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Spatial inhomogeneity of anions in ambient particulate matter collected on air filters: Determination using a drift-corrected ion chromatography technique

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ABSTRACT

The spatial inhomogeneity of anions in ambient particulate matter collected on filters has been investigated using two different sub-sampling techniques and with analysis by a drift-corrected ion chromatography technique. The results highlight the inhomogeneity in anion mass along the radius of the sampled filter, in agreement with analogous studies on metals in PM, and also, more surprisingly, significant random differences between sub-samples based on filter sectors. Implications for the sub-sampling of filters for the purposes of performing multiple analyses are discussed.

1. Introduction

The chemical composition of ambient aerosols continues to be a subject of great interest to the environmental and atmospheric chemistry communities [1]. The determination of the anionic content of particulate matter (PM) is of increasing interest in this context because of the requirement to work towards mass closure in PM studies, and also because the presence of many anions in PM arise as a result of conversion from primary air pollutants such as CO, SO_2 and NO_x [2]. Moreover anions in PM can be precursors for acid rain formation [3]. Therefore, there is a need to perform accurate and traceable measurements of the mass concentration of anions in ambient air, and the mass fraction of anions in PM, in order to provide reliable data sets to: measure the exposure of the general population to these compounds; assess compliance with legislative limits or similar target values; and inform policy development and assess the effectiveness of abatement strategies. To this end anion mass concentration in ambient air is currently measured daily at three sites in the UK as part of the UK Airborne Particulate Concentrations and Numbers Network [4]. Moreover the requirement to perform these measurements (together with measurements of cations) is mandated in the European Union (EU) [5] – and as a result of this requirement a standard method for the measurement of anions and cations in PM will be prepared by the European Committee for Standardisation's Technical Committee (TC) 264 Working Group (WG) 34. Motivated by the same legislative requirement, the sister group of WG 34 – namely TC 264 WG 35 – is developing methods for the measurement of organic and elemental carbon (OC/EC) in particulate matter which is required by the same EU legislation. This highlights the increasing requirement for multiple analyses to be made from sampled air filters to improve the cost effectiveness of ambient air monitoring. Multiple analyses are usually performed by taking sub-samples from the filter. The UK Airborne Particulate Concentrations and Numbers Network is a case in point where two sub-samples from the same filter are taken for the measurements of anions by ion chromatography and OC/EC by thermo-optical methods [6]. When taking sub-samples it is self-evidently important to ensure than this sub-sample is representative of the filter as a whole.

In this paper we present novel data concerning the homogeneity of anions within PM collected on filters, using ion chromatography employing a drift correction protocol, which removes any variability owing to changes in instrument sensitivity, therefore allowing real differences between measured samples to be more easily elucidated. The drift correction procedure is based on the repeated analysis of a quality control standard throughout the measurement series followed by correction of the intermediate measured responses according to the observed change in the response of the quality control standard in the time domain. There has been very little work on determining the homogeneity of pollutants contained within PM on air filter, save for our recent investigation of metals in PM using LA-ICP-MS [7]. We have also recently developed a

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novel extraction procedure for anions in PM to improve the accuracy of measured results [8], which we also employ in this study. However to the best of the authors' knowledge no study has examined specifically the spatial inhomogeneity of anions within PM on sampled air filters, although research into the general process of making measurements on ions in PM is ongoing currently [9].

2. Material and methods

2.1. General

All solutions were prepared in fully cleaned and dried (in a nitrogen flow (oxygen free nitrogen, BOC)) polypropylene labwear (Fisher) using deionised water (18.2 MΩ cm, Milli-Q system, Millipore). All chemicals were of high purity (+99.9%, Fisher) and were prepared according to the supplier's guidelines (drying at elevated temperatures for the inorganic salts). All solutions were prepared gravimetrically. The eluent used for the IC analysis and for extraction of the anions from the filters was an aqueous solution of 11 mM Na_2CO_3 and 2 mM $NaHCO_3$. All experimentation, except for the sample collection, was conducted in a temperature-controlled laboratory at 20 ± 2 °C.

