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Spider web biomonitoring: A cost-effective source apportionment approach for urban particulate matter

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Wolf von Tümpling:	Conceptualization, Supervision, Writing – Review & Editing
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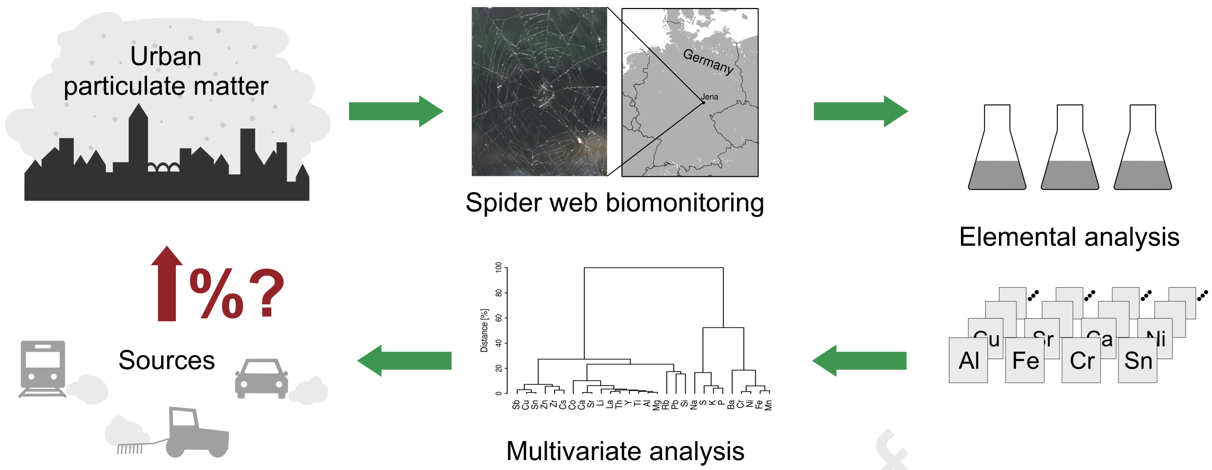
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Title page

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Spider web biomonitoring: A cost-effective source apportionment approach for urban particulate matter

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Abstract

Elevated levels of particulate matter (PM) in urban atmospheres are one of the major environmental challenges of the Anthropocene. To effectively lower those levels, identification and quantification of sources of PM is required. Biomonitoring methods are helpful tools to tackle this problem but have not been fully established yet. An example is the sampling and subsequent analysis of spider webs to whose adhesive surface dust particles can attach. For a methodical inspection, webs of orb-weaving spiders were sampled repeatedly from 2016 to 2018 at 22 locations in the city of Jena, Germany. Contents of Ag, Al, As, B, Ba, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Si, Sn, Sr, Th, Ti, V, Y, Zn and Zr were determined in the samples using inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-optical emission spectroscopy (ICP-OES) after aqua regia digestion.

Multivariate statistical methods were applied for a detailed evaluation. A combination of cluster analysis and principal component analysis allows for the clear identification of three main sources in the study area: brake wear from car traffic, abrasion of tram/train tracks and particles of geogenic origin. Quantitative source contributions reveal that high amounts of most of the metals are derived from a combination of brake wear and geogenic particles, the latter of which are likely resuspended by moving vehicles. This emphasizes the importance of non-exhaust particles connected to road traffic.

Once a source identification has been performed for an area of interest, classification models can be applied to assess air quality for further samples from within the whole study area, offering a tool for air quality assessment. The general validity of this approach is demonstrated using samples from other locations.

Capsule

Combining spider web biomonitoring and chemometrics allows for source apportionment of metals in urban particulate matter. Main sources in the study area are natural particles and brake wear.

Keywords

Spider Webs

Urban Particulate Matter

Trace Elements

Source Apportionment

Biomonitoring

Introduction

Atmospheric particulate matter (PM) is a global burden and has been identified as one of the major causes of diseases related to environmental pollution worldwide (Cohen et al., 2017; Landrigan et al., 2018). Known adverse effects on human health include – but are not limited to – premature mortality, respiratory illnesses, cardiopulmonary diseases, lung cancer, artherosclerosis, osteoporosis and adverse birth outcomes (Lelieveld et al., 2015; Lelieveld et al., 2019; World Health Organization (WHO), 2013). They have mainly been reported in urban areas where atmospheric loads of PM often exceed natural background values due to emissions from various anthropogenic sources (Fang et al., 2005; Hertel and Goodsite, 2009). As more than half of the world's population lives in cities, lowering atmospheric levels of PM wherever possible is one of the important but challenging tasks of the Anthropocene (Landrigan et al., 2018). To effectively tackle this task, a source apportionment with the identification and quantification of sources of PM is necessary.

Since levels and composition of air pollution can vary within short distances of tens or hundreds of meters, source identification approaches need to cover the high spatial variation (Apte et al., 2017). This cannot be realized solely with conventional monitoring stations, equipped most often with active samplers, which require space, maintenance and power supply. As a result, only one or maximum a few monitoring stations if any are established in urban areas (Capozzi et al., 2016; Kardel et al., 2011). A potential complement, for problems like the identification of sources or hotspots an alternative method, is the sampling and subsequent analysis of spider webs. The webs can capture particles from the atmosphere flowing through them similar to prey, accumulating up to high loads of particles (Rybak et al., 2012). Spider web biomonitoring for qualitative source identification has only been applied in few locations in Poland, China, Germany and Nigeria so far (e.g. Ayedun et al., 2013; Górka et al., 2018; Rachold et al., 1992; Rybak and Olejniczak, 2014; Rybak et al., 2015; Xiao-li et al., 2006), but has proven to be a promising method that might even be expanded to monitoring of indoor air pollution (Rutkowski et al., 2019; Rybak et al., 2019). Main advantages of this method are its low cost, easy operability and independence from both floor area and power supply (Rybak et al., 2012). Web weaving spiders can be found almost globally and they can withstand comparably high levels of pollution and mechanical stress (Yang et al., 2016). Therefore, this method could be applied worldwide, including areas with low public budget like developing countries that might not be able to afford more expensive monitoring equipment but often exhibit the highest levels of urban air pollution (Hertel and Goodsite, 2009). With regard to the analysis of the samples, trace element contents seem to be particularly suitable for source identification: Anthropogenic PM is most often enriched in heavy metals, their combination is expected to be source-specific and they are not degraded during atmospheric transport (Furusjö et al., 2007; Hovmand et al., 2008).

