filter. The authors' interpretation was that the DCA concentrations on the back filters were caused by the adsorption of gaseous organic species and that DCAs have a semivolatile behaviour. Low-volume TSP samplers were used in that study, the face velocity across the filter was about 22 cm/s, and the collection time per sample was around one week.

We conducted a similar study as that of Limbeck *et al.* (2001), but there were also substantial differences. The samplings for our study took place during summer campaigns in 2003 and 2006 at K-puszt, Hungary; we used a high-volume dichotomous sampler (HVDS), which provides separate fine (PM2.5) and coarse size fractions, the face velocity through the PM2.5 filters was 80 cm/s, and the collection time per sample was around 12 hours. Pre-fired Gelman Pall quartz fibre filters were used for both size fractions. During the 2003 campaign it was consistently warm and dry, but the 2006 campaign was divided in separate cold and warm periods (Maenhaut *et al.*, 2008). The front and back filters for the PM2.5 size fraction of all samples were analyzed

for OC, elemental carbon (EC), and total carbon (TC) with a thermal-optical transmission technique (Birch & Cary, 1996), for WSOC as described by Viana *et al.* (2006), and for water-soluble organic and inorganic anionic species by suppressed ion chromatography with conductometric detection. The median front filter concentrations for a number of components and the interquartile ranges of the back/front filter concentration ratios (both for PM2.5) are given in Table 1. The front/back filter ratios, as derived from the data of Limbeck *et al.* (2001), are included for comparison. Our back/front ratios for oxalic and succinic are low and clearly lower than those obtained by Limbeck *et al.* (2001); malonic was not present on the back filter in the earlier study, whereas we found larger back/front ratios than for oxalic and succinic; of the 4 DCAs studied by us, glutaric has the largest back/front ratio, but Limbeck *et al.* (2001) found an even greater back/front ratio for this species. It is clear that results from one site and sampler cannot be generalised to all sites and sampler types. Therefore, similar studies as the present one are being carried out for other sites in Europe.

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Table 1. Front filter median concentrations and interquartile ranges for the back/front filter concentration ratio (both for PM2.5 of the HVDS) at K-puszt. Comparison with data of Limbeck *et al.* (2001).

Species	Cold period 2006		Warm period 2006		2003		Limbeck <i>et al.</i> (2001) Mean back/ front ratio
	Median front conc. (ng/m <sup>3</sup> )	Interq. range for back/front ratio	Median front conc. (ng/m <sup>3</sup> )	Interq. range for back/front ratio	Median front conc. (ng/m <sup>3</sup> )	Interq. range for back/front ratio	
TC	2100	0.09 – 0.17	4600	0.12 – 0.16	4400	0.10 – 0.13	0.12
WSOC	970	0.17 – 0.26	2900	0.13 – 0.19	2600	0.15 – 0.19	
SO <sub>4</sub> <sup>2-</sup>	1790	0.00 – 0.00	3600	0.00 – 0.00	3500	0.00 – 0.01	
MSA	29	0.01 – 0.13	29	0.01 – 0.08			
Oxalic	73	0.01 – 0.02	210	0.01 – 0.03	196	0.01 – 0.03	0.14
Malonic	33	0.03 – 0.13	65	0.01 – 0.13			0.00
Succinic	32	0.02 – 0.08	142	0.01 – 0.05	41	0.01 – 0.03	0.26
Glutaric	7.1	0.17 – 0.35			7.8	0.15 – 0.22	0.38

## Determination of vertical distribution of air pollution over Budapest by aircraft based measurements

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Keywords: air pollution, mixing layer, Saharan dust, size distribution, trajectory.

Budapest (Bp) is the capital of Hungary, at the same time the largest city of the country. The air pollution of the city is principally determined by traffic related emissions however, contribution of industrial sources as well as pollution transport cannot be neglected.

Aircraft based measurement is an effective way to observe horizontal as well as vertical distribution of air pollution. Investigation of pollutant's vertical profile can provide additional information on the origin of the pollutants that helps the evaluation of urban air quality.