2.2. Sample collection

Samples were collected so as to replicate extremes of likely samples taken in the field by air quality networks. Weekly and daily samples were taken onto cellulose ester filters (GN Metricel, Pall) using a Partisol 2000 instrument, fitted with a PM_{10} sampling head sampling at 1 $m^3\,h^{-1}$, resulting in a total sample volume of approximately 168 m^3 on a 47 mm diameter filter. These samples were taken at the UK Heavy Metals Monitoring sites in Runcorn Weston Point, Walsall Willenhall and Chadwell St Mary [10,11] where relatively heavy mass loadings were expected. Daily samples were taken onto PTFE-bonded borosilicate glass filters (Emfab, Pall) using a Leckel KFG instrument, fitted with a $PM_{2.5}$ sampling head sampling at 2.3 $m^3\,h^{-1}$ resulting in a total sample volume of approximately 55.2 m^3 on a 47 mm diameter filter. These samples were taken at NPL's research air quality monitoring site at the north-western corner of the NPL compound in Teddington, adjacent to Bushy Park, where lighter mass loadings were expected. Both samplers used sampling heads employing impactor-style designs, with the sampled air finally being delivered down a tube orthogonal to the filter, the diameter of this tube being approximately half that of the filter and the centres of the filter and the tube being coincident.

2.3. Sub-sampling and extraction

Sampled filters were sub-sampled using ceramic scissors (Fisher, UK). Two types of sub-sample were taken. Sub-sample type (a) was taken by cutting the filter into eight equal filter sectors (i.e. a portion enclosed by two radii and an arc). Three daily PM_{10} samples were analysed using this method. Sub-sample type (b) was taken by cutting a rectangular strip approximately 10 mm wide and 20 mm long from the centre of the circle to its circumference along a radius of the filter, and then cutting orthogonally to this radius, starting from the filter centre, to produce 6 pieces of 10 mm by 3 mm, discarding the outermost couple of mm of the filter which may not be entirely covered by the sampled PM. This type of sub-sample allows assessment of the homogeneity of anion distribution along a radius of the filter. Each one of these sub-samples represented less than 2.5% of the whole filter area. Six weekly PM_{10} samples, three daily PM_{10} samples and three daily $PM_{2.5}$ samples were analysed using this method. These sub-sampling procedures are displayed diagrammatically in Fig. 1.

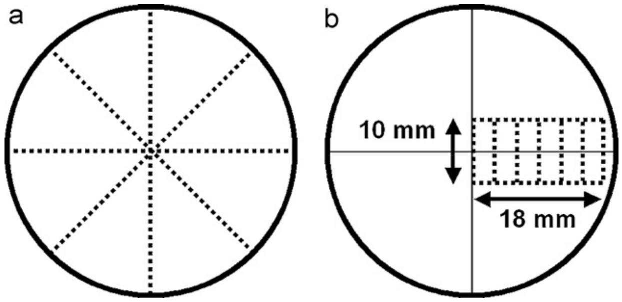

Fig. 1. Diagrammatic representation of the two types of filter sub-samples considered, indicated by the dotted lines: (a) cutting the filter into eight equal filter sectors, (b) cutting a rectangular strip approximately 10 mm wide and 20 mm long from the centre of the circle to its circumference along a radius of the filter, and then cutting orthogonally to this radius, starting from the filter centre, to produce 6 pieces of 10 mm by 3 mm, and discarding the outermost 2 mm; the solid lines are orthogonal diameters marking the centre of the filter as a guide to the eye.

The sub-samples taken were sonicated in an ultrasonic bath (37 kHz, 80 W RMS power, Ultrasonics Ltd.) in a weighed amount (approximately 20 g) of the IC eluent. Solutions were then filtered through 0.45 mm PPE filters (Whatman) as they were introduced into the ion chromatograph. Representative blank filters were also measured and these values subtracted from the measured masses of the anion in the PM. In all cases, for each filter material, these blank masses were small relative to the mass of anions collected (overall <2% of the total mass), such that their impact on the measured results was minimal.

