# Characterisation of temporal and regional differences in the elemental fractionation and mobility of urban particulate matter via online sequential extraction

Volker Nischwitz [1*], Jonas Bauer [2], Stefan Norra [2]

[1] Central Institute for Engineering, Electronics and Analytics, Analytics (ZEA-3), Forschungszentrum Juelich, 52425 Juelich, Germany

[2] Institute of Applied Geosciences, Working Group Environmental Mineralogy and Environmental System Analysis (ENMINSA), Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany

[*] Corresponding author: v.nischwitz@fz-juelich.de

ORCID Volker Nischwitz: 0000-0002-9261-3124

## Abstract

Numerous diffuse sources contribute in addition to industrial plants to atmospheric particulate matter (PM) concentrations causing concern regarding potential health effects and environmental impacts. Routine monitoring focuses on PM mass and determination of the total concentrations for selected elements. However, assessment of the (eco-)toxicological potential and the spatial distribution as well as the interaction in the environment requires suitable characterisation of the elemental speciation and mobility. Classical off-line sequential extraction techniques have been explored for this purpose but require high effort and were of limited suitability especially for low particle mass sampled on filters.

A novel online sequential extraction (OSE) technique was recently developed using low amounts of model dust samples with transient elemental monitoring by inductively coupled plasma mass spectrometry (ICP-MS) to overcome the challenges. However, application of this method to PM samples was not reported until now.

In the current study the OSE was adapted for application to punches of PM2.5 filter samples to achieve elemental fractionation with minimum manual input, low relative standard deviations and reduced risk of contamination or loss of residual sample material during solvent changes. Four samples from China and seven samples from Germany were exemplary investigated to identify regional and temporal changes in elemental fractionation and to highlight the potential of the OSE method for filter samples. Normalisation of the data as percentage of the aqua regia leachable fraction for each element demonstrated clear differences between the Chinese and the German samples. In particular fireworks affected samples showed a unique characteristic mobility pattern. In addition normalisation to the aqua regia leachable Mn content was performed to highlight the combination of the elemental fractionation pattern and the relative abundance between the various investigated samples. Thereby, a major improvement in the classification of the PM samples was achieved. Principal component analysis visualises the observed differences in 2-D plots with clusters of different regional and also partly different temporal samples. The obtained results indicate the potential of OSE for an improved understanding of chemical element patterns of PM samples in future studies.

**Keywords**

Aerosol; online sequential extraction; multi-element detection; ICP-MS; fireworks; source characterisation

## 1. Introduction

Air quality, specifically airborne particulate matter (PM), is of major concern to the population in urban areas both in China and in Germany [1,2]. Technical efforts have been made in the recent three decades in Germany to reduce fine dust emissions in particular from power plants, domestic heating devices and industrial processes [3]. As a consequence general pollution levels decreased [3]. However, recent results from air quality monitoring still indicate elevated levels especially of fine dust in certain urban areas. In addition, geogenic dust emissions are likely to increase as a result of climate change causing extended arid periods [4]. Discussion and dispute about the major emission sources and suitable reduction strategies are ongoing and highlighting that the current monitoring data is not sufficient for a clear identification of the various emission sources and for detailed evaluation of the potential health risk associated with fine dust.

For obvious simplification of routine monitoring, primarily the mass of fine dust i.e. particulate matter in the size <10 µm (PM10) or < 2.5 µm (PM2.5) is determined and compared with legal limits [3,5]. A recent study demonstrated the strong effects of fireworks and wildfires on PM2.5 levels based on a large number of low cost sensors monitoring PM concentrations [6]. Generally, total concentrations in the PM filter samples are determined for selected elements using either wet digestion followed by inductively coupled plasma mass spectrometry (ICP-MS) or direct solid sampling by X-Ray techniques [7, 8, 9].

Further characterisation of the soluble i.e. mobile fractions and their elemental composition is rarely performed for PM filter samples [10,11]. This data has the potential to support source identification and the toxicological assessment of inhaled or ingested particulate matter as well as assessment of the general environmental impacts. Considering the various PM emission sources including abrasion from vehicle tires and brakes, construction activities, domestic heating by fossil fuels or wood combustion, smoking, fireworks, agriculture and geogenic background in addition to the above mentioned industrial and power plant emissions at large scale it is obvious that the elemental composition is varying to significant extent not only regarding the total concentration levels but also regarding the elemental speciation. The latter aspect has major impact both, on the environmental mobility and thus on the distribution of aerosol borne elemental species and on toxicological relevance of aerosol exposure for humans [12,13,14].

From an analytical point of view the characterisation and quantification of elemental species in solid matrices such as dust at general urban load levels is still challenging. Direct solid sampling approaches like X-Ray techniques have the capability of providing elemental speciation data, however the instrumental effort and expense is rather high and the limits of detection are often not sufficient for metal species at trace concentrations. For example, a recent study applied X-ray absorption near edge structure (XANES) spectroscopy for determination of the percentage distribution of iron oxidation levels in rural and urban aerosols [15]. However, comparison with the water soluble Fe fraction showed no correlation indicating that the XANES data is not sufficient for assessment of Fe mobility in PM samples. Consequently, indirect approaches based on extraction of the PM followed by liquid based elemental detection are the only feasible alternative. In selected cases, species preserving extraction and species specific identification and quantification is possible. For example, vanadate, chromate, arsenate and molybdate were sufficiently stable under alkaline extraction conditions and could be determined by liquid chromatographic separation followed by elemental detection [16]. However, the majority of PM samples from various mixed emission sources contains a substantial percentage of not well characterised elemental species or species which are not stable under extraction conditions, for example metal carbonates or metals bound to iron oxides or macromolecular organic matter.