The aims of this work were (i) to study the homogeneity of the pollution in the mixing layer over the city; or (ii) find hot spots that can be associated to any specific emission source on the ground; (iii) to analyse the vertical profile of size fractioned aerosol concentration over downtown and suburban areas, in the mixing as well as the residual layer.

With this object fifteen flights were performed over Budapest and the surrounding area in June and September 2008, and January 2009. Aerosol count concentration and size distribution was measured by a Grimm 1.108 aerosol spectrometer. Black carbon concentration was measured by a Magee Scientific aethalometer. In addition, O<sub>3</sub> and CO concentrations were measured by Horiba gas monitors. The air pressure, temperature and relative humidity was registered by a compact meteorological sensor, while the geographical position was controlled and logged by GPS.

In the first figure concentration time series of two aerosol size fractions with particle diameter of 250nm and 700nm are presented together with the graph of the flying altitude on September 11, 2008. It is seen that until 15:30, while the flying altitude was varying around 400m AMSL the concentration of the two particle size fraction was correlated. After 15:30 the flying altitude increased. At 1400m AMSL, when the aircraft left the mixing layer the concentration of 250nm particles suddenly decreased, while concentration of 700nm particles increased. There was a significant drop in the O<sub>3</sub> concentration as well. These experimental facts together with the analysis of backward trajectories of air masses denote that Sahara originated air mass was sampled over the mixing layer.

Figure 2 shows results of air mass backward trajectory calculation by HYSPLIT model. It is seen

that air masses sampled under 1200m came from over the Atlantic Ocean, while air mass sampled at 1400m passed over the west part of Sahara before it reached European area. The air mass here picked up desert sand and transported into Europe.

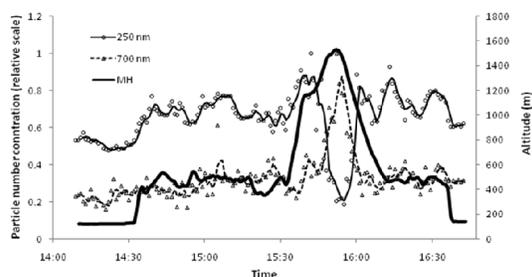


Figure 1. Count aerosol concentration of particles having 250 and 700nm diameter and flying altitude.

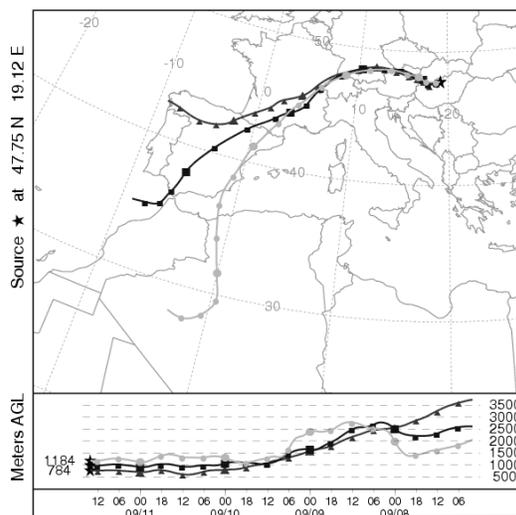


Figure 2. Backward trajectories of air masses sampled at 1000, 1200, 1400m AMSL over Bp.

It must be noted that over the mixing layer the calculated PM<sub>10</sub> concentration was low (around 7µg/m<sup>3</sup>) comparing to the urban pollution concentration. The Saharan dust pass was able to be identified alone over the mixing layer, where the background concentration is negligible. The results reveal the importance of transported pollution in the forming of urban background. Especially naturally generated aerosols can have significant contribution to the PM level in Europe that is not limited to intensive episodes only like Saharan dust events.