2.4. Analysis using ion chromatography

Analysis for chloride, sulphate and nitrate was performed with a Dionex ICS-1500 ion chromatograph (IC), with self-regenerating suppressor unit and conductivity detection as previously described [8]. A flow rate of 1.0 mL min^{-1} was used throughout. The volume of the sample injection loop was nominally 100 μL. Each sample extract was measured in duplicate. Quantification was performed with NPL's XLGenline software [12], using the peak areas provided by the proprietary software (Chromeleon software, Dionex).

2.5. Drift correction

Each set of sub-samples from the same filter was analysed in one analysis run which, as the key data are presented in relative terms, gives more confidence that any uncertainty owing to reproducibility between analytical runs is not an important factor in the interpretation of the results. Prior to this analysis run multicomponent calibration solutions were prepared and measured such that the solutions requiring measurement were approximately located towards the centroid of the calibration curve wherever possible, and usually constituted of at least four solutions of different concentration plus a blank solution. Calibration was only necessary in this case to make a determination of the total mass of anions present on each filter – which is only supplementary information in respect of the main study presented. After the set of calibration standards, the first sub-sample extract was measured. Next the calibration standard closest in peak area to the initial sub-sample measurement was re-run as a drift correction standard. Then a further sub-sample extract was measured, then the same drift correction standard, and so on, alternating sub-sample and drift correction standard until the end of the measurement series. The peak areas for the drift correction standards were then normalised to their average over the measurement series. An example of the plot produced is shown in Fig. 2. This shows the magnitude of variability that may be expected over the measurement peri-

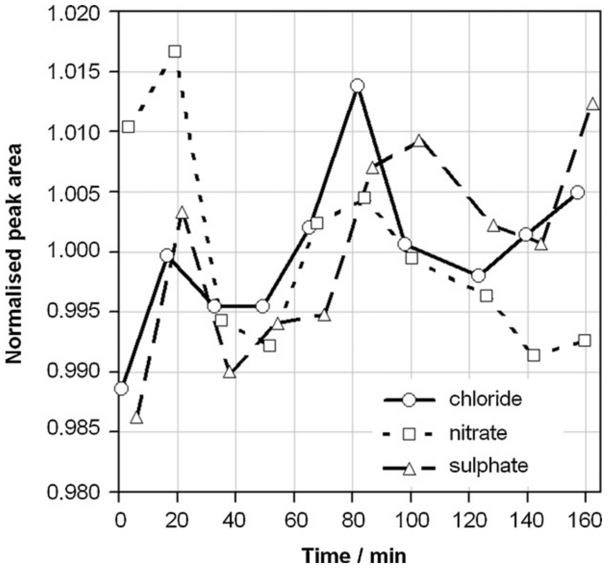

Fig. 2. Exemplar normalised response from a multi-component drift correction standard measured ten times over an extended period. The retention times for chloride, nitrate and sulphate were 4.5, 7.1, and 9.6 min respectively.

ods employed, and that this drift is usually random with zero sum difference over time, and not monotonic. The peak area measured from a sample extract during the measurement series may then be corrected for drift according to:

$$A_{\text{corr},t} = \frac{A_{\text{meas},t}}{\varepsilon_{\text{drift}}(t)} \tag{1}$$

where $A_{\text{meas},t}$ is the peak area measured for sample extract analysed at time t, $A_{\text{corr},t}$ is the drift-corrected peak area measured for sample extract analysed at time, and $\varepsilon_{\text{drift}}(t)$ is the peak area of the drift correction standard normalised to its average value over the measurements series at time t. $\varepsilon_{\text{drift}}(t)$ is a function of t, and is most pragmatically evaluated at time t as a linear function between the two adjacent measurements of the drift standard, thus:

$$\varepsilon_{\text{drift}}(t) = \varepsilon_{\text{drift}}(t_{-1}) + \frac{(t - t_{-1})}{(t_{+1} - t_{-1})}(\varepsilon_{\text{drift}}(t_{+1}) - \varepsilon_{\text{drift}}(t_{-1})) \tag{2}$$