A high number of sampling locations as well as variations of them can be realized with manageable effort, rendering spider web biomonitoring a promising method for subsequent source apportionment. To our knowledge only three studies, all performed in the city of Wrocław, Poland, have been published on source identification so far (Rybak, 2015; Rybak and Olejniczak, 2014; Rybak et al., 2019) with one of them regarding metal contents (Rybak, 2015). They indicate an applicability of the method on a small scale. However, a broader approach with high numbers of sampling locations, samples and components determined in them is regarded in this work for a more reliable source identification and general review of the method. Source contributions should be calculated in addition as they will allow a target-oriented reduction of atmospheric levels of PM. The approach includes repeated sampling at various locations to check for both temporal and spatial variation. Such a repeated sampling (2016-2018) is regarded in this work, including webs from 22 locations in the city of Jena, Germany. Orb webs, that often persist for only one day, were sampled instead of funnel webs (persistent for up to months) as performed so far (e.g. Górka et al., 2018; Rybak, 2015), both to test their usability and to allow for a higher temporal resolution. Contents of 34 elements, mainly heavy metals, were determined and evaluated, applying multivariate statistics. One purpose has been to check if the method works for source identification in general by regarding a broader dataset from a city with different (urban) topography, meteorological conditions and pollutant emitters than Wrocław. Rather general sources of PM like traffic should be further differentiated if possible and their contributions shall be quantified. Another purpose has been to test the representativeness and transferability of the results, both within the city of Jena and for other cities.

Material and Methods

Study Area

Spider webs were sampled at 22 locations in the city of Jena, Germany (Fig 1). Jena is a medium-sized city located in a valley shaped by the river Saale. With a mean annual temperature of 9.6 °C and mean annual precipitation of 489 mm (2009–2018) it exhibits a rather arid climate for a German city (Koch, 1953; Max Planck Institute for Biogeochemistry, 2019). This as well as the resulting elongated orientation following the course of the river can be found for various cities grown around a river worldwide. No big particle emitting industries are located in the city of Jena, but a motorway, two federal highways and two railroad lines. Nearby the city there is only a cement production as a potential source of PM which, due to the main wind direction, has no significant influence on urban PM. Therefore, traffic is expected to be the major source of PM in Jena. In accordance with this expectation, the sampling locations were named according to the most nearby type of traffic: car traffic (prefix CA), tram and/or train traffic (TR) and areas with only pedestrians and cyclists (PD).

Sampling

A repeated, periodic sampling has been performed at all sampling locations from 2016 to 2018, yielding a total of 265 samples (Supplementary A). Samples were collected from April to September, as in the colder period of the year no sufficient number of webs could be found. 28 additional samples were collected at different locations in Jena (n = 4) as well as other locations in Germany (n = 24) with similar most nearby types of traffic to revise the calculations for the repeated sampling afterwards. Webs of orb-weaving spiders were sampled from handrails, mainly of bridges (up to 1.25 m above ground level), by coiling up all webs still in use per location and sampling day on a plastic straw (polypropylene, PP) to form one sample. Orb webs were chosen as they are the most common ones and mostly persist for only one day, allowing for a high temporal resolution of the data (Nentwig, 1980; Saravanan, 2006). Webs on the lower half of all handrails have been excluded as they are expected to be influenced by wear of the underlying road surface as well as water bouncing back from it during rainfall events. For transportation, each sample was stored in an individual polyethylene (PE) bag.

Sample preparation and chemical analysis

In the lab, the samples were detached from the plastic straws and coarse objects (insects, hairs, etc.) were removed with tweezers of polyoxymethylene. All samples were dried at 40 °C and digested with aqua regia according to DIN EN 16174 (Deutsches Institut für Normung e. V., 2012) using the microwave-assisted pressure digestion system MARS 5 Xpress with vessels of perfluoroalkoxy alkane (both: CEM GmbH). 2 ml 65% HNO_3 (Merck, subboiled) and 6 ml 35% HCl (supra quality, Carl Roth) were added to a maximum of 200 mg of each sample. After a pre-reaction at ambient conditions for 20 min the vessels were closed, heated to 175 °C within 15 min and kept at this temperature for 10 min. The cooled mixtures were transferred to volumetric flasks (25 ml, polymethylpentene, PMP, Vitlab GmbH), filled up with ultrapure water (genPure UV-TOC, Thermo Fisher Scientific) and transferred to 50 ml centrifuge tubes (PP, Greiner Bio-One GmbH) for centrifugation at 3000 rpm for 15 min. The clear supernatants were stored in 30 ml sample bottles (Nalgene high-density polyethylene, Thermo Fisher Scientific) until analysis.