## The effect of season and microenvironment type on measurement bias of a photometer DustTrak

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Keywords: Aerosol measurements, Atmospheric Aerosols, Personal sampling, Nephelometer, PM

In the last decade, light scattering devices (or photometers) have been widely used for continuous recording of particulate matter concentrations in exposure assessment studies. The principal advantage of these instruments is that they can be used not only for static but also for personal monitoring since they are portable and can operate on batteries which sustain usually longer than 24 hours. One of the most widely used devices is the DustTrak nephelometer (TSI, Model 8520). It is a real time photometer suitable for determination of aerosol mass concentrations between 0.001 and 100mg/m<sup>3</sup> for particles ranging in size from 0.1 to 10µm. As the instrument is calibrated by the manufacturer for Arizona dust (ISO 12103-1, A1 test dust) the values obtained from measurements performed in various types of indoor and outdoor microenvironments where the particles differ substantially are not actual gravimetric values. In previous studies using this type of device several attempts have been made to establish a recalculation/correction factor according to which the DustTrak data can be transformed into “real” gravimetric values (Chung et al., 2001; He et al., 2004; Heal et al., 2000; Jenkins et al., 2004; Lehoczy a Williams, 1996; Levy et al., 2003; Moosmüller et al., 2001; Morawska et al., 2003; Ramachandran et al., 2003; Yanoski et al., 2002 and others). We present here the results of a long term collocation of Dustrak (PM<sub>2.5</sub>) and a cascade impactor (PCIS). Our results showed that the correlation coefficients between the DustTRak and PCIS PM<sub>2.5</sub> concentrations were reasonably high, 0.922 and 0.936 for the outdoor and indoor microenvironments respectively.

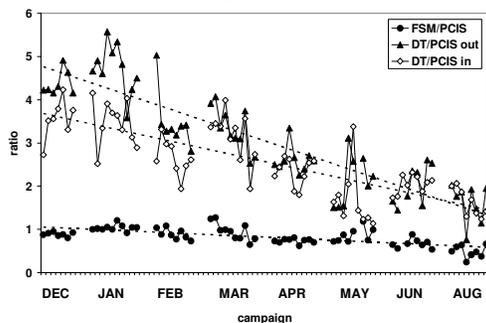


Figure 1: Ratio between PM<sub>2.5</sub> measured during different seasons in indoor and outdoor microenvironments by DustTrak and two other methods (PCIS and  $\beta$ -attenuation).

However, the 24-hour DustTrak values were in all cases higher than the PCIS ones (Fig. 1). The photometer gave values ranging from about less than 2 to over 5 times higher than the reference method. Higher DT/PCIS ratios were found in winter and in situations when smaller particles were abundant in the measured aerosol mixture.

Together with other authors we conclude that DustTrak is a good device for recording relative changes in aerosol concentrations but cannot be used for estimation of real PM mass concentration. However, with parallel gravimetric measurements a correction factor can be obtained and used in short term exposure assessment studies. When no simultaneous reference measurements are available, recalculations of DustTrak readings to gravimetric values cannot be simply made on the basis of the existing literature data. Seasonal (temperature and relative humidity), specific microenvironmental characteristics (indoor, outdoor) and type of aerosol sources should be taken into account.

Support: MSM 0021620831

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## Novel approach to identifying size dependent losses of semivolatile compounds during room temperature storage of sampled aerosol matter

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Keywords: Aerosol sampling, aerosol size distribution, cascade impactor, semivolatile, salt aerosol.

In recent studies we have discussed negative artefacts associated with the loss of semivolatile compounds of aerosol matter. It is well known – but not often fully appreciated – that the processes leading to such artefacts during sampling are in most cases quite significant (Wittmaack and Keck, 2004; Keck and Wittmaack, 2005). Less well studied are losses that can occur during subsequent storage of aerosol matter on filters or on collection plates of impactors. Unpublished data suggest that even after several years of storage the losses might not be complete.

This study was performed to explore a novel ‘soft’ approach to identifying the total amount of matter that can be lost due to volatilisation during sample storage. In order to determine the size dependence of the effect, sampling was performed in impactors. Two essentially identical 8-stage cascade impactors (Berner type) were operated in parallel at flow rates of 30 L/min. PM<sub>2.5</sub>, PM<sub>10</sub> and TSP mass concentrations were also determined by filter sampling. Particle size distributions in the range above 0.3 µm were recorded using an optical counter (Grimm model 1108). The results discussed here relate to 24-h sampling in late winter with temperatures around 0°C.