where $\varepsilon_{\text{drift}}(t_{-1})$ is the peak area of the drift correction standard normalised to its average value over the measurements series at time t_{-1} corresponding to the measurement point immediately prior to the measurement of the extract undergoing correction and $\varepsilon_{\text{drift}}(t_{+1})$ corresponds to the analogous measurement point at time t_{+1} immediately after the measurement of the extract undergoing correction. (An alternative method of producing drift correction of this type is polynomial fitting [13], but there were normally too few points in a measurement series to use such a method in this case.) In general the observed difference between drift correction points (<2% relative) is small compared to the difference observed in the measured samples, as will be shown later, but it is good measurement practice to include this in the measurement procedure to give confidence that any effects observed are real. All presented data has been drift corrected in this manner.

3. Results and discussion

The total masses of chloride, nitrate and sulphate measured on each of the filters examined in this study are given in Table 1.

The measurement of the first type of sub-sample, based on the eight filter sectors, served to act as a type of control experiment for the subsequent investigations of anion distribution along a filter radius. Based on previous results from other studies [7] and knowledge of the sampling system, it was expected that there would be no significant difference between the anion loadings measured on the filter sectors. The results from the analysis of these filters are displayed in Fig. 3. The measurements for each anion for each filter were normalised to their average and then the whole set of values was ordered and plotted with respect to their ranking in this order. Surprisingly, relatively large differences were observed between the filter sectors, ranging from 0.75 to in excess of 1.4 times the average level observed on each filter. Moreover, evidence that these observations are not an analytical artefact comes from the correlation between nitrate and sulphate masses on the same sections, shown in the inset to Fig. 3. Because these two species are found in secondary aerosols formed by very similar processes the correlation between the observed concentrations of these species is often strong at the same monitoring site [4]. Hence the good correlation

Table 1
Sampled volume and measured mass for the filters used in this study.

Filter	Sample volume/m^3	Anion mass on whole filter/μg		
		Chloride	Nitrate	Sulphate
FS 1	55.2	541	549	318
FS 2	55.2	38	515	525
FS 3	55.2	218	532	317
WR 1	168	511	879	494
WR 2	168	440	921	678
WR 3	168	461	1130	544
WR 4	168	544	821	523
WR 5	168	523	942	553
WR 6	168	1038	209	486
DR(10) 1	24	35	351	170
DR(10) 2	55.2	99	278	148
DR(10) 3	55.2	128	190	160
DR(2.5) 1	55.2	30	244	367
DR(2.5) 2	55.2	33	280	173
DR(2.5) 3	55.2	81	380	329

Filter labelling is as follows: FS – filter used for filter sector sub-sampling; WR – filters sampled over a week with a PM10 head and used for filter radius sub-sampling; DR(10) – filters sampled over a day with a PM10 head and used for filter radius sub-sampling; DR(2.5) – filters sampled over a day with a PM2.5 head and used for filter radius sub-sampling. In the cases of the WR and DR samples these total masses have been calculated assuming that the average mass loading found on the sub-samples measured were replicated across the whole filter area.

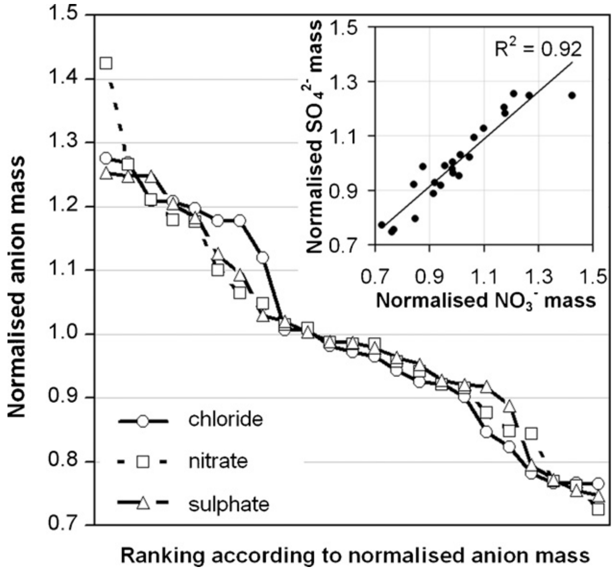

Fig. 3. Anion mass measured on each filter sector normalised to the average measured across each of the filters analysed. This has been plotted, for each anion, in order of the normalised mass. The inset shows the relationship between the normalised nitrate and sulphate masses measured on individual filter sectors.