For quality control some samples were also subjected to total digestion in a pressure digestion system (DAS, Pico Trace) with vessels of polytetrafluoroethylene. 2.5 ml 65% HNO_3 (Merck, subboiled) were added to 50 mg of each sample. For pre-reaction, the mixtures were heated to 45 °C within 1 h and kept at this temperature for 1 h. 2.5 ml 40% HF and 3 ml 70% $HClO_4$ (both: Suprapur®, Merck) were added to the cooled mixtures, the closed vessels were heated up to 180 °C within 8 h and kept at this temperature for 12 h. After cooling, the mixtures were heated up again to 180 °C within 4–5 h and kept at this temperature for 14 h in the evaporation mode to remove the acids. 2 ml HNO_3 (Merck, subboiled), 0.6 ml HCl (supra quality, Carl Roth) and 7 ml ultrapure water were applied to dissolve the remaining solids at 150 °C within 8 h and the solutions were filled up to 25 ml with ultrapure water in volumetric flasks (PMP, Vitlab).

Contents of Al, Ca, Fe, K, Mg, Mn, Na, P, S, Si, Sr, Ti and Zr in the digestion solutions were determined with inductively coupled plasma-optical emission spectroscopy (ICP-OES, 725 ES, Agilent Technologies) while contents of Ag, As, B, Ba, Cd, Co, Cr, Cs, Cu, La, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Th, Ti, V, Y, Zn and Zr were determined with inductively coupled plasma-mass spectrometry (ICP-MS, XSeries II, Thermo Scientific).

Data Analysis

Data pre-treatment and descriptive statistics were calculated with MS Excel 2016 (Microsoft Corporation). Values below the limit of detection (LOD) were replaced by a random value between zero and the LOD due to limited availability of the accurate measurements of those values. Elements with more than 5% of contents below the LOD were excluded from further examination (Ag, As, B, Cd, Mo, V). In addition, the data was tested for outliers (P = 99%, Grubbs, 1969) and normal distribution (P = 99%, David et al., 1954). Enrichment factors (EFs), comparing contents in the samples with contents in the upper continental crust (UCC), were calculated according to Eq 1, using Al as normalizing element and contents in UCC given by Wedepohl (1995):

$$EF_i = \frac{\left(c_{i,sample} / c_{Al,sample} \right)}{\left(c_{i,UCC} / c_{Al,UCC} \right)} \qquad \textbf{Eq 1}$$

with EF_i: enrichment factor of the element i, $c_{i,sample}$: content of the element i in the sample, $c_{Al,sample}$: content of Al in the sample, $c_{i,UCC}$: content of the element i in UCC and $c_{Al,UCC}$: content of Al in UCC. Multivariate analyses of autoscaled data were performed with the software R (version 3.6.0) and RStudio® (version 1.1.453) using basic packages as well as ggplot2, grid, MASS and psych. As a first step, a cluster analysis was calculated in the object space using Ward's algorithm and squared Euclidean distances. Principal component analysis (PCA) with varimax rotation was applied to visualize sources of PM. Five samples with high leverage and high sum of squared residuals were removed prior to the calculation and a number of six principal components was selected, taking into account the Guttman-Kaiser criterion (Yeomans and Golder, 1982), the screeplot and prior knowledge on the occurrence of the elements. Results of the PCA were also used to quantify contributions of the identified sources to total PM in the study area using the approach by Thurston and Spengler (1985). To review the results and check how representative they are, linear discriminant analysis (LDA) was applied.

Quality Control

For quality control two blanks were generated per each twelve samples during aqua regia digestion and measured accordingly. Standard reference material (SRM) 1648a Urban Particulate Matter (National Institute of Standards and Technology) has been prepared and analyzed in the same way as the samples. Considering also the spider web material itself, for which no reference material has been available, contents after aqua regia digestion were compared to contents after total digestion, the latter of which are expected to be closest to actual contents. Most recovery rates were satisfactory (≥ 85%, for numbers see Supplementary B). In addition, the rates compared to the SRM and those compared to the results of the total digestion were very similar, indicating that proportions dissolved from spider web samples are comparable to those dissolved from pure PM. Low rates were only found for Al, Cs, Rb, Ti, Y and Zr as well as Cr, K and Na in SRM 1648a. These elements occur in silicates like feldspar or titanite, that are likely parts of natural, geogenic PM, and cannot be dissolved completely by aqua regia (Salminen et al., 2005). Still, aqua regia digestion is regarded as pseudo-total and suitable for environmental studies as this one (Deutsches Institut für Normung e. V., 2012). Contents of selected lithophile elements might not represent total contents, but element patterns and correlations can be regarded. They focus on variance of the data for which precision, which is good in this study, is of higher importance than accuracy (Spijker et al., 2005).

Results and Discussion

Enrichment of Trace Elements in Spider Webs

An overview on element contents in the samples can be found in Table 1. Most of the elements are trace components (1000 µg/g ≥ median ≥ 1 µg/g), ranging from median contents of 1.14 µg/g for Th to 379 µg/g for Zn. These contents exhibit mostly the same order of magnitude as contents found in other studies (Hose et al., 2002; Rybak et al., 2012; Rybak et al., 2015; Xiao-li et al., 2006). Those studies focused on funnel webs with longer exposure periods of several weeks to months whereas the orb webs sampled in the current work were exposed to ambient air for only about a day. This shows that even short exposure periods in combination with sticky webs are sufficient to bind measurable contents of elements, allowing for a better temporal resolution of the sampling and a potential detection of short-term effects. Sampling in this study for example was done every two weeks at four selected locations without any significant reduction in the number of webs available. Highest contents are in the range of minor components (10% ≥ median ≥ 1000 µg/g) and were found for Al, Ca, Fe, K, Mg, Na, P, S and Si, elements that occur to a great extent in geogenic material (Salminen et al., 2005; Sternbeck et al., 2002). This is a first indication that geogenic particles make up a significant part of PM suspended in the air of Jena. Since K, Na, P and S do also occur in the webs themselves, they are not regarded as clear indication for either geogenic or anthropogenic particles in the following (Rachold et al., 1992; Work and Young, 1987).