The collected masses were first determined by gravimetry. Thereafter one set of impactor samples was transferred into a vacuum chamber and stored at < 10<sup>-6</sup> hPa. The mass losses that occurred in vacuum were determined at storage times between 18 h and three weeks, at which point the losses had stabilized.

The water soluble fractions of the impactor deposits were carefully extracted and analysed by ion chromatography. Size distributions of SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup>, measured with as-sampled and vacuum treated impactor deposits, are presented in Figs. 1(a) and (b). Within experimental uncertainty the results for SO<sub>4</sub><sup>2-</sup> are the same, indicating that this component did not suffer from any losses in vacuum. By contrast, NH<sub>4</sub><sup>+</sup> was lost very significantly throughout the whole spectrum, with possible exceptions at the lower and upper end of the spectra. Large losses were also observed with NO<sub>3</sub><sup>-</sup>, see Fig. 1(c) and, to a lesser extent, for Cl<sup>-</sup> (not shown).

Interpretation of the results was assisted by measuring the time dependence of mass losses in vacuum for the pure salts NH<sub>4</sub>NO<sub>3</sub> and NH<sub>4</sub>Cl.

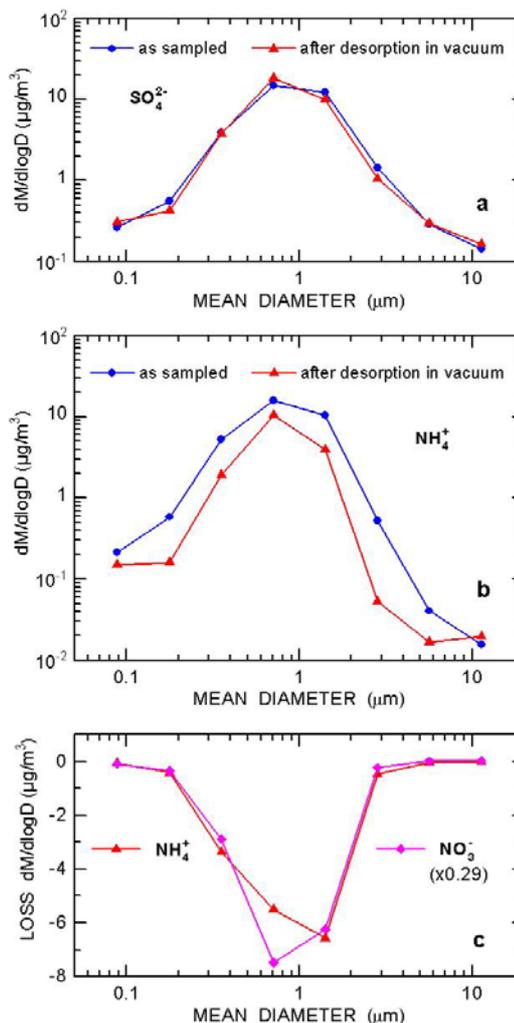


Figure 1. Comparison of the mass spectra of (a) SO<sub>4</sub> and (b) NH<sub>4</sub> ions in impactor deposits without and with long-term storage in vacuum. (c) Comparison of mass losses for NH<sub>4</sub> and NO<sub>3</sub>.

Thanks are due to E. Schneider-Kracke for the mass measurements, to H. Halder for assistance with the vacuum treatment of the samples and to L. Keck for the ion chromatography analysis.

Wittmaack, K., & Keck, L. (2004). *Atmos. Environ.*, 38, 5205-5215.

Keck, L. & Wittmaack, K. (2005). *Atmos. Environ.*, 39, 4093-4100.