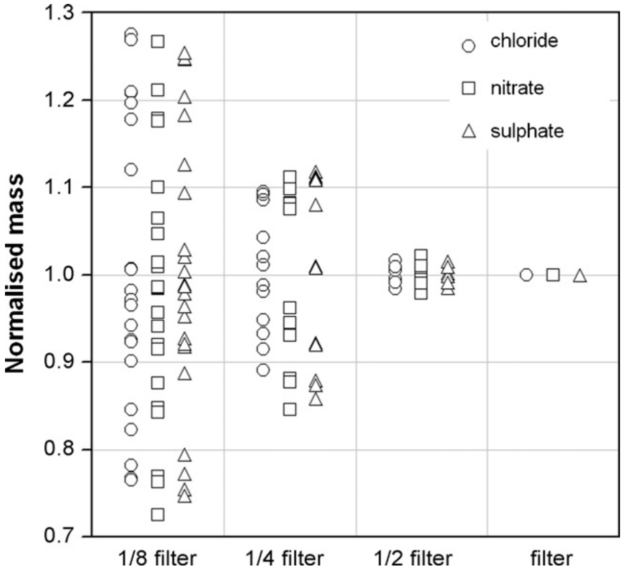

Fig. 4. Distribution of normalised masses of anions (as indicated on the chart) measured on the filter sectors and normalised to the average measured across each of the filters. Each filter is considered in eighth portions (far left), quarter portions, half portions, and as the whole filter (far right).

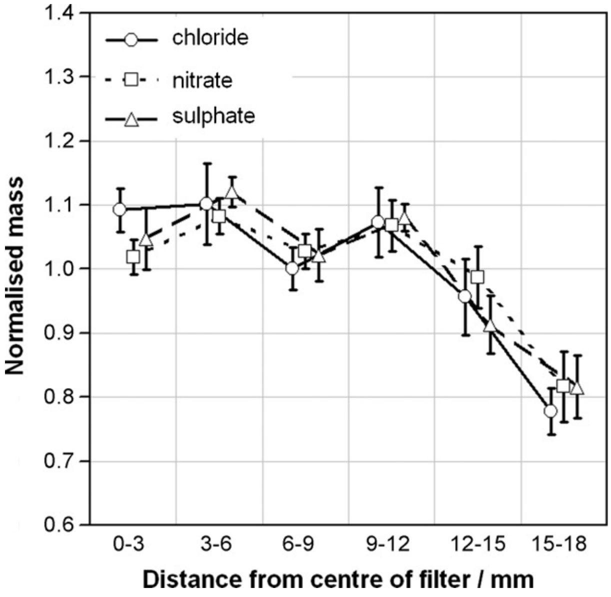

Fig. 5. Measured mass, normalised to the average of each filter, for each anion (as indicated on the chart) on weekly filters sampling PM_{10}, with respect to distance from the centre of the filter. The error bars represent the standard error of the mean over the entire filter set.

(with a squared correlation coefficient (R^2) value of 0.92) between the masses of sulphate and nitrate found on each filter sector is a good indication that this is a real result and not an analytical artefact. The correlation between chloride and sulphate, and chloride and nitrate, are both very small on the filter sectors (with R^2 equal to 0.10 and 0.15 respectively) – this is expected since chloride is a primary aerosols originating from different sources. The differences observed between different filter sectors were not related to position within the filter, that is to say no obvious pattern was observed as one moves from sector 1 to sector 8 around each filter. The reasons for this apparent variability within filter sectors is not entirely clear, but may be as a result of non-homogeneous flow characteristics within the sampler, or possibly uneven thickness of the filter material allowing different flow rate though different filter sectors. This inhomogeneity rapidly disappears (as of course would be expected simply as a function of regression to the mean) when results are averaged over larger portions of the filter, as shown in Fig. 4. This shows that quarter filters show a maximum deviation of between 10 and 15% of the filter average, whilst half filters show less than 2.5% deviation from the filter average. This supports the previous hypotheses that when taking radial sub-samples it is best to make these as large as possible [7]. Further work on this topic is required to understand better the nature and origin of this observed variability, including examination of this effect for higher sample loadings where distribution may be more even.