To assess if an element is of rather natural or anthropogenic origin, EFs can be regarded (Table 1). They compare an element's content with its natural abundance in form of its content in UCC, as described above. An element is regarded as being derived mainly from anthropogenic sources if the enrichment factor exceeds 10 (Enamorado-Báez et al., 2015; Zhu et al., 2015). In the present dataset this can be found for Cr, Cu, Ni, Pb, Sb, Sn and Zn of which Sb exhibits the highest median EF of 456 and EFs for Cu, Sn and Zn are greater than 100. It is therefore assumed that Cu, Sb, Sn and Zn are almost exclusively derived from anthropogenic sources in this study. Comparably high EFs for P and S are again ascribed to the spider web material itself and do not indicate for certain an anthropogenic origin.

Identification of Sources of Urban Particulate Matter

It is expected that elements with similar behavior, for example a similar spatial distribution, are emitted by the same source (e.g. Ordóñez et al., 2003). To reveal those groups of elements a cluster analysis has been performed, the resulting dendrogram is shown in Fig 2. At a relative distance of 25% four clusters can be found. The first cluster (I) comprises of Cs, Cu, Sb, Sn, Zn and Zr, four of which have already been found to be derived from anthropogenic sources. The cluster analysis leads to the more detailed conclusion that this anthropogenic source might be car traffic, since Cu, Sb, Sn and Zn correlated with each other are most often ascribed to brake wear (Heinrichs and Brumsack, 1997; Johansson et al., 2009). With Al, Ca, Co, La, Li, Mg, Rb, Si, Sr, Th, Ti and Y cluster II is mainly formed by elements that occur to a great extent in geogenic material (Salminen et al., 2005). As the sampling area lies in a valley surrounded by hillsides with partly exposed rocks and adjacent agricultural fields, eroded rock and soil particles have likely been blown into the valley.

While clusters I and II form a joint cluster at around 30% of relative distance, clusters III and IV are totally different from them and more stable. Cluster IV consists of Ba, Cr, Fe, Mn and Ni, elements that can be found in a variety of anthropogenic products. A plausible group of products that can contain all of them and occur as PM in urban areas are steel alloys (Johansson et al., 2009; Lahd Geagea et al., 2007). Since there are no major steel processing companies in the sampling area and its surroundings cluster IV is ascribed to abraded steel particles in general and needs to be further specified by additional methods. The four elements K, Na, P and S (cluster III) occur in the webs themselves and are expected to describe the biological carrier material of the samples.

For more details and to confirm the primal source identification, results of the PCA are regarded. Six principal components (PCs) were extracted and all elements show high loadings for a limited number of PCs (Supplementary C). It has to be noted that for all components, high positive scores are connected to high contents of the elements with which they are highly loaded. PC 1 confirms the finding that geogenic particles make up a significant part of PM in the study area. It explains about half of the variance explained by the PCA and is highly loaded mainly with elements that have already been ascribed to geogenic particles (Al, Ca, Co, La, Li, Mg, Pb, Sr, Th, Ti, Y, see cluster II) as well as Cs, Zn, Zr (cluster I) and Mn (cluster IV). The latter are allocated to more than one group of elements and consequently to more than one source of PM, which is more probable than a limitation to one source as done when using only the cluster analysis. A geogenic origin is also assigned to PC 6, which is highly loaded with Si and has been extracted separately as otherwise it would have been merged with elements of rather biological origin.

Scores for component 2 (Fig 3a), highly loaded with Cs, Cu, Sb, Sn, Zn and Zr, confirm the assumption that those elements describe brake wear from traffic as a source of PM. Highest scores (> 2.0) belong to samples from locations CA_3 and CA_6 located at frequented junctions where cars have to brake. PC 3 is highly loaded with Ba, Cr, Fe, Mn and Ni (equivalent to cluster IV) that have been ascribed to steel abrasion in general. The evaluation of the scores (Fig 3a) narrows this down. High scores are found only for samples from locations with tram and/or train traffic and highest scores belong to samples from location TR_3 with both tram and train traffic but without any car traffic nearby. Ba, Cr, Fe, Mn and Ni are therefore expected to be derived from abrasion of tram/train tracks. Compared to previous studies, this is a further piece of information since abraded steel particles were often ascribed to brake wear or steel parts of cars in general (e.g. Furusjö et al., 2007; Huber et al., 2016).

A temporal influence is found to be described by component 5 with a high positive loading for Rb and a high negative loading for Na. High scores are exclusively found for samples of a single sampling campaign in late April 2018 (Fig 3b). This period has been characterized by warm temperatures (mean: 14 °C) several degrees higher than the longtime average while only two weeks before temperatures were below 0 °C (Ernst-Abbe-Hochschule Jena, 2019). Pollen of various plants have likely developed quickly at the same time in this period and ended up in the samples. This would explain the enrichment of Rb, a tracer for plant biomass, but no other metals in the samples while diluting the web biomass containing Na (Megido et al., 2017). Further groupings of the samples in the spaces of the six factors were checked for but could not be found. This does include facts that were considered possibly influencing the particle retention of the webs like wind direction and wind force.