## What's up with the European PM reference methods?

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Keywords: PM10/PM2.5, PM reference method, PM artefacts, Filters

Quite recently it has become clear that the European reference methods for measuring **PM<sub>10</sub> (EN12341)** and **PM<sub>2.5</sub> (EN14907)** can lead to much larger ranges of results than what was first assumed. It turns out that certain artefacts were underestimated or even unknown when the standards were created. In the last couple of years the Flemish Environment Agency has carried out a range of experiments and tests in order to investigate some of the issues, and to put them on the agenda of CEN TC264 WG15 (which created both standards).

Some 5 years ago various types and brands of 47-mm filters were used in parallel in several field campaigns. To our surprise the differences between the different variations of the reference method were sometimes as high as 25% (as campaign averages). Of the two filters that were used the most, the **Whatman QM-A** (which contains 5% borosilicate and is pre-fired in the factory) gave results that were on average 14% higher than **Macherey-Nagel QF10** (a 100% pure quartz fiber filter). Tests with the standard EMERY 3004 aerosol (a poly alpha olefin) showed that the observed differences were not due to variations in physical separation efficiency, as all filters scored better than 99.9%.

In a more recent project ("Chemchar PM<sub>10</sub>" a chemical characterisation project) the Whatman QM-A filters (which were extra pre-fired to obtain lower OC blanks) captured on average 7% more mass than teflon filters (Pall Teflo) that were sampled in parallel. Part of this difference was due to the higher blanks for the QM-As (112 µg absolute resulting in ± 2 µg/m<sup>3</sup>) than for the teflon filters (56 µg absolute resulting in ± 1 µg/m<sup>3</sup>).

A 3-step experiment with 5 filter types (Table 1) was done to investigate both the effects of pre-firing and the use of the 'Amsterdam' approach (= 'pre-conditioning' the blank filters by exposing them to 100% humidity for some weeks, before weighing and sampling). Each set of a filter type consisted of 3 new, identical filters.

In the first step of the experiments types 3 and 5 were fired (by Ghent University) for 24 h at 550 °C. This led to a mass loss of 10 mg for the QF10s and 2 mg for the QM-As.

Table 1: Filter types used in 3-step experiment.

1. Pall Teflo	teflon
2. Macherey-Nagel QF10	100% quartz
3. Macherey-Nagel QF10*	100% quartz
4. Whatman QM-A	95% quartz + 5% glass
5. Whatman QM-A*	95% quartz + 5% glass

\*to be fired in step 1

In the second step all 5 sets of filters were exposed to 100% relative humidity (RH) for 9 weeks (Fig 1). All quartz filters showed a rapid increase in the first couple of days and did not stabilise within the 9 weeks. Similar profiles, but in a lower mass range, had already been obtained at 50% RH and for field blanks.

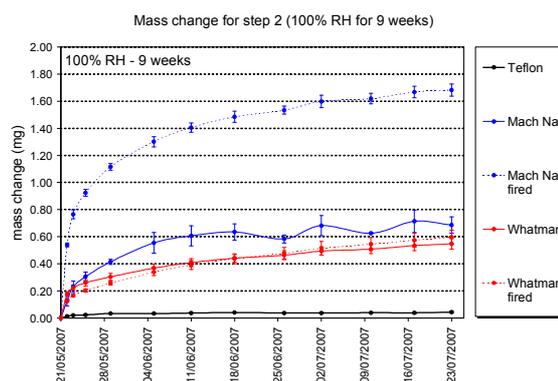


Figure 1: Mass change for step 2, at 100% RH.

In the third step all the filters were exposed to 50% humidity for 30 weeks. The results of the first 4 weeks are presented in Fig 2 and show that 3 of the 4 types of quartz filters reach an equilibrium weight within 48 h. For these 3 types this weight turned out to be the same as the weight they had after exactly 3 weeks in step 2 (at 100% RH) indicating that at least 3 weeks of 'pre-conditioning' is desirable. The 4<sup>th</sup> quartz type, the pre-fired QM-A showed only a small loss in mass and even started gaining weight again after 3 days. After the full 30 weeks this type had gained about 100 µg compared to the start of step 3. For the other types the mass was constant or less than 50 mg from the equilibrium weight.