The results from the analysis of the second type of sub-sample are shown in Figs. 5–7. Because of the presentation of normalised results from these sub-samples any sectoral inhomogeneity will not have any bearing on the conclusions drawn with respect to the inhomogeneity observed along filter radii. These measurements were very challenging because of the very small portion (approximately 2.5%) of the total filter area being analysed for each sample. These notwithstanding the results were generally less variable than were observed with the filter sector sub-samples. For the weekly PM_{10} samples (Fig. 5) there is a strong correlation between the trends displayed by each of the three anions. The observed mass distribution of anions is higher in the centre of the filter, at about 1.1 times the filter average, with this mass possibly decreasing very slightly as one moves out towards the middle of the filter radius. Further towards the outside of the filter the anion mass shows a much more dramatic drop-off reaching approximately 0.8 of the filter average at the outer edges of the filter. The confidence in this trend is quite high because of the very small variability observed across the filter set measured, resulting in small standard errors of the mean for each point.

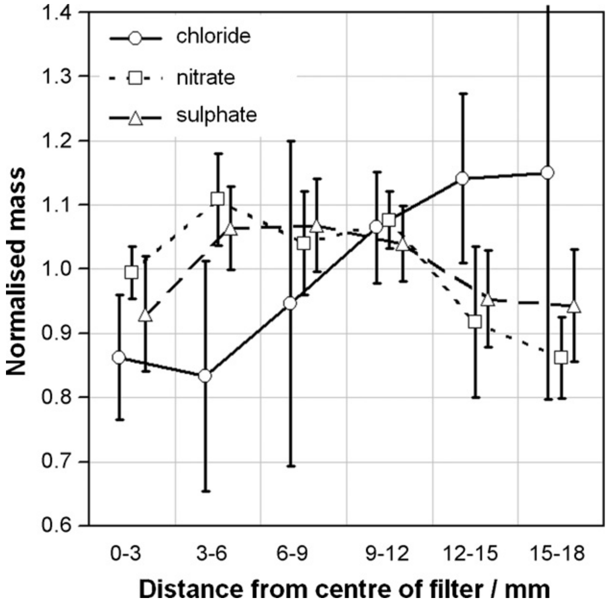

Fig. 6. Measured mass, normalised to the average of each filter, for each anion (as indicated on the chart) on daily filters sampling PM_{10}, with respect to distance from the centre of the filter. The error bars represent the standard error of the mean over the entire filter set.

These results have been compared with those obtained from directly analogous samples (also taken from the UK Heavy Metals Monitoring Network) measured using LA-ICP-MS for metals distribution along the filter radius, in Fig. 8. (In this figure the y-axis uncertainty bars represent twice the average standard error of the mean over the three anions measured, giving a rough estimate of the expanded uncertainty at the 95% confidence interval. The x-axis uncertainty bars indicate that the anion data is not continuous in

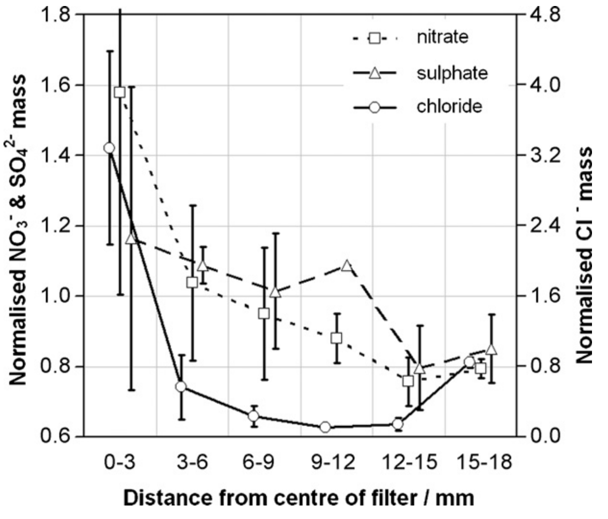

Fig. 7. Measured mass, normalised to the average of each filter, for each anion (as indicated on the chart) on daily filters sampling $PM_{2.5}$, with respect to distance from the centre of the filter. The error bars represent the standard error of the mean over the entire filter set. Normalised chloride masses are plotted on a separate scale on the right hand *y*-axis.