In total, the dendrogram allows for a primal identification of natural dust, brake wear and steel abrasion as main sources of PM in Jena. The results of the PCA confirm these findings and narrow down the rather vague source of steel abrasion to abrasion of tram/train tracks. Furthermore, the close link between brake wear particles (cluster I) and geogenic particles (cluster II) indicates that they occur at the same locations. Particles of an initially natural origin like soil erosion are likely resuspended by driving vehicles, a process that can be regarded as an anthropogenically induced amplification of the burden of natural PM and is pointed out by this result. Only by combining the two evaluations the clear split of traffic-related sources as well as the connection with geogenic particles could be revealed.

This matches findings for PM from the two German cities Erfurt and Leipzig, that are located 40 km west and 72 km northeast respectively of the study area. Elements like Al, Ca, Si and Ti have been identified as soil/crustal elements in those studies (Cyrys et al., 2003; Fomba et al., 2008; Vallius et al., 2005) and a link to resuspended road dust has been drawn by van Pinxteren et al. (2016). Fomba et al. (2018) did point out that Cu and Ni are derived from different sources in Leipzig, matching the findings of this study where the two elements are ascribed to two different traffic-related sources. Also, Yue et al. (2008) did find airborne soil and two different traffic-related factors among the relevant sources of PM in Erfurt.

Quantification of the Source's Contributions to Element Loads of Urban Particulate Matter

Expanding the results of the PCA, source contributions were calculated. They allow for a better estimation of the importance of sources as they quantify the proportion of each element's total burden derived from each source/component (Table 2). By this, most important sources (highest proportional contribution) can be identified for each element. For about half of the elements (Al, Ba, Ca, Co, Cs, La, Li, Mg, Mn, Pb, Rb, Sr, Th, Ti, Y, Zn, Zr) resuspended geogenic particles (PC 1) are the most important source, making up for 36% (Ba) to more than 80% (Al, Li, Y) of the element's total load in PM. The most important source for Cu, Sb and Sn is brake wear (PC 2) with a contribution to the elements' total load in PM of 53–56%. Gu et al. (2011) did find similar contributions in a source apportionment study in Augsburg, Germany (300 km south of Jena) with 53% of Cu and 54% of Sb in PM being derived from brake wear. At a location with high amount of car traffic in Leipzig even more than 75% of Cu and Sb in total PM were ascribed to traffic (Fomba et al., 2018).

Resuspended geogenic particles and brake wear do also substantially (more than 10%) contribute to the loads of other elements with many of them featuring the other of the two sources as their most important one. In detail, those are Cu, Fe, Na, Sb, Si and Sn (from resuspended geogenic particles) as well as Al, Ba, Ca, Co, Cr, Cs, Fe, La, Mg, Mn, Na, Ni, Pb, Rb, S, Si, Sr, Th, Ti, Y, Zn and Zr (from brake wear). In sum, most of the elements are derived mainly from geogenic dust and brake wear, exceeding contributions of 85% for Al, Ca, Co, Cs, Cu, La, Li, Mg, Pb, Rb, Sb, Sn, Sr, Th, Ti, Y, Zn, Zr. It is expected that geogenic dust and brake wear get mixed during resuspension by driving vehicles at the roads. This finding hence highlights the importance of non-exhaust car traffic related PM. A similar mixing of resuspended geogenic particles and abraded particles from car traffic has been found in studies for Leipzig (Fomba et al., 2018; van Pinxteren et al., 2016). Since mainly heavy metals were regarded in this study, a possible detection of car exhaust particles would not be straightforward. However, fuel combustion has been connected to the joint occurrence of Cr, Cu, Ni and Pb (e.g. Vuković et al., 2016), a pattern that has not been found in this study. Therefore, it is assumed that non-exhaust car emissions are more important than exhaust emissions in the study area.

In contrast, steel abrasion (PC 3) does add substantial portions of only a few elements. It is the main source of Cr, Fe and Ni (40–62%) and also substantially emits Ba, Mn and Na. With 48% the main source of Si are naturally occurring silicate minerals (PC 6). The quantification does also show that short-term effects as the one of pollen evolution on PM detected by PC 5 do likely not contribute remarkably to the elements' total burden in PM. It has to be noted that elements occurring in the spider web material (K, P, S) are not derived primarily from PM in the samples. This results in substantially negative contributions for component 1 and excessively high contributions for other components as the output of the mathematical model. Those elements were therefore not regarded for source contributions and should be excluded from future studies of spider web material.

Most of the minor but still substantial sources of elements (e.g. Ba from geogenic dust or Fe from brake wear) were not regarded when applying only the PCA, as they exhibit small loadings for the particular component. This highlights the importance of performing a quantification to assess the real burden of each source which might not be grasped totally when regarding only the variance as done with PCA. However, the easier structure of a PCA loadings table is needed to identify sources in the first place.

Classification Models as a Tool to Check the Transferability of the Results

Since amount and composition of PM vary on a local scale, the transferability of the results should be checked. To do this, an LDA was calculated with the same data as the PCA. Three classes were selected, resulting from the anthropogenic sources identified: car traffic (Fig 1, CA, n = 133), pedestrian areas (PD, n = 76) and tram/train traffic (TR, n = 51). The classification model is credible with rates of correct classification of 92% (reclassification) and 90% (cross-validation with ten splits of the data). It allows for the assignment of further samples to classes, based on their measured element contents. This has been done for 28 new samples from different locations in Jena and Germany to check if the data from the repeated sampling is representative also for other locations. All of the "Tram/train" samples and all but one of the "Pedestrian" samples are correctly classified. Only about half of the "Car" samples are falsely classified as "Pedestrian". This leads to a summarized rate of correct classification of 61% (detailed information can be found in Supplementary D). Fig 4 shows that the confidence ellipses overlap to a small extent and samples that are not correctly classified lie in this area of overlap. Additional samples taken in Jena are correctly classified, showing that samples from different locations but within the area of the sampling performed to build the model can be classified nicely. That's why on a regional scale, the classification model is well usable. Regarding samples from other places, several of them (from areas with both high and low amounts of car traffic) are assigned to the class "Pedestrian". Those samples have been taken in cities/areas that exhibit both a smaller size (fewer inhabitants) and a different urban geography than the city of Jena. Local climate influencing PM distribution and resuspension as well as a potential influence by the total amount of car traffic in a city are therefore deduced to affect the model. As a result, it is recommended to do individual source identifications and build individual models for all areas of interest, covering all major sources of PM. This might be a useful tool, for example for decision-makers: Classification models allow for a simplified assessment and comparison of dust samples, considering a great amount of information (e.g. element contents) but regarding only a small number of classes.