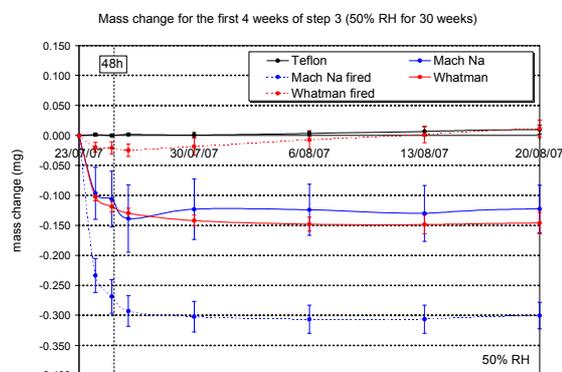


Figure 2: Mass change for step 3, at 50% RH.

## Organic Carbon in Whatman-QMA field-blanks

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Keywords: filter-blanks, OC, artefact

Guideline EN-12341 prescribes the use of quartz fibre filters in the reference sampling of PM<sub>10</sub>. It is well-known that quartz fibre filters exhibit artefacts. They take up volatile OC during sampling and may lose semi-volatile OC (Turpin et al. 2000). Adsorption is in general the most important artefact.

A large number of samples has been taken by now in EU counties with quartz fibre filters over the years and the OC-artefact must have lead to an appreciable artificial increase in the amount of PM<sub>10</sub>. However, searching for information we could not find data on the importance of this artefact.

A minimum value for the adsorption artefact may be provided by the so-called field blanks. These are filters that are put in the sample holders without being loaded. The filters take up OC via diffusion.

The networks in the US report field blanks that are large in comparison with the actual OC-data. Only some scattered data are available in Europe (e.g., Vecchi et al. 2009).

Filters as received from the manufacturer often contain OC and they are therefore cleaned by pre-firing in scientific studies. The commonly used Whatman-QMA filters are pre-fired in the factory, according to information from the manufacturer.

In order to assess the current uncertainties around field blanks and lot-blanks in the PM-studies in the Netherlands we performed a dedicated study on the two types of blanks with Whatman-QMA filters as used in the national reference sampling for PM<sub>10</sub>.

### Field blanks

The study was part of a one-year investigation to assess the composition of PM in the Netherlands at regional and urban/kerb sites. Filter sampling was performed with automated reference samplers (KFG-Leckel) on 47 mm Whatman-QMA filters. Field blanks were filters that were in the Leckel filter carousels.

There are two carousels, one with the fresh filters from which every day a new filter is shifted into the filter holder. After sampling the filter is moved to a second carousel. 150 field blanks were taken evenly distributed between the two carousels and over the stations.

Analysis of the set of field blanks showed quite a variation in the OC-values. The average was 68 ug with an SD of 31 ug. The mentioned value for a total filter corresponds to a concentration of OC of 1.3 ug m<sup>-3</sup>. This translates into a value of Organic Matter (OM) of close to 2 ug m<sup>-3</sup>.

There was no systematic difference in the blanks from the urban sites versus those from the three regional sites, which seems to indicate that the filters are saturated with OC. This could imply that the field blanks can serve as a proxy for the adsorption artefact during sampling.

### Lot blanks

In addition to the field blank we made a study of the "lot"-blanks, i.e., Whatman-QMA as received from the factory. These "lot"-blanks were taken from batches that were unsealed immediately before analysis. Filters from three batches were analysed.

It was consistently observed that filters from the top of a stack contained high OC values. These values were higher than the average field blank.

Further down the stack of filters the values rapidly decreased. In two of the batches these were still appreciable with an average value of 25 ug, but in one batch the values were at the detection limit of 3 ug.

The bottom filters had (again) higher values.

### Addendum: blanks for NO<sub>3</sub>, SO<sub>4</sub> and NH<sub>4</sub>

The average value in the (150) field blanks was resp. 1.1%, 2.1% and 0.7% of the average value in the actual samples.

### Acknowledgement

The investigation was performed in the framework of Netherlands Research Programme on Particulate Matter (BOP)

Turpin et al., (2000). *Measuring and simulating particulate organics in the atmosphere: problems and prospects*. Atmos. Environ. 34, 2983-3013

Vecchi et al. (2009). *Organic and inorganic sampling artefacts assessment*. Atmos. Environ. 43, 1713-1720

## Water uptake and retention by filter material used for PM sampling

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Keywords: PM measurements, artifacts

Water uptake by atmospheric aerosol particles under conditions of elevated relative humidity is a well known phenomenon. Several models exist to predict the amount of water associated with the particles from their chemical composition. For PM measurements, weighing protocols have been developed that specify equilibration of filters at 50% humidity and 20°C for 24 hours before weighing. Under these conditions, most of the water should have evaporated from the particles. Recently, equilibration at 35% relative humidity has been suggested.

The question whether the filter material itself adsorbs water has been mentioned several times, but very few actual measurements (e.g. Demuyneck, 1975; Hänninen et al., 2002) can be found in the open literature. If sampling was performed at elevated humidities and the filter material retains appreciable amounts of water vapor at the specified humidity for weighing even after the required equilibration time, measured PM mass concentrations will be overestimated. As filter masses are much higher than deposit masses, even mass increases below the percent range will add a substantial bias to the measured deposit mass.

In this study, we investigate the changes in filter mass for different filter types (e.g. Quartz fibre, cellulose ester, glass fibre, polycarbonate filters) after 24 hr exposure to different humidities. We used the humidity chamber developed at the University of Vienna (Hitzemberger et al., 1997, current design: see Lehtinen et al., 2003). In this chamber (Figure 1), samples are put on an aluminum tray which is connected through a sealed opening to a semi-microbalance (Mettler AT 201, accuracy  $\pm 10\mu\text{g}$ ) mounted above the chamber. Humidity is controlled by using aqueous solutions of salts (in this study, we used  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) of different concentrations.

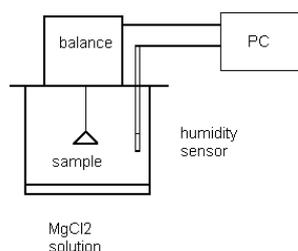


Figure 1 schematic set-up of the humidity chamber

Measurements started at ambient humidity in the laboratory (usually around 50%), when the balance is tared so the mass readings during the measurement cycle directly correspond to the mass of water taken up by or lost from the filters. Mass, temperature and humidity are recorded automatically. In a typical measurement, filters are first exposed to a nominal humidity of 30% (in some cases 40%) and subsequently to 50%, 90%, 50% and 30% (or 40%)40%. Exposure time at each of these humidities was  $> 24$  hrs.

First results showed that during the periods at high humidities, filters can take up appreciable amounts of water. For 5 different 47 mm diameter Quartz fiber filters (Pallflex Tissuequartz 2500 QAT-UP), masses increased on average by 6.13 mg when humidities were increased from 43 to 87%. Most of this mass is lost again, but at 53 % the average mass increase is still 1.4 mg (compared to the initial 43%). The filters do not reach their initial mass when humidities are reduced back to 43%, but still retain 0.54 mg on average. In terms of filter mass, this mass increase is negligible (average mass of filters: 130.5 mg), but in terms of deposit mass, this mass retention could lead to large errors at low mass deposits.

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## Level of uncertainty on PM<sub>2.5</sub> mass concentrations introduced by inorganic sampling artifacts

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Inorganic aerosol compounds such as reactive acidic (SO<sub>2</sub>, HNO<sub>2</sub> and HNO<sub>3</sub>) and basic gases (NH<sub>3</sub>) contribute to positive and negative artefacts significantly affecting PM<sub>2.5</sub> mass concentrations. The evaporative loss of the semi-volatile ammonium nitrate from the aerosol phase (negative artefact) or adsorption of nitric acid and sulphur dioxide gases (positive artefact) can occur during or after sampling. This work presents results obtained during a campaign for the assessment of sampling artefacts on the gravimetrically determined PM<sub>2.5</sub> mass concentration during winter.