Therefore, a more flexible fractionation approach with multi-element capability is required to characterise the relevant speciation information from PM samples. Sequential extraction schemes have been applied in large extent for operationally defined elemental fractionation of sediment and soil samples [10]. Due to the low available amount of PM obtained from routinely applied particle size selective sampling devices i.e. impactors, few applications of sequential extraction for PM filter samples have been reported. For example, Schleicher et al. performed the first multi-element sequential extraction of urban particulate matter from Beijing concluding that the approach provides important additional information regarding potential health effects but also that the procedure is very complicated and time-consuming and therefore not suitable for routine application [11]. Classical extraction schemes suffer from frequent solvent changes and washing steps, which are associated with partial loss of residual solid sample material causing increased uncertainty for subsequent extraction steps. In case of 1 g aliquots of soil this is less critical compared to <<10 mg of PM aliquots on a filter punch. The lower the sample amount the higher the challenge for the operator to separate the individual fractions from the particulate residue causing high effort on human resources and limiting throughput and efficiency.

Recently, a novel online sequential extraction (OSE) approach was developed and verified based on road dust at sample aliquots <5 mg [17]. The automated extraction method included four steps: water soluble fraction, exchangeable fraction, acid soluble fraction and reducible fraction. The residual fraction containing in particular metal oxides of low solubility, particulate organic matter and silicates was not determined online due to incompatibility of the required strong acids and elevated temperature with the OSE setup. The application to bulk road dust showed high repeatability and reasonable agreement with offline sequential extraction of the same sample. The sample was introduced into a small cartridge with 0.45 μm outlet frit and subsequently extracted by four solvents pumped through the cartridge using a high performance liquid chromatography (HPLC) system. The eluting elemental species were introduced online into an ICP-MS and the transient multi-element signals were monitored. Major advantages are the reliable separation of the residual PM material from the extractants via the frit in the flow path and the automated sequential extraction within 80 minutes requiring minimum manual input. Moreover, an important aspect is the continuous exchange of the solvent during online extraction. The extracted elemental species and matrix components of the sample are immediately separated from the solid residue and transported out of the sample cartridge preventing the risk of re-adsorption known from classical batch-wise extractions. Matrix effects on the extraction are minimised in case of mixed samples containing road dust with high amount of water soluble Na by rapidly purging the Na out of the sample cartridge. In contrast, during classical batch extraction the dissolved Na is incubated with the residual PM for at least 1 hour and may influence extraction behaviour of other elemental species due to increased ion strength of the “deionised water” used for extraction.

Following the verification of the novel OSE method on model bulk dust samples, our current study focuses on the application of the OSE to urban PM obtained from routine sampling devices both in China and in Germany. Selected elements were monitored during the 4-step OSE scheme. In addition, the fifth residual fraction was determined as difference between aqua regia leaching of the non-extracted PM samples and the sum of the OSE extracted fractions. The obtained multi-element fractionation profiles enable regional comparison of PM composition and elemental mobility between Chinese and German samples. Temporal comparison was performed for the German samples collected at the same location on seven different time points.

## 2. Experimental

### *2.1 Chemicals and reagents*

Hydrochloric acid (mass fraction 30%, suprapur), nitric acid (mass fraction 65%, suprapur), acetic acid (mass fraction 100%, glacial, suprapur) and hydroxylammonium hydrochloride were obtained from Merck, Darmstadt, Germany. Ammonium nitrate was purchased from

Sigma Aldrich (Schnelldorf, Germany). High purity deionised water was prepared by a Merck Millipore system (Darmstadt, Germany).

### *2.2 Sample collection*

Four PM 2.5 samples (BWG 61, BWG 86, BWG 170, IMG 1624) were collected on quartz fibre filters within an earlier study at the campus of the China Research Academy of Environmental Sciences (CRAES), Beijing, China, during the intervals 4.1.-11.1.2010, 14.12.-21.12.2009, 15.3.-23.3.2010 and 27.4.-4.5.2009 including a blank filter (BWG 31). Collection period was one week at a flow of 100 L $h^{-1}$ (Mini-Volume Sampler, Leckel, Berlin, Germany) leading to gravimetric PM mass in the range of 1-5 mg.

Seven PM 2.5 samples (12_1_D_P2, 12_15_D_P2, 12_30_D_P2, 12_31_D_P2, 12_52_D_P2, 16_15_D_P2, 17_33_D_P2) were collected at the same sampling location in the center of Karlsruhe, Germany, at a busy cross road (Durlacher Tor) in week 1, 15, 30, 31 and 52 of the year 2012, in week 15 of the year 2016 and in week 33 of the year 2017 including four blank filters (12_31_D_P0, 12_51_D_P0, 16_17_D_P0, 17_33_D_P0). Sampling period was also one week at a flow of 2.3 $m^3$ h-1 (Low Volume Sampler, Comde-Derenda, Stahnsdorf, Germany). The samples from week 1 and week 52 include fireworks events at the beginning and end of the year.