Conclusions

Measurable and reasonable contents of elements were found in orb spider webs, acting as a natural collector of PM, despite their short exposure period to ambient air. Multivariate evaluations of the element contents in the samples can be applied to identify and quantify sources of PM. While both cluster analysis and factor analysis can be used for identification, a combination of them has been found to yield more detailed information, including also potential relations between the sources. It is therefore recommended to apply both methods when possible. With this approach, geogenic particles and non-exhaust emissions from different types of traffic were found to be the major sources of PM in the city of Jena.

Most of the elements regarded in this work are attributable to a large extent to a combination of brake wear and geogenic particles, ranging between a contribution of 54% (Ba) of the element's total load in PM and 97% (Y). The two sources are interconnected since the influence of geogenic/natural particles has been shown to be anthropogenically increased as they get resuspended by car traffic. Abrasion of steel tracks, present at locations with tram/train traffic, could be identified as another source accounting for major proportions of Cr, Fe and Ni (48–62%) in the samples.

Repeated sampling campaigns should be performed prior to the evaluation, to cover both spatial and temporal variation and build up a dataset large enough for multivariate analyses. It could be shown that, by this, noteworthy short-term effects can be revealed that might not be revealed by other passive sampling strategies.

The source identification is representative for the study area, the city of Jena, covering also locations apart from the ones sampled. It is therefore possible to build classification models, defining classes in compliance with the local sources. This might be a useful tool for air quality assessment or the detection of changes in sources for future campaigns. Similar classification models are expected to be calculable for other cities if the samples used to build the model cover their specific features with regard to PM.

Tables

Table 1: Element contents in spider web samples (n = 265) from the city of Jena and the corresponding interquartile range (IQR). Outliers according to Dixon (1951, P = 99%) were removed prior to the calcuations (marked by *, n = 264 in those cases). Underlined elements do not exhibit a normal distribution according to David et al. (1954, P = 99%). Median enrichment factors (EFs) are listed in addition, dividing contents in the samples by contents in the upper continental crust given by Wedepohl (1995), with both normalized to contents of Al.

Element	Median [µg/g]	IQR [µg/g] ($q_{0.75}$ - $q_{0.25}$)	EF	Element	Median [µg/g]	IQR [µg/g] ($q_{0.75}$ - $q_{0.25}$)	EF
Ca	14,600*	15,200	8	Sr	66.2*	63.9	3
Fe	11,300	11,400	4	Cr	38.0*	43.1	14
K	10,000	4,090	5	Ni	18.0*	18.5	12
P	9,330	5,790	203	Rb	14.6*	7.08	2
S	7,150*	3,050	108	Pb	14.0*	11.8	12
Si	6,140	4,760	0	Sn	13.4*	27.9	102
Al	5,100	5,270	-	Zr	8.50*	8.21	1
Na	3,430*	2,310	2	Sb	8.10	14.4	456
Mg	3,150	2,960	4	Li	7.60	8.60	5
Zn	379*	503	140	La	4.30*	4.82	2
Ti	338	449	2	Co	3.00*	2.81	4
Mn	211	158	5	Y	2.42*	2.52	2
Ba	194*	202	3	Cs	1.22*	1.39	3
Cu	82.5*	146	107	Th	1.14	1.32	2

Table 2: Contributions [%] of the sources identified by principal component analysis to the element's loads in the samples. Contributions not accounted for by the PCA are not regarded as they are negligibly small.

Element	PC 1 Resuspended geogenic particles	PC 2 Brake wear	PC 3 Abrasion of steel tracks	PC 4 Spider web material	PC 5 Effect of pollen (April 2018)	PC 6 Silicate minerals
Al	81	14	0	0	1	4
Ba	36	18	35	10	1	0
Ca	59	32	0	3	0	6
Co	75	13	10	1	0	1
Cr	7	28	62	0	1	2
Cs	63	25	8	0	2	2
Cu	32	53	9	0	1	5
Fe	25	25	48	0	0	2
K	-71	1	24	123	12	11
La	79	14	5	0	2	0
Li	87	8	2	0	1	2
Mg	70	24	0	0	0	6
Mn	45	29	21	1	0	4
Na	25	16	18	37	0	4
Ni	37	21	40	0	0	1
P	-56	9	33	104	5	5
Pb	64	26	3	2	2	3
Rb	75	12	4	3	6	1
S	-19	23	29	66	2	0
Sb	34	53	8	0	0	5
Si	25	11	0	16	0	48
Sn	39	56	3	0	0	2
Sr	74	20	4	0	2	0
Th	79	15	4	1	1	0
Ti	74	21	1	0	1	3
Y	84	13	1	0	2	0
Zn	49	41	5	1	0	4
Zr	70	23	4	0	1	2