The field campaign was carried out at the “Demokritos” urban background site in the periphery of the Athens Metropolitan area, Greece. An annular denuder system (ADS) and a filter pack (FP) were deployed in parallel for the evaluation of mass concentrations. A cyclone inlet preceded the annular denuder/filter pack system in order to remove coarse particles, while gases and fine particles are quantitatively transferred into the annular denuder and filter pack components. SO<sub>2</sub>, HNO<sub>2</sub> and HNO<sub>3</sub> vapours are trapped by a Na<sub>2</sub>CO<sub>3</sub> – coated annular denuder. A second Na<sub>2</sub>CO<sub>3</sub> – coated annular denuder is used to retain excess nitrate and nitrite. The third denuder was coated with citric acid for trapping NH<sub>3</sub>. The filter pack after the denuders contained a Teflon filter where the particulate matter was collected, a KOH coated cellulose filter where the gases evaporating due to the disequilibrium between gas and particulate phase were collected and a citric acid coated cellulose filter where the evaporating NH<sub>3</sub> was collected. The annular denuders and the triple filter pack together comprised the annular denuder sampling system (ADS). An identical triple filter pack equipped with a cyclone inlet was also sampling in parallel. Samples were collected at 24h intervals, where the sampling flow rate was set at 10 lt/min and values of ambient temperature, R.H. and pressure were monitored. After sampling, the aerosol mass concentration was determined gravimetrically on the Teflon filters from the ADS and FP systems. Filters were conditioned in a 20 °C and 50 % R.H. weighing room for 24h before and after sampling. Weighing was performed on a 10<sup>-5</sup> gr resolution Sartorius Balance.

A control experiment was performed comparing the mass concentrations on Teflon filters obtained by an un-denuded ADS system and the filter pack,

when sampling in parallel. Mass concentrations displayed an excellent correlation ( $R^2 = 0.99$ ) and a ratio of 0.8 for the FP concentration over the ADS concentration. Results of the equivalent mass concentrations measured by the ADS and FP during the winter period (February – March – April) are shown in Fig 1.

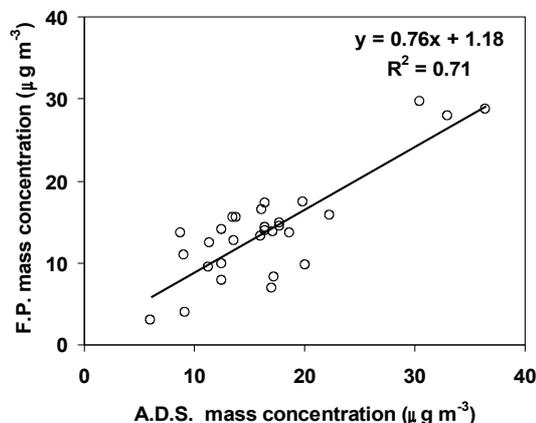


Figure 1. Relationship between denuder and filter pack system concentration in PM<sub>2.5</sub> samples

Preliminary conclusions from the current results indicate that increased scatter in the data is apparent when the ADS and FP ratios are compared to the control experiment data. This is due to the variability in positive/negative artifact due to the disequilibrium between gas/particle phases at variable conditions. Below the effect of increasing RH is demonstrated to lead to FP/ADS ratio closer to unity as the particulate phase is favoured.

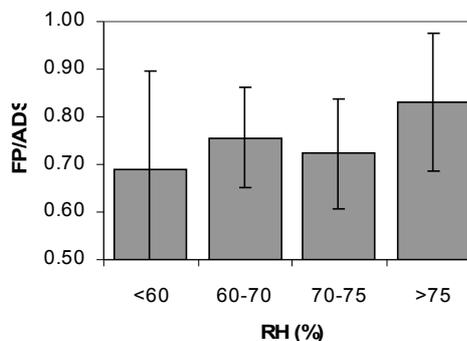


Figure 2. FP/ADS ratios with respect to ambient RH