### *2.3 Aqua regia leaching*

Triplicate punches of 6 mm diameter were subsampled from each PM filter sample and leached with aqua regia (2 mL hydrochloric acid mass fraction 30% and 0.7 mL nitric acid mass fraction 65%) in closed microwave Xpress vessels using a MARS 5 (CEM, Kamp-Lintfort, Germany). The vessels were heated within 15 min to 160°C and kept at this temperature for 25 min. The leachates were transferred and made up to 10 mL with deionised water. Two replicate dilutions

(20-fold) were analysed by sector field ICP-MS (Thermo Element 2, Thermo Scientific, Bremen, Germany) using external calibration with Rh as the internal standard. $^{23}$Na, $^{24}$Mg, $^{27}$Al, $^{34}$S, $^{49}$Ti, $^{52}$Cr, $^{55}$Mn, $^{56}$Fe, $^{59}$Co, $^{60}$Ni, $^{65}$Cu, $^{66}$Zn, $^{121}$Sb, $^{138}$Ba, $^{140}$Ce were monitored in medium resolution mode and $^{39}$K, $^{71}$Ga, $^{85}$Rb, $^{88}$Sr, $^{120}$Sn, $^{207}$Pb in high resolution mode. NIST 1633b (fly ash) and ERM-CC141 (loam soil) were leached and analysed in the same way for quality control. In addition the natural water reference material NIST 1640a was used to verify the calibration. Recoveries are summarised in Table S1 (Supplementary Information). The recoveries for the NIST 1640a are in a good range between 93% and 106% with exception of Fe showing elevated recoveries (most likely due slight contamination at the low level of 3 µg L$^{-1}$ (ten-fold dilution); verification of the Fe calibration was confirmed by an independent commercial multi-element standard solution at 96% recovery). The results for ERM-CC141 from pressurised aqua regia digestion exceed the certified aqua regia soluble fractions partly, but agree well with the total concentrations. Predominantly residual/silicate-bound elements such as Al, K, Ti, Cr and Fe are leached by aqua regia in a range of about 20-50%. The fly ash NIST 1633b contains higher percentage of residual bound elemental fractions and therefore recoveries are lower compared to soil.

### *2.4 Online sequential extraction with ICP-MS detection*

The same instrumentation, extractants and parameters were used as described in our previous work [17]. In brief, two Bischoff 2250 HPLC pumps (Bischoff Analysentechnik, Leonberg, Germany) were used in connection with switching valves for time programmed sequential supply of four extractants at a flow rate of 0.3 mL min$^{-1}$. Deionised water was used in step 1 for 15 min, followed by 50 mmol L$^{-1}$ ammonium nitrate for 20 min in step 2. Acetic acid (0.11 mol L$^{-1}$) was used in step 3 for 16 min and 0.04 mol L$^{-1}$ hydroxyl ammonium chloride (adjusted to pH 2 with nitric acid) for 29 min in step 4. Equilibration with deionised water for 10 min followed prior to the next sample run. An inline filter cartridge with 0.45 µm frits on both ends was used as sample container. A 6 mm diameter punch of the PM filter samples was placed inside the sample container with minimum dead volume (Figure 1A) and then the sample container was connected to a manual injection valve instead of the sample loop. Sequential extraction was started manually via the injection valve triggering the HPLC system and the ICP-MS detection as described below.

Hyphenation with an Element 2 sector field ICP-MS (Thermo Scientific, Bremen Germany) was realised via polyether ether ketone (PEEK) tubing. An internal standard solution (Rh in diluted nitric acid prepared by addition of 5 µL Rh stock solution (1 g $L^{-1}$) and 5 mL nitric acid (mass fraction 65%) to 495 mL deionised water) was mixed with the OSE eluate at a flow rate of about 0.4 mL $min^{-1}$ via a T-piece for dilution prior to entering the ICP-MS. The isotopes $^{23}$Na, $^{24}$Mg, $^{27}$Al, $^{34}$S, $^{39}$K, $^{49}$Ti, $^{52}$Cr, $^{55}$Mn, $^{56}$Fe, $^{59}$Co, $^{60}$Ni, $^{65}$Cu, $^{66}$Zn, $^{71}$Ga, $^{85}$Rb, $^{88}$Sr, $^{120}$Sn, $^{121}$Sb, $^{138}$Ba, $^{140}$Ce, $^{207}$Pb and $^{103}$Rh were analysed in medium resolution mode. Calibration was performed by introducing multi-element standards via the internal standard line while the OSE was operated with deionised water flow [17]. The OSE transient data were converted to mass flow fractograms and the absolute extracted mass of each monitored element was determined by peak integration. Blank runs were analysed and evaluated in the same way as the samples. Limits of detection were calculated from the mean and three-fold standard deviation of replicate blank runs. The mean blank was subtracted from the PM sample runs.

### *2.5 Multivariate Data analysis*

Principal component analysis (PCA) of the autoscaled obtained data was performed with Origin Pro 2021. OSE fractions 1 to 4 and the residual fraction were evaluated as percentage data based on the aqua regia leachable content of the same non-extracted PM sample for each element. Results below limit of detection (LOD) were replaced by zero to avoid bias due to different LODs for the Chinese and the German filter samples.

In addition, OSE fractions 1 to 4 and the residual fraction were evaluated after normalisation by the aqua regia soluble Mn contents using BWG61 as reference (100%). More specifically, the contents of all monitored elements were divided by the aqua regia leachable Mn content of the same sample and multiplied by the respective Mn content of the sample BWG61. Also in this case the results below limit of detection were replaced by zero.

For comparison, aqua regia leachable elemental fractions (µg per filter punch) were evaluated by PCA without normalisation to PM mass or sampled air volume. Results below limit of detection were replaced by the limit of detection. In addition the aqua regia leachable elemental data were normalised to Mn using BWG61 as reference as described above. 2D-Plots of the first and second extracted principal components are presented for the scores and the loadings.

## 3. Results and Discussion

### *3.1 Adaption of the OSE method to PM filter samples*

The inline filter cartridges used in the development of the OSE method based on bulk model dust samples are well compatible with 6 mm punches of the PM filter samples [17]. The frits of the cartridge have the same diameter as the punch and the sample is well contained with minimum dead volume when closing the cartridge. After extraction the residue of the sample and filter can be removed by purging with deionised water followed by short drying and insertion of the next sample. Analysis of blank filter punches provided negligible blank peaks for most of the elements apart from minor instrumental blank signals for example in case of Fe, Mn, Co and for example in case of Na and K from the filter material itself. Limits of detection (3σ) were calculated from six replicate runs over five days of one blank filter representative for the Chinese samples (BWG) and from four blank filters (DT) analysed in duplicate (with one exception, i.e. a total number of 7 blank runs) over four days for the German samples. Results are given as absolute amount of metal per 6 mm filter punch (Table 1).

Depending on filter blanks, reagent blanks and instrumental blanks contributing to the recorded element levels during blank OSE runs, the LODs range from 0.01 ng to 4 µg for the monitored elements. In most cases the LODs for the filters of the two locations are the same. However, in particular for Na, K and Zn 10-fold or even higher differences were obtained which are assigned to elevated blank levels in one of the filter materials. Repetitive blank runs provided repeatable blank signals with few outliers which were eliminated prior to calculation of the LODs.

The technical operation of the OSE worked well without leaks or blockage of the frits of the sample container. Triplicate OSE runs of two samples resulted in mean relative standard deviations of the extracted metal fractions of 11% (SD 3%) (sample 12_31_D_P2) and 6% (SD 7%) (sample 17_33_D_P2) for step 1, 4% (SD 2%) and 5% (SD 2%) for step 2, 7% (SD 4%) and 8% (SD 2%) for step 3 as well as 9% (SD 4%) and 10% (SD 4%) for step 4 (mean and standard deviation (SD) across the relative standard deviations of all monitored elemental fractions above LOD per extraction step). Superimposed fractograms of triplicate OSE extractions of a PM sample are shown in Figure 1B for Pb. The three mass flow fractograms are nearly congruent demonstrating the high repeatability of both the extraction peak shapes and the calculated mass flows. These results indicate reliable fractionation patterns of the PM samples by OSE with ICP-MS detection.

For completion of the fractionation pattern, the residual fraction was calculated as difference of the aqua regia leachable content (obtained from parallel non-extracted punches of the same sample) and the summed OSE fractions one to four for each element and PM filter sample. Experimental determination of the residual fraction from the remaining material in the cartridge after OSE extraction was not suitable due to technical difficulties in recovering the residue from the cartridge and due to the associated dilution with water during cleaning of the sample cartridge. However, the calculation enabled the interpretation of the residual fraction which was not considered as fifth fraction in the original development of the OSE method but provides an important contribution to the characterisation of elemental (im)mobility. In few cases the sum of the OSE fractions one to four exceeded the aqua regia leachable fraction resulting in negative residual fractions which are typically associated with high standard deviations due to low elemental concentrations. Potentially, in such cases OSE might dissolve elemental species which are not accessible by aqua regia leaching.

### *3.2 Element specific extraction pattern of PM samples*

The extracted mass per element for the sequential steps of a filter punch is dependent on the sampled air volume, on the PM concentration in the air and on the composition and mineral phases of the particulate matter. In addition, stable long term operation of the sampling device (impactor) under field weather conditions needs to be guaranteed to achieve homogeneous deposition of the PM on the filter material. The current study aims to compare PM samples from China and Germany collected in different environments. In order to avoid uncertainties due to different instrumentation and operating conditions, the OSE results are not corrected for air volume or PM mass.

For comparison of the element specific mobility pattern the extracted elemental mass for each OSE step and for the fifth residual fraction was divided by the aqua regia leachable fraction of the element obtained from parallel punches of the same PM filter. This resulted in percentage distribution of the elemental content across the four OSE fractions and the residual fraction. Examples are shown in Figure 2 for Pb (A), Ba (B) and Fe (C). The standard deviations included in the figures were calculated by propagation of error. In case of low residual fraction the SD is partly rather high due to combined SD from the four OSE steps and the aqua regia leaching. Significant differences in the mobility between the investigated PM samples are indicated. The water soluble Pb fraction (step 1) is below 10% in the Chinese samples, while it reaches 8% to 30% in the German samples. The exchangeable Pb fraction is in similar range with exception of the samples 12_1_D_P2 and 12_52_D_P2 accounting for 69% (SD 28%) and 47% (SD 17%) of aqua regia leachable Pb. The unusual fractionation pattern of these two samples is likely an effect of fireworks affecting PM composition as discussed in more detail in the following [18]. Lead tetroxide is used as oxidiser in fireworks resulting in divalent lead reaction products, which are consistent with the observed increased abundance of Pb in the exchangeable fraction [19].The acid soluble fraction (step 3) and the reducible fraction (step 4) are in similar range for all samples. However, the residual fraction is much higher in the Chinese samples (27%-37%; SD 5-15%) than in most of the German samples (<10%) apart from 16_15_D_P2 (21% with SD 29%). The partly negative residual fractions and the associated rather high SDs for the German samples indicate that this fraction is not relevant and mostly affected by propagation of error. The much higher residual Pb fraction in the Chinese samples may be assigned either to geogenic dust emissions or to emissions from combustion processes resulting in Pb species of low mobility. An earlier study on Pb fractionation in Chinese PM samples did not report similarly increased residual fractions based on offline sequential extraction including experimental determination of the residual fraction [11].

In case of Ba the relative distribution over the five fractions is rather different from Pb. The residual fraction is predominant in the Chinese samples with >70% apart from BWG_170 with about 40% each in the exchangeable and the residual fraction. The exchangeable fraction is by far most abundant (>60%) in the German PM samples except for the sample from 2016, which shows the same pattern as BWG_170. An unique distribution was obtained for the samples from week 1 and week 52 in 2012, which are affected by fireworks known to contain significant amounts of Ba [18, 20]. The water soluble fraction is unusually high accounting for 60% and 48% of Ba, followed by the residual fraction with 26% and 38% while the exchangeable fraction accounts for less than 15%. This suggests two major groups of Ba species originating from fireworks aerosol: easily water soluble Ba salts and far less mobile Ba species formed in high temperature combustion processes. Apart from the special contribution by fireworks these samples include seasonal contributions from various heating devices during winter time which are represented in lower extent in weeks 15, 30 and 31. The residual Ba species are also dominant in the Chinese aerosol possibly due to coal combustion [2].

As a third example Fe shows even clearer than Ba the predominant residual fraction (>90%) in the Chinese samples. In case of IMG1624 all OSE fractions were below limit of detection and thus calculation of the residual fraction makes no sense. Schleicher et al. reported about 50% of Fe in the residual fraction for Chinese PM2.5 samples [11]. Also in the German PM samples the residual fraction is most abundant with 48% to 91%. However, significant amounts of water soluble Fe are present in the range of 7% to 40% indicating Fe species with higher mobility.

The corresponding figures for further elements (Al, Mn, Cu, Sr) are included in the electronic supplementary information (Figures S1 to S4). The percentage distribution for Al is very similar to Fe with clearly higher water soluble fraction in the German samples. Sample 16_15_D_P2 is also for Al very similar to the Chinese Samples. For Mn the acid soluble fraction occurs only in the Chinese samples, for Cu the reducible fraction was detected in most, but not all of the German samples. The aqua regia leachable fraction of Sr is close to the limit of detection for several samples causing high standard deviations. The percentage Sr distribution of the German sample 16_15_D_P2 is similar to the Chinese BWG samples as observed for Pb and Al. The exchangeable, acid soluble and reducible Sr fractions of the other German samples (apart from week 1 and 52) are below LOD.

The discussed elements demonstrate clear differences in the percentage distribution of the fractions normalised by the aqua regia leachable content of the respective element in the sample. This approach allows the identification of different elemental speciation and consequently different mobility and potentially different toxicological impact of the monitored PM samples. In future studies with larger number of analysed samples, changes in PM sources can be identified as discussed for the simple example of fireworks aerosol and offer the potential for source apportionment in combination with statistical models such as positive matrix factorisation [21].

### *3.3 Relative abundance of elemental fractions in PM samples*

The discussed element specific extraction pattern has the great benefit of comparing the species distribution independent of the abundance in the various samples. For example the distribution pattern for Sr (Figure S4) looks quite similar for all investigated PM samples. However, the source characteristic of PM emissions is not only determined by the presence of different species of the monitored elements but also by changes in the relative abundance of species of various elements. For example, the samples of week 1 and 52 including fireworks aerosol contain much higher Sr levels than the PM samples from the same location but other time points during the year.

Therefore, a second set of normalised data is important for comprehensive understanding and interpretation of the OSE fractionation results. As outlined in the previous paragraph, correction with aerosol mass or sampled air volume for absolute quantification is associated with various technical uncertainties such as variation of the sampled air flow, different weather conditions and uncertainty of the gravimetric evaluation of the filter samples. Therefore, it is more efficient to choose the aqua regia soluble content of one suitable reference element for normalisation of the fractionation results of all monitored elements in the investigated samples.

In order to select a suitable reference, elements with aqua regia leachable concentrations above limit of detection in all samples were considered. Relative ratios (%) between the various samples were calculated for each element based on one sample as reference (100%). Graphical display of the obtained ratios for the selected elements and the mean ratio of all elements is shown in Figure S5 (electronic supplementary information). Sulphur is matching best with the mean ratio while Cu is strongly affected by the fireworks aerosol and manganese is not affected by the fireworks aerosol causing deviation from the mean. However, the standard deviations of the aqua regia leachable contents of S and Cu are elevated for some samples and therefore Mn was chosen as reliable reference.

Complementary to the differences in the percentage Pb fractionation pattern in Figure 2A, the Mn normalised Pb results in Figure 3A highlight also significant differences in the abundance of the Pb fractions in the investigated PM samples. The acid soluble (carbonate) fraction, the residual fraction and partly the exchangeable fraction are clearly present at higher concentrations in the Chinese samples. However, exceptions are the German samples from week 1 and 52 with exchangeable and acid soluble fractions at similar levels exceeding the usual concentrations at the German sampling location. This demonstrates the effect of fireworks on the PM samples even clearer compared to the relative Pb species distribution in Figure 2A.

The fireworks related impact on PM elemental fractionation is even more pronounced for the Mn normalised Ba results (Figure 3B). The water soluble Ba fraction is 130-fold to 300-fold higher than the usual levels in the German PM samples, the exchangeable fraction is 5-fold to 17-fold higher and the residual fraction 17-fold to 450-fold higher. This example impressively demonstrates the effect of general non-industrial emission sources on the elemental fractionation levels in urban PM samples. Characteristic for the Chinese PM samples is the residual fraction in 3 out of 4 samples, which is up to about 100-times higher than in the general German samples, but lower compared to the fireworks related samples.

Fe fractionation levels are less affected by fireworks (Figure 3C). The residual fraction is predominant both in the Chinese and in the German samples. Residual Fe levels are higher in the fireworks related German samples and in the samples from 2016 and 2017 compared to the general levels from 2012. The increase in 2016/2017 might be caused by rail building activities near the PM sampling location.

The corresponding Mn normalised figures for Al, Mn, Cu and Sr are shown in the electronic supplementary information (Figures S6 – S9). The predominant residual fraction of Al is present in similar extent in the Chinese samples and in the German samples of years 2016 and 2017 as well as in the fireworks affected samples from 2012. The latter samples are characterised by increased water soluble Al fractions. The graphic display for Mn is identical with the percentage distribution (Figure S2) apart from the y-axis scale because Mn was selected for normalisation. While the percentage distribution graph for Cu (Figure S3) was indicating minor differences between the samples, the Mn normalised data including the relative abundance clearly show higher relative Cu levels in the German samples in particular for the fireworks affected samples. The rather high water soluble fraction of the latter samples is much more obvious in this presentation of the data. Also for Sr the relative abundance graph impressively highlights the outstanding fireworks contribution. The low standard deviations confirm that the OSE operation is reliable and that the partially large variation observed in Figure S4 is mainly caused by the uncertainty of the aqua regia soluble Sr fraction used for normalisation in this case.

The presented results demonstrate even for the limited set of eleven selected PM samples the potential of OSE to identify temporal and regional changes in PM samples due to source variation both via changes in the relative speciation pattern and via changes in the abundance level of elemental species. The discussed examples are just few insights into the obtained data set. Multivariate statistical evaluation including results from all monitored elements is discussed in the following section.

### *3.4 Multivariate statistical evaluation of OSE results for PM samples*

The examples in the figures 2 and 3 highlight several changes and differences in the elemental fractionation pattern for individual elements. Combined evaluation of the results from multiple monitored elements is possible via classification techniques such as cluster analysis, principal component analysis (PCA) and factor analysis [22]. In the figures 2 and 3 results below limit of detection were not included to focus on the clearly detected fractions. However, the classification techniques require complete data matrices. Therefore, the results below LOD were replaced as described in the experimental section.

Principal component analysis was selected as classification strategy considering the limited data set of this initial feasibility study resulting in larger number of variables than cases which excludes the application of factor analysis. PCA offers the advantage of extracting meaningful information from the data set and enabling even for the relatively small number of cases improved correlation between cases and variables compared to cluster analysis.

First, the data set "element specific extraction pattern" i.e. the OSE fractions plus the residual fraction as percentage of the aqua regia soluble content of each monitored element was explored by PCA. Initially the data of all five fractions was processed separately for each element and the obtained 2D plots of the first and second principal components were checked. For most elements reasonable separation of the main types of PM samples (Chinese, German general, German fireworks) was achieved. However, for Na, Ti, Ni, Zn and Sn unclear results were obtained partly due to many fractions below limit of detection. Therefore, these elements were not included in the further evaluation. The PCA result obtained for the remaining 16 elements is shown in Figure 4. Ten eigenvalues above 1 were obtained with cumulative explained variance of 100%. The first principal component (PC1) separates the Chinese samples (positive loading) from the German samples (negative loading), while the second principal component (PC2) mostly separates the fireworks affected samples (negative loading) from the other German samples taken at the same location (positive loading). Overall, the PCA plot achieves three clusters containing the Chinese BWG samples, the general German Samples and the fireworks affected German samples, respectively. Exceptions are the German sample from 2016 with similar distribution pattern as the Chinese samples for some elements (see discussion in previous section) and the Chinese IMG Sample from a different campaign and thus varying in sampling time and location. It is important to keep in mind that this data set includes only the percentage distribution across the five fractions for each element but does not consider the absolute or relative abundance of the fractions in the various samples. The obtained classification was achieved solely based on differences in the mobility of the extracted elements proving the suitability of OSE for characterisation of differences in PM caused by regional or temporal variation of dust sources. The corresponding diagram of the loadings in Figure S10 (Supplementary Information) matches well with the discussed differences in the previous sections. For example, negative loading of PC2 associated with fireworks aerosol includes water soluble Ba and exchangeable Pb, while positive loading of PC1 includes residual Ba, Pb and Al as discussed for the Chinese samples. The table with the factor loadings is also included in the supplementary information (Table S2).

The Mn normalised OSE fractions and the residual fraction representing the relative abundance of the fractions in addition to the percentage distribution were classified by PCA in the same way. Eight eigenvalues above 1 were obtained with cumulative explained variance of 98%. The resulting 2D plot in Figure 5 shows improved clustering of the three types of samples in our data set. The excessive contents of some characteristic element fractions in the fireworks aerosol dominate PC1 with positive loadings while PC2 mostly separates the Chinese samples (positive loading) from the general German samples (negative loading). Even the "outliers" IMG1624 and 16_15_D_P2 are now well included in the cluster of their respective region. A larger number of PM samples is required in the future to investigate in more detail whether the changes in elemental speciation of the latter two samples indicated in Figure 4 are significant for these sampling locations or sampling time, respectively. The corresponding loadings are shown in Figure S11 and Table S3 (Supplementary information). Many characteristic fractions are identified both in Figure 4 and Figure 5. However, when focusing only on the top 20% loadings of the corresponding principal components, some aspects identified from the percentage data such as water soluble Pb, Cu and Al in the German samples and residual Ba and Pb in the Chinese samples are included in the PCA of the percentage distribution data, but not in the PCA of the Mn normalised data. This indicates that both types of normalisation are important for interpretation of the OSE data and provide complementary information.

For comparison PCA was also performed for the aqua regia soluble fractions of the elements in the eleven PM samples. The 2D plot including the factor scores and loadings is shown in Figure S12 for the data without any correction for PM mass or sampled air volume (four eigenvalues above 1; cumulative explained variance is 96%). This resulted in one major mixed cluster and two Chinese samples as well as one fireworks sample separately. Considering the fact that the usual correction for sampled air volume is just a constant factor per sample and thus not affecting the elemental pattern within the sample, it is surprising that the classification is rather poor. There is no logic separation of the regional or temporal samples evident.

When normalising the aqua regia leachable contents to Mn in the same way as described in the previous section for the OSE results there is a major improvement in the classification of the PM samples (Figure S13) (three eigenvalues above 1; cumulative explained variance is 89%). The two fireworks PM samples are clearly separated by positive values of PC1, while the

Chinese samples are characterised by negative PC1 values and positive PC2 values and the remaining German samples by negative PC1 and negative PC2 values. The improved classification supports the suitability of Mn normalised data for comparison of the PM elemental profiles. The cluster of the general German samples is however less focused compared to the Mn normalised OSE results (Figure 5). The maximum distance between two samples within the cluster is about 1.1 compared to 0.6. Corresponding is the minimum distance between this cluster and the Chinese samples 0.75 for the Mn normalised aqua regia soluble data compared to 1.2 for the Mn normalised OSE data. The loadings indicate that few elements (Fe, Cr, Pb, Ga) are mainly supporting the classification of Chinese and German samples while in case of OSE a much larger number of fractions supports the classification.

## 4. Conclusion

The investigated set of PM samples from China and Germany demonstrates the feasibility of OSE with ICP-MS detection for reliable multi-element fractionation of low mass aerosol samples on filter punches with minimum requirement for sample preparation. The programmed 4-step sequential extraction achieves simultaneous extraction and detection of elemental species with reliable separation of the dissolved fractions from the residual solid via frits in the sample cartridge. In classical offline sequential extraction substantial amount of human effort, skill and work time is required to achieve this critical task of reliable separation of the extract from the residual solid without significant loss.

Although a limited number of four Chinese and seven German samples with corresponding blanks was analysed in this initial application of the method to PM samples, the resulting fractionation pattern shows clear differences between samples from different regions and also from different time points as demonstrated by the fireworks affected German samples with unique outstanding elemental pattern. Normalisation of the obtained data as percentage per element or normalisation to Mn was suitable for comparison of the samples from different campaigns without the need for correction by sampled air volume or PM mass. Principal component analysis identified the known major structure within the analysed samples.

Future studies with larger number of PM samples enable the possibility for more robust multivariate data analysis and therefore identification of additional minor dust sources contributing to changes in regional or seasonal elemental fractionation. Apart from this classification in respect to source apportionment, the obtained elemental mobility data support assessment of the environmental behaviour as well as potentially of the (eco)toxicological impact.

## Disclosure Statement

There is no conflict of interest.

**Table 1** Limits of detection (µg) obtained from six replicate runs of a blank filter (BWG) representative for the Chinese samples and from seven replicate runs of four blank filters (DT) (each in duplicate with one exception) representative for the German samples using the OSE method with ICP-MS detection. LODs are given as 3 times the standard deviation. Differences between both filter types are marked in bold print.

| | **Water Soluble** | | **Exchangeable** | | **Acid Soluble** | | **Reducible** | |
|---|---|---|---|---|---|---|---|---|
| | BWG | DT | BWG | DT | BWG | DT | BWG | DT |
| **Na** | **4** | **0.8** | 0.02 | 0.01 | 0.009 | 0.009 | 0.02 | 0.01 |
| **Mg** | **0.09** | **0.03** | 0.004 | 0.004 | 0.002 | 0.003 | 0.003 | 0.002 |
| **Al** | **0.05** | **0.02** | **0.003** | **0.001** | 0.01 | 0.007 | 0.005 | 0.003 |
| **S** | 0.05 | 0.09 | **0.02** | **0.1** | **0.01** | **0.09** | **0.04** | **0.2** |
| **K** | **0.1** | **2** | **0.1** | **2** | **0.07** | **1** | **0.1** | **2** |
| **Ti** | **0.001** | **0.0003** | 0.0001 | 0.0001 | 0.0002 | 0.0001 | **0.00004** | **0.0001** |
| **Cr** | **0.001** | **0.01** | 0.0007 | 0.0004 | **0.001** | **0.0004** | **0.002** | **0.0008** |
| **Mn** | 0.001 | 0.0005 | 0.0008 | 0.001 | **0.0003** | **0.001** | 0.002 | 0.002 |
| **Fe** | **0.02** | **0.004** | 0.005 | 0.006 | **0.02** | **0.005** | 0.01 | 0.006 |
| **Co** | 0.00001 | 0.00001 | 0.00002 | 0.00002 | **0.00001** | **0.00003** | 0.00005 | 0.00003 |
| **Ni** | 0.001 | 0.001 | 0.001 | 0.002 | 0.002 | 0.001 | 0.001 | 0.003 |
| **Cu** | 0.0003 | 0.0005 | 0.0004 | 0.0003 | 0.003 | 0.004 | **0.02** | **0.003** |
| **Zn** | 0.02 | 0.02 | 0.01 | 0.02 | **0.2** | **0.02** | **0.2** | **0.02** |
| **Ga** | 0.00002 | 0.00001 | 0.00001 | 0.00001 | 0.00002 | 0.00001 | 0.00004 | 0.00002 |
| **Rb** | 0.0001 | 0.0001 | 0.00003 | 0.00002 | **0.00004** | **0.00001** | **0.00004** | **0.00001** |
| **Sr** | 0.0005 | 0.0003 | 0.0002 | 0.0001 | **0.0001** | **0.00002** | 0.0002 | 0.0001 |
| **Sn** | 0.0003 | 0.0004 | 0.0002 | 0.0002 | 0.0003 | 0.0002 | 0.0004 | 0.0004 |
| **Sb** | 0.0003 | 0.0002 | 0.0001 | 0.00005 | 0.00005 | 0.00003 | **0.0001** | **0.00003** |
| **Ba** | 0.0009 | 0.0007 | 0.0008 | 0.0009 | 0.0002 | 0.0002 | 0.0003 | 0.0006 |
| **Ce** | 0.00001 | 0.00001 | 0.00001 | 0.00001 | 0.00001 | 0.00001 | 0.00002 | 0.00001 |
| **Pb** | 0.0005 | 0.0004 | 0.0005 | 0.0005 | **0.001** | **0.0003** | **0.0007** | **0.0003** |

## Figure legends

**Figure 1** PM filter sample and OSE cartridge (A) and overlaid OSE fractograms (B) of triplicate analysis of PM2.5 filter punches from the same aerosol filter sample showing the mass flow for Pb.

**Figure 2** Percentage distribution of lead (A), barium (B) and iron (C) in the OSE fractions and the residual fraction of four PM samples from China (BWG, IMG) and seven PM samples from Germany (DT). Negative residual fractions are not fully displayed and OSE fractions below limit of detection are also not shown.

**Figure 3** Absolute extracted OSE fractions and the residual fraction of lead (A), barium (B) and iron (C) normalised to the aqua regia leachable Mn contents.

**Figure 4** Principal component analysis of the element specific extraction pattern data set including OSE steps 1 to 4 and the residual fraction as percentage of the aqua regia soluble content of each monitored element (without Na, Ti, Ni, Zn and Sn). The corresponding loadings are shown in Figure S10 and Table S2 (Supplementary Information).

**Figure 5** Principal component analysis of the Mn normalised OSE results including steps 1 to 4 and the residual fraction (without Na, Ti, Ni, Zn and Sn). The corresponding loadings are shown in Figure S11 and Table S3 (Supplementary Information).

## References

---

[1] K. W. Fomba, D. van Pinxteren, K. Müller, G. Spindler and H. Herrmann, Atmos. Env. **176**, 60 (2018).

[2] S. Zhao, Y. Duan, L. Chen, Y. Li, T. Yao, S. Liu, M. Liu and J. Lu, Env. Pollut. **226**, 404 (2017).

[3] Feinstaubbelastung in Deutschland, Umweltbundesamt, (2009).

[4] P. Achakulwisut, L.J. Mickley and S.C. Anenberg, Environ. Res. Lett. **13**, 054025 (2018).

[5] C. Ehrlich, G. Noll, W.D. Kalkoff, G. Baumbach and A. Dreiseidler, Atmos. Env. **41**, 6236 (2007).

[6] K.E. Kelly, W.W. Xing, T. Sayahi, L. Mitchell, T. Becnel, P.E. Gaillardon, M. Meyer and R.T. Whitaker, Env. Sci, Technol. **55**, 120 (2021).

[7] F. Zereini, F. Alt, J. Messerschmidt, C. Wiseman, I. Feldmann, A. von Bohlen, J. Müller, K. Liebl and W. Püttmann, Environ. Sci. Technol. **39**, 2983 (2005).

[8] K.W. Fomba, N. Deabji, S.E.I. Barcha, I. Ouchen, E.M. Elbaramoussi, R.C.E. Moursli, M. Harnafi, S.E. Hajjaji, A. Mellouki and H. Herrmann, Atmos. Meas. Tech. **13**, 4773 (2020).

[9] E. Dabek-Zlotorzynska, T.F. Dann, P.K. Martinelango, V. Celo, J.R. Brook, D. Mathieu, L. Ding and C.C. Austin, Atmos. Env. **45**, 673 (2011).

[10] P. Smichowski, G. Polla and D. Gomez, Anal. Bioanal. Chem. **381**, 302 (2005).

[11] N.J. Schleicher, S. Norra, F. Chai, Y. Chen, S. Wang, K. Cen, Y. Yu and D. Stüben, Atmos. Env. **45**, 7248 (2011).

[12] A. D. Brown, B. Yalala, E. Cukrowska, R.H.N. Godoi and S. Potgieter-Vermaak, Environ. Geochem. Health **42**, 1127 (2020).

[13] B.T. Sendja, G. Aquilanti, I. Vassura and M. Giorgetti, J. Physics **712**, 012087 (2016).

[14] P. Apostoli, R. Cornelis, J. Duffus, P. Hoet, D. Lison, D.M. Templeton, S. Hahn, J. Kielhorn, M. Nordberg, V. Riihimaki and A. Aitio, Environ. Health Criteria **234**, ix (2006).

[15] J.R. Salazar, D.J. Pfotenhauer, F. Leresche, F.L. Rosario-Ortiz, M.P. Hannigan, S.C. Fakra and B.J. Majestic, Earth and Space Science **7**, e2020EA001262 (2020).

[16] A. Drincic, J. Scancar, T. Zuliani, I. Nikolic and R. Milacic, J. Anal. At. Spectrom. **32**, 2200 (2017).

[17] N. Asante and V. Nischwitz, Spectrochim Acta B **174**, 105993 (2020).

---

[18] C. Hickey, C. Gordon, K. Galdanes, M. Blaustein, L. Horton, S. Chillrud, J. Ross, L. Yinon, L.C. Chen and T. Gordon, Particle Fibre Toxicology **17**, 28 (2020).

[19] M. Koga, M. Matsumoto, A. Miyahara, S. Yoshinaga, J. Japan Explosives Society **57**, 197 (1996).

[20] J.D. Rindelaub, R.K. Davy, N. Talbot, W. Pattinson and G.M. Miskelly, Env. Sci. Pol. Res. **28**, 21650 (2021).

[21] P.K. Hopke, in *Chemometrics in Environmental Chemistry*, edited by J.W. Einax (Springer, Heidelberg, 1995) p. 47-86.

[22] J.W. Einax, H.W. Zwanziger and S. Geiss: *Chemometrics in Environmental Analysis* (VCH, Weinheim, 1997).