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Figure Captions

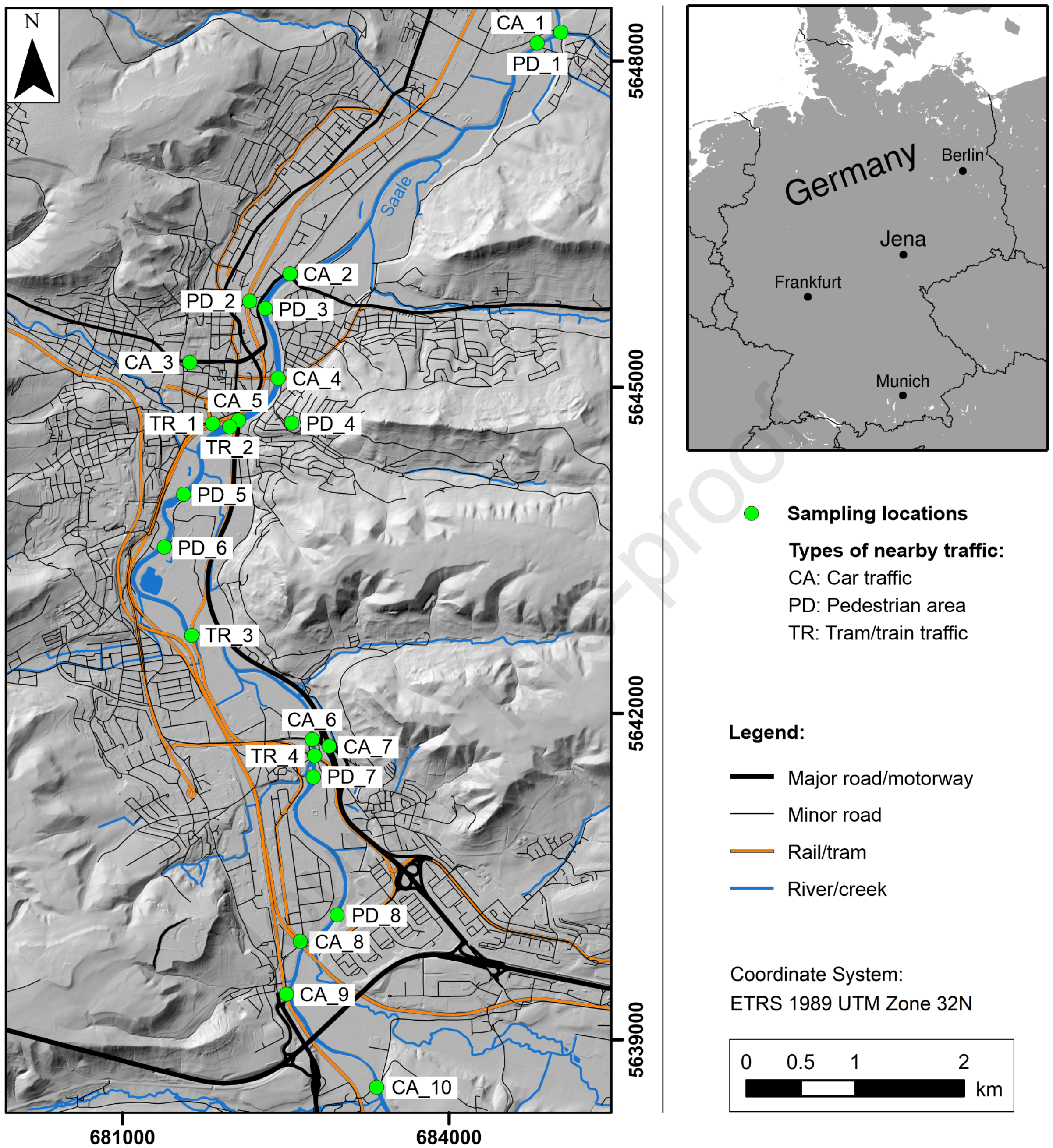
No colors should be used for any of the figures in print!

Fig 1 (2-column-fitting image) Map of the city of Jena, showing the sampling locations of spider webs as well as traffic routes. Sampling locations were named according to the most nearby type of traffic. CA: car traffic, PD: areas with only pedestrians, TR: tram and/or train traffic. Information on traffic routes and elevation above sea level has been derived from Thüringer Landesamt für Bodenmanagement und Geoinformation (2019).

Fig 2 (1-column-fitting image) Dendrogram (Ward's algorithm, squared Euclidean distances) resulting from the cluster analysis of element contents in spider web samples in the object space. Four clusters that can be found at a relative distance of 25% are regarded.

Fig 3 (2-column-fitting image) Plots of the scores of a principal component analysis (PCA, varimax rotation) of 260 spider web samples from the study area. a) PCs 2 and 3, coded according to the type of most nearby traffic. b) PCs 1 and 5 color coded according to the date of the sampling.

Fig 4 (1-column-fitting image) Plot of 260 spider web samples (used to calculate the model) in the space of the two discriminant functions of a linear discriminant analysis. Original class memberships to the three classes "Car", "Pedestrian" and "Tram/train" are depicted in greyscale and the 95% confidence ellipses of the calculated classes are shown. Orange squares show three exemplary additional samples and how they are classified by the model.