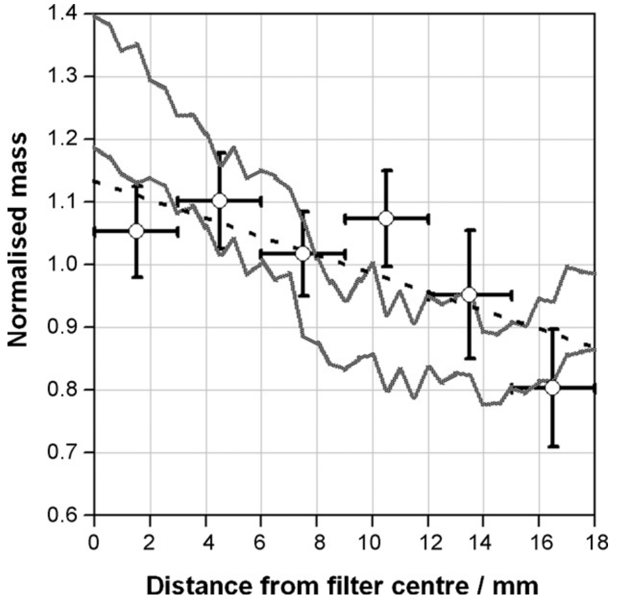

Fig. 8. Comparison of the mass of analyte measured, normalised with respect to the average value between 0 and 18 mm, with respect to distance from the filter centre, for the average of the three anions measured in this paper (open circles) and a set of ambient metals measured in reference [7] where the two solid grey lines represent the upper and lower uncertainty limit of this measurement at the 95% confidence interval. The dotted line is a generalised least squares line of best fit through the anions data, calculated using NPL's XLGenline software, assuming a linear relationship.

nature and represent the measurement from a portion of the filter of 3 mm in width.) There is general agreement between the two data sets in Fig. 8 as they both show higher mass loadings in the centre of the filter than at the outside, with the changes observed across a filter radius being of a similar size. However, for the metals data set the main drop in mass loading seems to occur near to the centre of the filter, whereas for the anions data the sharpest drop occurs towards the outside of the filter. Robust comparison of these data sets is made difficult because the anions data are comprised of discrete data points whereas the metals data have (almost) continuous values. This notwithstanding the best fit line through the anions data (assuming a linear relationship) compares well with the range of values obtained for the metals mass distributions. Differences between these data may be a result of metals and anions being contained within different size distributions of particulate matter, changing flow characteristics of the samplers, or variation in filter collection characteristics or filter thicknesses.

For the daily samples in Figs. 6 and 7 the trends are somewhat less clear owing to the increased variability between filters, leading to larger standard errors of the mean. For the PM_{10} samples the trend is very similar to that observed for the weekly samples but with a lower mass loading at the centre of the filter. The daily $PM_{2.5}$ samples show the most marked decrease in mass loading between the centre of the filter and the outside. This observation could be explained if fine particles initially accumulate towards the centre of the filter at low samples volumes. As sulphate and nitrate are mostly present in the fine fraction this would explain why the trend in Fig. 7 is so clear, whereas in Fig. 6 any sulphate and nitrate was present in the $PM_{2.5}$ to PM_{10} coarse phase may act to counterbalance the trend observed in Fig. 7, especially as these coarse particle dominate in terms of mass. Some supporting data for this hypothesis comes from the chloride trends in Figs. 6 and 7 where there is some evidence that the mass loading of chloride, which is expected to be predominantly in the coarse phase, increases as one moves towards the outside of the filter. This is very much the case for the PM_{10} daily sample in Fig. 6. Fig. 7, where any chloride collected must be in the fine phase, shows a large mass loading in the centre of the filter, dropping off sharply as one moves towards the outside, before increasing again at the edge of the filter. However, interpretation of the daily chloride data is very challenging because of the relatively low masses collected, meaning that the mass of chloride on each sub-sample is less than 1 μg. For the results from the low sample loadings observed in Figs. 6 and 7, it is very difficult to draw firm conclusions. Other factors such as variability in filter thickness and therefore flow rate through the filter, may also play a role in the distribution of collected PM.

The reason for the general observation across Figs. 5, 6 and 7 that mass loadings are greater in the centre of the filter than at the outside is thought to be similar to that proposed in [7] which ascribes this effect to the final sample tube from the impactor head being centred on the centre of the filter, delivering the PM onto the filter from above, and being of a diameter about half that of the filter such that PM is preferentially likely to build up in the centre of the filter immediately below the final sample tube. Furthermore the observation that inhomogeneity is greater for higher sample loadings (Fig. 5) than for lower sampler loadings (Figs. 6 and 7) is consistent with a previous WD-XRF study of heavy metals on filters [14]. This study observed no inhomogeneity below element loadings of 3300 ng cm^{-2}, which would correspond approximately to a 2–3 day exposure period for a fairly abundant element such as Fe or Zn, i.e. somewhere between the exposure period represented by Fig. 5 and that represented by Figs. 6 and 7.

4. Conclusion

Two different types of sub-samples from real samples of ambient PM on air filters have been taken and measured using ion chromatography with a drift correction procedure. This has shown, perhaps surprisingly, that filter sector sub-samples differed by up to 25% from the filter average. This was confirmed to be a real effect by the strong correlation between nitrate and sulphate on each filter sector (as one would expect from masses on a whole filter). However, this variation showed no pattern with respect to the position of the filter sector and, as expected, decreased as larger filter sectors were considered such that filter halves showed less than 2.5% relative difference form the filter average. The reasons for this apparent variability within filter sectors is not entirely clear, but may be as a result of non-homogeneous flow characteristics within the sampler, or possibly uneven thickness of the filter. However, further investigation of this phenomenon at higher mass loadings is required before definitive conclusions may be drawn.

Measurement of anion mass along the line of the filter radius, from the second type of sub-sample, showed a decrease from the centre to the edge of the filter for most samples. The pattern observed for the weekly samples with higher particle loadings showed a strong and repeatable correlation between the anions measured and also compared well with previous studies of this type for metals in PM [7] but with a slightly different profile. Observed differences for weekly samples ranged from 10% higher that the filter average in the centre of the filter to 20% lower at the outer edge of the filter. Trends for the daily samples with lower particle loadings showed similar trends but with poorer repeatability. It was noted that interpretation of the daily chloride data was challenging because of the relatively low masses collected. Further work is required to understand fully the subtleties of the trends observed for the daily samples in both PM_{10} and $PM_{2.5}$. The reason for the general observation that mass loadings are greater in the centre of the filter than at the outside is thought to be the same as that proposed in [7] which ascribes this to the geometry and diameter of the final sample line within the sampler with respect to the filter which is collecting the PM. Because of this explanation it is not unreasonable to expect that the distribution of water-soluble cations (such as Na^+, K^+, $NH_4{}^+$, etc.) would be similar to the patterns observed here and in [7].

This study highlights implications for sub-sampling filters, especially for anion analysis. It is important to ensure that the subsample taken is as representative as possible of the filter as a whole. The most sensible and reliable way to do this is to use as much of the filter as possible. Small sub-samples taken from along the filter radius not only contain relatively little analyte mass, making analysis more uncertain, but also are likely to suffer from the inhomogeneity observed along filter radii. The preferred method is to take filter sector sub-samples that will contain a greater mass of analyte. This study has highlighted that these filter sectors still need to be as large as possible to avoid the random variability between filter sectors observed in this study – at least filter quarters, but preferably filter halves.

Acknowledgements

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