N
CA_1
PD_1
Saale
CA_2
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TR_1
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TR_3
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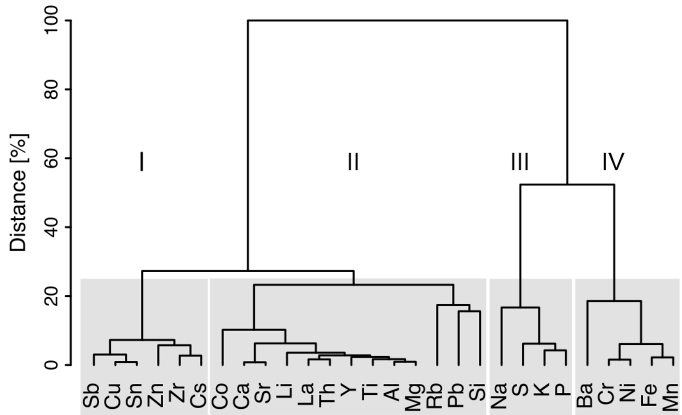
CA_7
TR_4
PD_7
PD_8
CA_8
CA_9
CA_10
5648000
5645000
5642000
5639000
681000
684000
Germany
Berlin
Jena
Frankfurt
Munich
Sampling locations
Types of nearby traffic:
CA: Car traffic
PD: Pedestrian area
TR: Tram/train traffic
Legend:
Major road/motorway
Minor road
Rail/tram
River/creek
Coordinate System:
ETRS 1989 UTM Zone 32N
0
0.5
1
2
km


Distance [%]
0
20
40
60
80
100
I
II
III
IV
Sb
Cu
Sn
Zn
Zr
Cs
Co
Ca
Sr
Li
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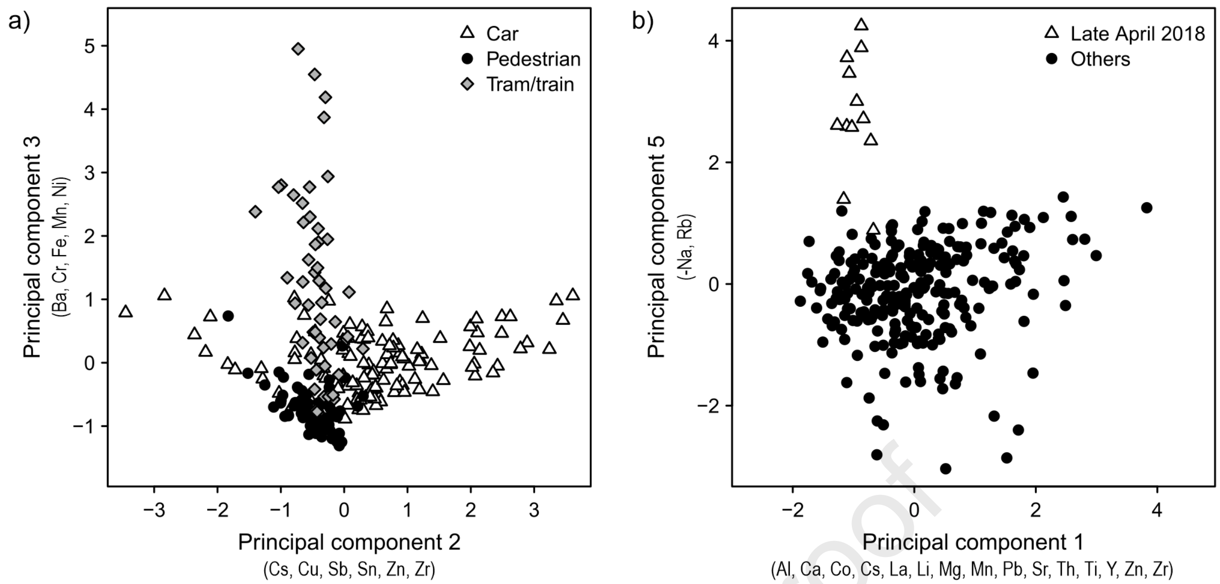
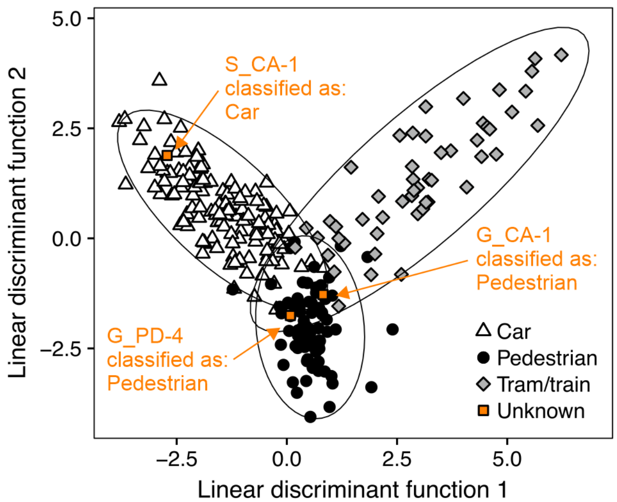
Cr
Ni
Fe
Mn


a)
Car
Pedestrian
Tram/train
Principal component 3
(Ba, Cr, Fe, Mn, Ni)
Principal component 2
(Cs, Cu, Sb, Sn, Zn, Zr)
b)
Late April 2018
Others
Principal component 5
(-Na, Rb)
Principal component 1
(Al, Ca, Co, Cs, La, Li, Mg, Mn, Pb, Sr, Th, Ti, Y, Zn, Zr)



Linear discriminant function 2
Linear discriminant function 1
5.0
2.5
0.0
–2.5
–2.5
0.0
2.5
5.0
S_CA-1
classified as:
Car
G_CA-1
classified as:
Pedestrian
G_PD-4
classified as:
Pedestrian
Car
Pedestrian
Tram/train
Unknown

Highlights

- Orb spider webs enable biomonitoring of particulate matter with high spatiotemporal resolution
- Metal contents in webs can be exploited to identify and quantify sources of urban particulate matter
- Combining clustering and principal component analysis yields the best source identification
- Non-exhaust traffic related metals are most important in the study area
- Classification models are a promising tool for future air quality assessment

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: