https://doi.org/10.5194/acp-2022-843
Preprint. Discussion started: 9 January 2023


Atmospheric Chemistry and Physics Discussions

# A new method for the quantification of ambient particulate matter emissions

Stergios Vratolis[1], Evangelia Diapouli[1], Manousos I. Manousakas[2], Susana Marta Almeida[3], Ivan Beslic[4], Zsofia Kertesz[5], Lucyna Samek[6], and Konstantinos Eleftheriadis[1]

[1]ERL, Institute of Nuclear & Radiological Sciences & Technology, Energy & Safety, National Centre for Scientific Research "Demokritos", 15310 Ag. Paraskevi, Attiki, Greece
[2]Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, Villigen-PSI, 5232, Switzerland
[3]Department of Nuclear Sciences and Engineering & C2TN, Instituto Superior Técnico, Universidade de Lisboa, Bobadela, Portugal
[4]Environmental Hygiene Unit, Institute for Medical Research and Occupational Health, Zagreb, 10000, Croatia
[5]Institute for Nuclear Research (ATOMKI), Bem tér 18/C, Debrecen, 4026, Hungary
[6]AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, ul. Mickiewicza 30, 30-059, Krakow, Poland

**Correspondence:** S. Vratolis (vratolis@ipta.demokritos.gr)

**Abstract.** An inversion method has been developed in order to quantify the emission rate of certain aerosol pollution sources across a wide region in the Northern hemisphere, mainly in Europe and Western Asia. The data employed are the aerosol contribution factors (sources) deducted by Positive Matrix Factorization (PMF) on a $PM_{2.5}$ chemical composition dataset from 16 European and Asian cities for the period 2014 to 2016. The spatial resolution of the method corresponds to the geographic grid cell size of the Lagrangian particle dispersion model (FLEXPART) which was utilized for the air mass backward simulations. The area covered is also related to the location of the 16 cities under study. Species with an aerodynamic geometric mean diameter of 400 $nm$ and 3.1 $\mu m$ and geometric standard deviation of 1.6 and 2.25 respectively, were used to model the Secondary Sulfate and Dust aerosol transport. PSCF analysis and Generalized Tikhonov regularization were applied so as to acquire potential source areas and quantify their emission rate. A significant source area for Secondary Sulfate on the East of the Caspian Sea is indicated, when data from all stations are used. The maximum emission rate in that area is as high as 10 $g * m^{-2} * s^{-1}$. When Vilnius, Dushanbe and Kurchatov data were excluded, the areas with the highest emission factors were the Western and Central Balkans and South Poland. The results display many similarities to the $SO_2$ emission map provided by ECLIPSE database. For Dust aerosol, measurements from Athens, Belgrade, Debrecen, Lisbon, Tirana and Zagreb are utilized. The west Sahara region is indicated as the most important source area and its contribution is quantified, with a maximum of 17.5 $g * m^{-2} * s^{-1}$. When we apply the emission rates from every geographic grid cell (1° x 1°) for Secondary Sulfate aerosol deducted with the new method to air masses originating from Vilnius, a good approximation to the measured values is achieved.

https://doi.org/10.5194/acp-2022-843
Preprint. Discussion started: 9 January 2023


Atmospheric Chemistry and Physics Discussions

## 1 Introduction

Atmospheric aerosol particles affect air quality, human health, atmospheric visibility, and the climate (Laden et al., 2006; Lohmann and Feichter, 2005; Pope and Dockery, 2006). The identification and quantification of sources and corresponding source areas of aerosols require significant effort by the Scientific Community. When these information are at hand, mitigation measures can be applied and air quality can be improved. Source apportionment methods can support air quality planning activities, by providing information on the relationship between air pollutant sources and their concentrations. Reliable and quantitative information on the origin of pollution and on pollution sources is required in order to support the design of air quality plans and explain the origin of exceedances. This information regarding the quantification of the sources of air pollution, both in terms of their sectorial and spatial origins, constitutes an essential step of the air quality management process (Wesseling et al., 2019).

This work is the follow up of the article by Almeida et al. (2020). In order to find the source areas for the pollution sources in the aforementioned publication we followed the Potential Source Contribution Function analysis (PSCF) (Eleftheriadis et al., 2009) and a discrete, deterministic approach (Tikhonov regularization, (Tikhonov et al., 1995)). Discrete, deterministic approaches have a long and distinguished history in geophysics. The major advantage of these methods is their computational efficiency, with costs governed by the number of discrete basis functions used. This allows researchers to limit the scale of their inference task to suit available resources, but imposes strong assumptions about the properties of the model sought: we assert that it can be well-represented using the chosen set of basis functions. An obvious drawback of any deterministic approach is the presumption that there is a single 'answer' that can explain observations. In many geophysical settings, it is apparent that this cannot be true: available data plainly lack the sensitivity required to properly constrain all components within the basis function expansion. This motivates strategies that seek to identify the full range of models that might be compatible with observations (Park et al., 2018).

This study aims to introduce a two-step method for the quantitative estimation of emissions from geographic areas using in situ stations measurement data. In the first step, the PSCF analysis for each measurement station is produced for the target species. Based on the results, we evaluate if at a measurement station the target species are mainly transported or locally produced. In the second step, including only stations for which the target species are transported, we employ the Tikhonov regularization method in order to acquire emission rates from each geographic source area. The use of this method can reduce the uncertainty of emission factors, especially from those areas in which the emission inventories have high uncertainty. Numerous source apportionment studies have been conducted on many European and Asian cities in the past, and this method can identify the source areas of transported aerosols and quantify their emissions.

In the present work no a priori information was used, and a smooth solution was sought. The smooth solution is justified by the fact that $SO_2$ emissions are gradually converted to Secondary Sulfate aerosol as they travel along with the air masses (Seinfeld and Pandis, 1998). This process takes many hours, covering probably more than one geographic grid cell (1° x 1°). Dust aerosol possibly originates from multiple neighboring cells (i.e. in North Africa) and therefore a smooth solution is suitable for this case too.

https://doi.org/10.5194/acp-2022-843
Preprint. Discussion started: 9 January 2023


Atmospheric Chemistry and Physics Discussions

## 2 Materials and Methods

### 2.1 PM sampling stations and filter analysis

More than 2,200 $PM_{2.5}$ samples were collected in urban and sub-urban background stations from 16 European and Central Asian cities. Sampling was performed mostly in 24-h periods, every third day, between January 2014 and December 2016. Particles were sampled on PTFE, polycarbonate, cellulose nitrate, cellulose and quartz filters by means of low and medium volume samplers.

Before and after sampling, filters were weighed in the laboratories located in each city by means of a microbalance using the procedure described in $EN12341$. Filters were subsequently analyzed by several analytical techniques for the determination of major and trace elements, elemental and organic carbon, black carbon, and water soluble ions.

The Positive Matrix Factorization receptor model (EPA PMF 5.0) was applied and sources were acquired for each city.

Due to the high number of cities involved in this work, it was not possible to fully harmonize the used methods, which introduces a level of uncertainty in the obtained results and especially in their comparison. Source apportionment of $PM_{2.5}$ was performed by receptor modelling that is based on the mass conservation principle. Further uncertainties to the source apportionment results are introduced by the fact that the stations of Chisinau, Sofia, Niksic, Lisbon, Ankara and Vilnius have available only 50 filter samples. More details can be obtained in (Almeida et al., 2020), where the measurement stations, $PM_{2.5}$ analysis techniques used, and PMF results are described in detail.

### 2.2 Flexible Particle Dispersion Model (FLEXPART)

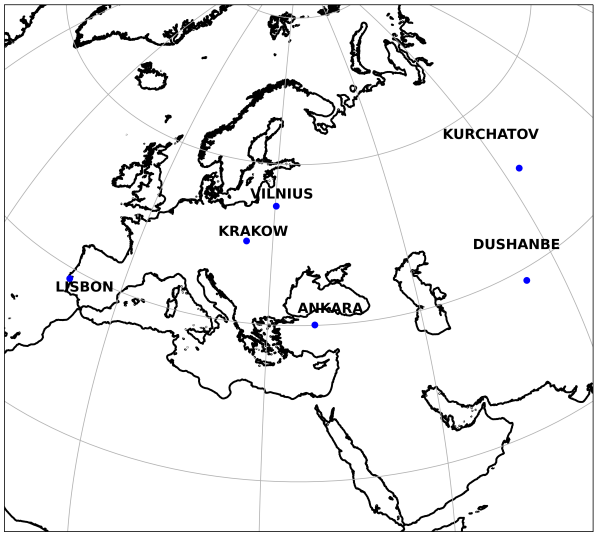
The Flexible Particle Dispersion Model (FLEXPART) was used in order to acquire residence times over geographic grid cells (sensitivity) (Stohl et al., 2005, 2009). These residence times indicate how sensitive the measurements at a station are to emissions occurring at each geographic grid cell. FLEXPART runs account for grid scale wind as well as for turbulent and mesoscale wind fluctuations. Drift correction, to prevent accumulation of the released computational particles, and density correction, to account for the decrease of air density with height, were both applied. Twenty-day backward runs with the release of $4 \times 10^4$ air parcels every 3 hours beginning from each station were produced. The aerosol species carried by the air parcels were Secondary Sulfate (400 $nm$ aerodynamic geometric mean diameter, 1.6 standard deviation) and Dust (3.1 $\mu m$ aerodynamic geometric mean diameter, 2.25 standard deviation). Wet and dry deposition of these species was also included in the results. Residence times in each grid cell, for a height range from 0 to 500 m above ground level (agl), are used for this study. The height was chosen so as to include sources within the boundary layer for all geographic grid cells.

The properties of the species were chosen based on the work published by (Gini et al., 2022), where an 11 stage low pressure Berner impactor was used. The Berner impactor cut sizes range from 0.03 $\mu m$ to 13.35 $\mu m$ at a flow rate of 26 $l * min^{-1}$. Gini et al. (2022) determined the elemental composition of the collected samples by energy dispersive X-ray fluorescence spectroscopy (XRF).

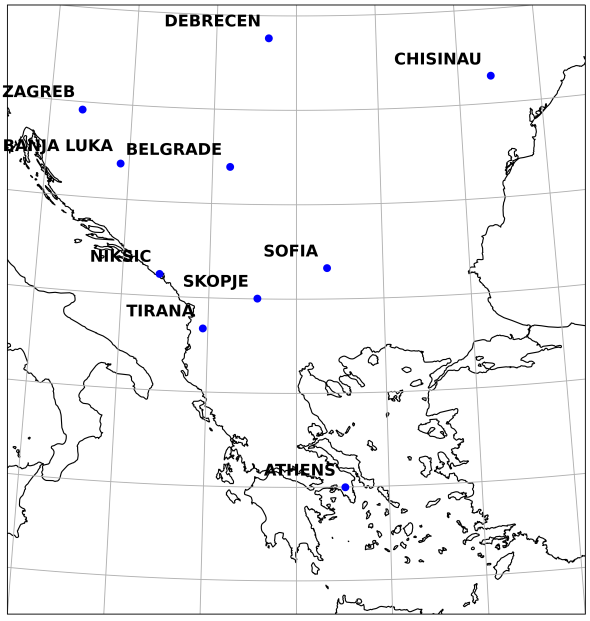
https://doi.org/10.5194/acp-2022-843
Preprint. Discussion started: 9 January 2023




Atmospheric Chemistry and Physics Discussions




(a) Ankara, Dushanbe, Kurchatov and Lisbon sampling locations




(b) Athens, Banja-Luka, Belgrade, Chisinau, Debrecen, Niksic, Skopje, Sofia, Tirana and Zagreb sampling locations

**Figure 1.** Urban background and suburban background measurement stations included in the study.

### 2.3 Tikhonov regularization

We are concerned with the solution of minimization problems of the form

$$min\|Ax - b\| \tag{1}$$

$x \epsilon R^n$ where $\|\|$ denotes the Euclidean norm, A $\epsilon$ $R^{m*n}$ is an ill-conditioned matrix, and the data vector $b \epsilon R^m$ is contaminated by an unknown error $e \epsilon R^m$ that may stem from measurement inaccuracies and discretization error (Park et al., 2018). Thus, $b = b_{exact} + e$. We are interested in computing the solution $x_{exact}$ of minimal Euclidean norm of the least-squares problem with error-free data vector,

$$min\|Ax - b_{exact}\| \tag{2}$$

$x \epsilon R^n$ associated with (2). The desired solution $x_{exact}$ will be referred to as the exact solution. Since $b_{exact}$ is not known, we seek to determine an approximation of $x_{exact}$ by computing a suitable approximate solution of (2).

https://doi.org/10.5194/acp-2022-843
Preprint. Discussion started: 9 January 2023


Atmospheric Chemistry and Physics Discussions

Due to the ill-conditioning of the matrix $A$ and the error $e$ in the data vector $b$, straightforward solution of the least- squares problem (2) generally does not give a meaningful approximation of $x_{exact}$ . Therefore, the minimization problem of equation (2) is commonly replaced by a penalized least-squares problem of the form

$$min\|Ax - b\| + \lambda^2\|Lx\|^2 \tag{3}$$

$x \epsilon R^n$

This replacement is known as Tikhonov regularization. The parameter $\lambda \geq 0$ is the regularization parameter that balances the influence of the first term (the fidelity term) and the second term (the regularization term), which is determined by the regularization matrix $L \ \epsilon \ R^{p*n}$. Here p is an arbitrary positive integer. The purpose of the regularization term is to damp undesired components of the minimal-norm least-squares solution of (1). The minimization problem (3) is said to be in standard form when L is the identity matrix $I$, otherwise the minimization problem is said to be in general form. We are interested in Tikhonov regularization in general form, because for a suitable choice of regularization matrix $L \neq I$ the solution of (3) can be a much better approximation of $x_{exact}$ than the solution of (3) with $L$ = $I$. In our particular case, $A$ matrix corresponds to FLEXPART model sensitivity (residence time in each grid cell), $b$ corresponds to the actual species mass concentration, while $x$ is the emissions of a specific source from each geographic grid cell.

We expect that uncertainties associated with the $PM2.5$ measurements, chemical analysis and PMF model application will be attributed as unknown error $e$ in the regularization term. Cavalli et al. (2016) report a positive sampling artefact of 0.4 to 2.8 $\mu g \ C/m^3$ for PM collection on quartz fibre filters corresponding to 14 - 70% of the total carbon collected. Viana et al. (2006) report that approximately 14% of the $PM2.5$ mass may result from the adsorption of gaseous organic and inorganic compounds onto the filter or the particles already collected on it (positive artefact). They also state that prolonged sampling times may lead to greater negative artefacts (i.e. loss of semi-volatile organic compounds and of ammonium nitrate). The uncertainty of the XRF, EC/OC and IC measurements range between less than 10% (IC) and up to 20% (XRF) (Manousakas et al., 2017; Panteliadis et al., 2015; Mantas et al., 2014; Vratolis et al., 2018). According to AIRUSE 2016 EU project final report (Deliverable B2.4), PMF results standard error was estimated for the Secondary Sulfate source to be below 10%, while the Dust source standard error ranged from below 5% to 40% ($PM2.5$ filters). An overall uncertainty approximating 30% in the results obtained from the filter analysis and source identification for each city is therefore expected.

### 2.4 $L - curve$ method

Commonly, if only a single regularization parameter needs to be determined, the norms of model and residuals are plotted against one another, to give an $L - curve$. This name comes from the curve's characteristic shape, and the preferred regularization parameter is then chosen by identifying the "elbow" of the curve. The strategy is justified based on the principle of Occam's razor, which advocates reliance on the simplest (in the present context, smallest) model that can explain observations (Valentine and Sambridge, 2018; Hansen, 1992).

https://doi.org/10.5194/acp-2022-843
Preprint. Discussion started: 9 January 2023


Atmospheric Chemistry and Physics Discussions

### 2.5 Potential source contribution function (PSCF)

Twenty-day backward FLEXPART runs were used to acquire the residence time over each geographic cell for each measurement and for all stations. For each cell the PSCF ratio was calculated.

$$PSCF_{i,j} = weight_{i,j} * m_{i,j}/n_{i,j} \quad (4)$$

where $m_{i,j}$ is the sum of residence times (sensitivity) in a cell for concentrations higher than the $90^{th}$ percentile and $n_{i,j}$ is the sum of residence times for all measurements. $PSCF_{i,j}$ is the measure of probability of a grid cell (1° x 1°) to contribute to the concentration of the pollutant measured at the receptor site considered (Perrone et al., 2018). In order to acquire the weight factor used for each cell, total residence times in cells were divided in percentiles. The weight coefficients 0.25, 0.5 and 0.75 were used for cells with total residence times up to the $25^{th}$, $50^{th}$, $75^{th}$ percentiles, respectively. Twenty day backward runs were used to asses species with high residence times in the atmosphere like Sahara dust.

## 3 Results and Discussion

### 3.1 Secondary sulfate aerosol

The Secondary Sulfate source identified in each station was simulated by an aerosol lognormal distribution with an aerodynamic geometric mean diameter of 400 $nm$ and a standard deviation of 1.6. From each station the aerosol mass was released every 3 hours (within $4 \times 10^4$ discrete finite air masses) and followed backward in time for 20 days. The result obtained by FLEXPART was the residence time in each geographic cell. In Figure 2 the PSCF results for Zagreb, Athens, Krakow and Dushanbe are displayed. In appendix A1 we display the PSCF results for the Secondary Sulfate source for all cities with a Secondary Sulfate species that are not displayed in Figure 2.

We did not exclude any station with an identified Secondary Sulfate source from the analysis for this species, as we consider that Secondary Sulfate and its precursor gases are emitted from many source areas in Europe and Asia (14 out of 16 stations were included). In this case we produced three emission results: One including only measurements from Zagreb (around 600 measurements), one including all participating European cities except Vilnius (around 1,800 measurements), and one including all cities (around 2,050 measurements).

In Figure 3 the emission factors for Secondary Sulfate aerosol calculated by the Tikhonov regularization method for 1° x 1° cells are presented. We used this resolution in the range of latitudes from -30° to 90° and longitude from -40° to 140°. This corresponds to a 120*160 (19,200 unknown factors) emission cell matrix, a number much higher than the total number of measurements. We have to keep in mind that not all sources are measured at all stations and even when a source exists at a station, it may not be present in all samples.

As already mentioned earlier, a high level of uncertainty is expected in our input data. In order to exclude data with high uncertainty, only the measurements for which Secondary Sulfate source contribution was positive were included in the calculations.

https://doi.org/10.5194/acp-2022-843
Preprint. Discussion started: 9 January 2023


Atmospheric Chemistry and Physics Discussions

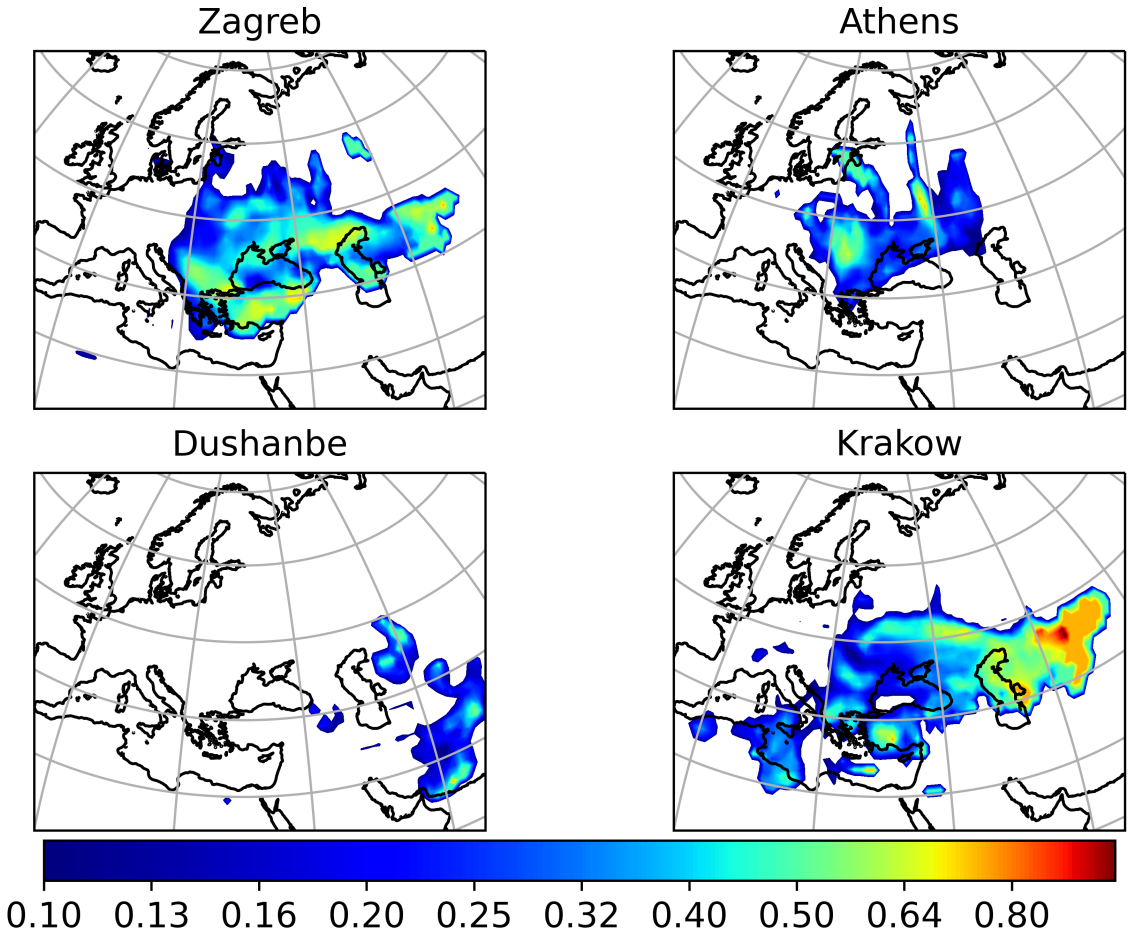
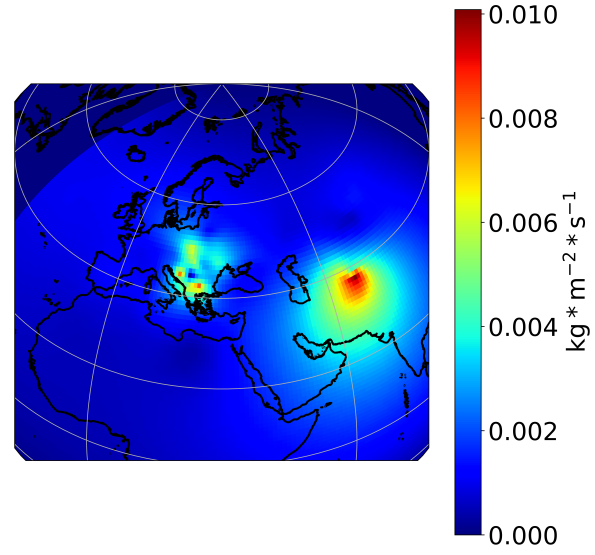



**Figure 2.** PSCF analysis at the $90^{th}$ percentile for Secondary Sulfate aerosol, Zagreb, Athens, Dushanbe, Krakow.

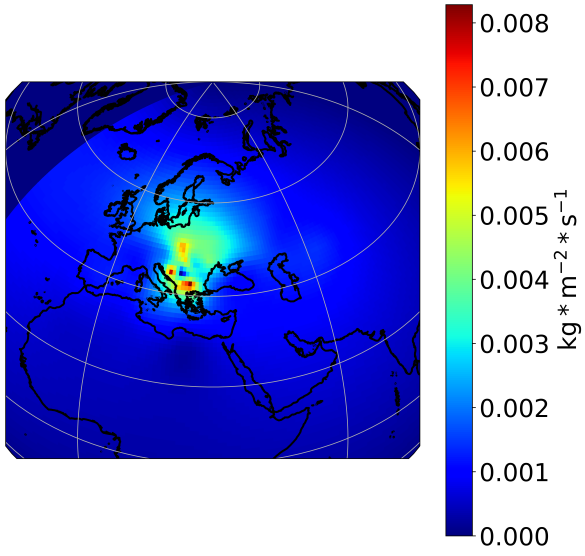
The result for Zabreb could not be computed in detail due to the small number of measurements (562 samples with positive Secondary Sulfate source values) used in relation to 19,200 unknown factors. Therefore, the result lacks specificity, indicating Poland and Eastern Europe in general as the main source area for Zagreb. We included the emission results for Zagreb as it was the station with the largest number of filter samples that participated in the study. This case indicates the results we could expect when we use data from a single station.

When we compare the Eclipse emission map for $SO_2$ and the emission map acquired by the Tikhonov regularization for the investigated European cities excluding Vilnius, we observe many similarities. The hotspots in Balkans and South Poland are apparent in both maps.

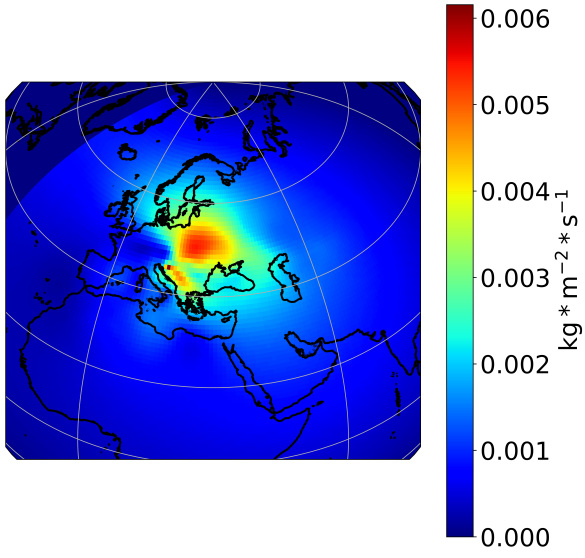
https://doi.org/10.5194/acp-2022-843
Preprint. Discussion started: 9 January 2023

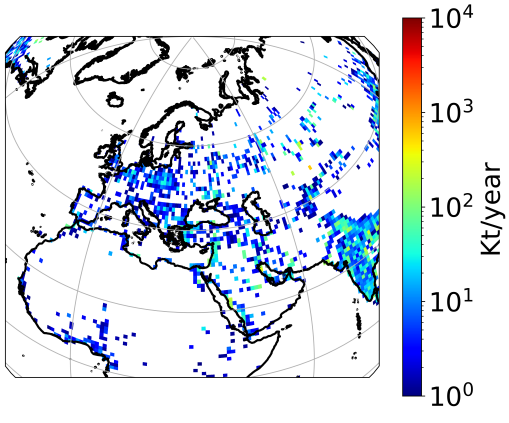

(a) Solution when data from all stations are included, Secondary Sulfate aerosol




(b) Solution excluding data from Vilnius, Dushanbe, Kurchatov, Secondary Sulfate aerosol




(c) Solution for Zagreb station data, Secondary Sulfate aerosol

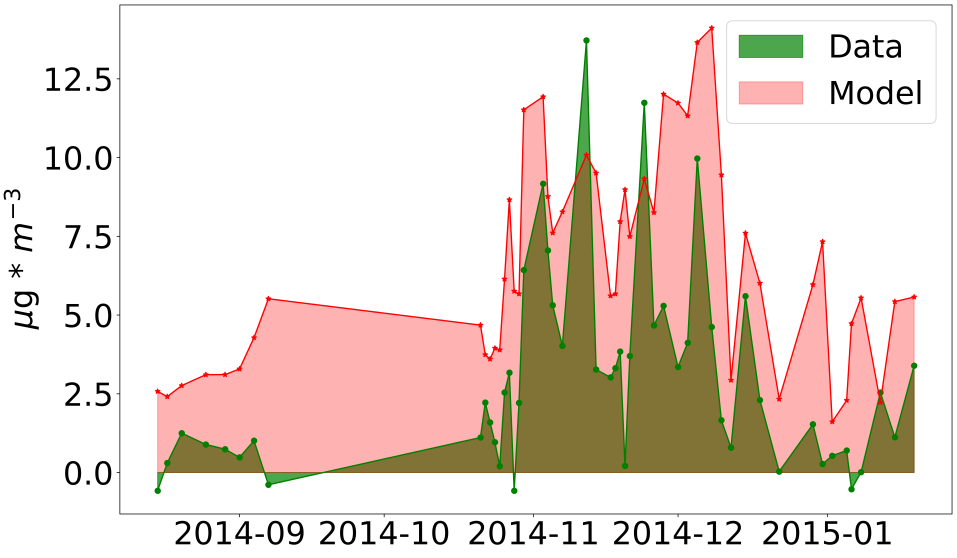



(d) ECLIPSE V6b database $SO_2$ emissions, 2015

**Figure 3.** Secondary Sulfate aerosol Tikhonov regularization, 1° x 1° emission factors.

https://doi.org/10.5194/acp-2022-843
Preprint. Discussion started: 9 January 2023


Atmospheric Chemistry and Physics Discussions




(a) Vilnius result, 1° x 1° solution

**Figure 4.** Comparison of modeled and measured Secondary Sulfate aerosol concentration at Vilnius. The solution used is the one acquired when Vilnius, Dushanbe, Kurchatov data are excluded.

We also find similarities between the PSCF analysis and the regularization result when all cities are included. In particular, the area east of the Caspian Sea appears to contribute significantly in the PSCF performed for Zabreb and Krakow, as well as in the Tikhonov regularization solution.

The PSCF result for Dushanbe indicates the areas east and south east of the Caspian Sea as potential sources. This is also apparent in the solution when we include all stations and the Eclipse emission map for $SO_2$. Central Asia, comprising Kazakhstan, Kyrgyzstan, Tajikistan, Uzbekistan and Turkmenistan, has developed rapidly in terms of population, industrialization and urbanization over the past few decades, accompanied by increased anthropogenic emissions. These emissions, along with regional and local dust, are often subject to long-range atmospheric transport by westerlies toward the Tian Shan and the Tibetian plateu. Biomass burning is a significant contributor to primary organic carbon emissions (Chen et al., 2022).

The center of the Balkans appears as a source area according to the PSCF for Zagreb and Athens, as well as the Tikhonov regularization solution.

### 3.1.1 The case of Vilnius

In Figure 4 we compare the modeled and measured Secondary Sulfate aerosol concentration at Vilnius with the 1-degree resolution model. We used the result of the Tikhonov regularization when we excluded the data from Vilnius, Dushanbe and Kurchatov to acquire the modeled values. In general we observe good agreement between the modelled and the measurement

https://doi.org/10.5194/acp-2022-843
Preprint. Discussion started: 9 January 2023


Atmospheric Chemistry and Physics Discussions

data. The agreement is not good for very low measured concentration values of Secondary Sulfate. This could be partly attributed to local precipitation episodes that brought significantly more rain than the atmospheric transport model predicted, leading to very low $PM2.5$ concentration values and subsequently low Secondary Sulfate aerosol attribution (i.e. Secondary Sulfate is transported to the site but local precipitation might decrease the aerosol load significantly). July to September are the months with the most precipitation in Vilnius (WMO, 2013). Vilnius station was chosen for the demonstration of the results as it is situated on the edge of the area that the rest of the European stations of the study cover.

### 3.2 Dust aerosol

The first step in order to identify potential source areas was to apply the PSCF analysis on all cities. Meaningful results, in the sense that the indicated potential source areas do indeed emit Dust aerosol, were acquired only in the cases of Athens, Belgrade, Debrecen, Lisbon, Tirana and Zagreb. In Figure 5 the PSCF results for these stations are displayed.

Potential source areas for Athens were North Africa and the Middle East, for Belgrade North-East Africa and the Middle East, for Debrecen Western Africa and the Middle East, for Lisbon Western Africa, for Tirana North Africa and for Zagreb North Africa. The PSCF results for the rest of the stations indicated that their Dust aerosol was mainly of local origin (Dust re-suspension).

In the second step, in order to quantify the Dust aerosol emitted from each geographic grid cell, the Tikhonov regularization was applied to the data from Athens, Belgrade, Debrecen, Lisbon, Tirana and Zagreb, excluding negative values (1,320 measurements were used). In Figure 6 it is apparent that the North-West Africa region was the most important source area and its contribution was quantified. North-East Africa also had a hotspot, but its contribution was significantly lower when the data from these 6 stations are combined.

Stohl et al. (2009), referring to halocarbons, state that small negative "emissions" are not unrealistic in regions remote from industrial sources given that chemical and ocean sinks exist. They also suggest an iteration method so as the sum of all negative emissions is less than 3‰ of the sum of the positive emissions. In our case with the Dust aerosol we allow small negative emission values (-2.5 $g * m^{-2} * s^{-1}$).

## 4 Summary and Conclusions

Source areas of Secondary Sulfate and Dust aerosol were identified and their transport contribution was quantified based on measurements in 16 stations in Europe and Asia.

For Secondary Sulfate, in the case that data from all stations were incorporated, the main source areas for Europe were found to be North Poland, Central Europe, Central and Western Balkans. In Asia, the North-East area of the Caspian Sea was indicated as the most significant source. This result is probably attributed to the fact that measurements mainly in Dushanbe covered this area. The maximum emission rate in the area was as high as 10 $g * m^{-2} * s^{-1}$.

https://doi.org/10.5194/acp-2022-843
Preprint. Discussion started: 9 January 2023

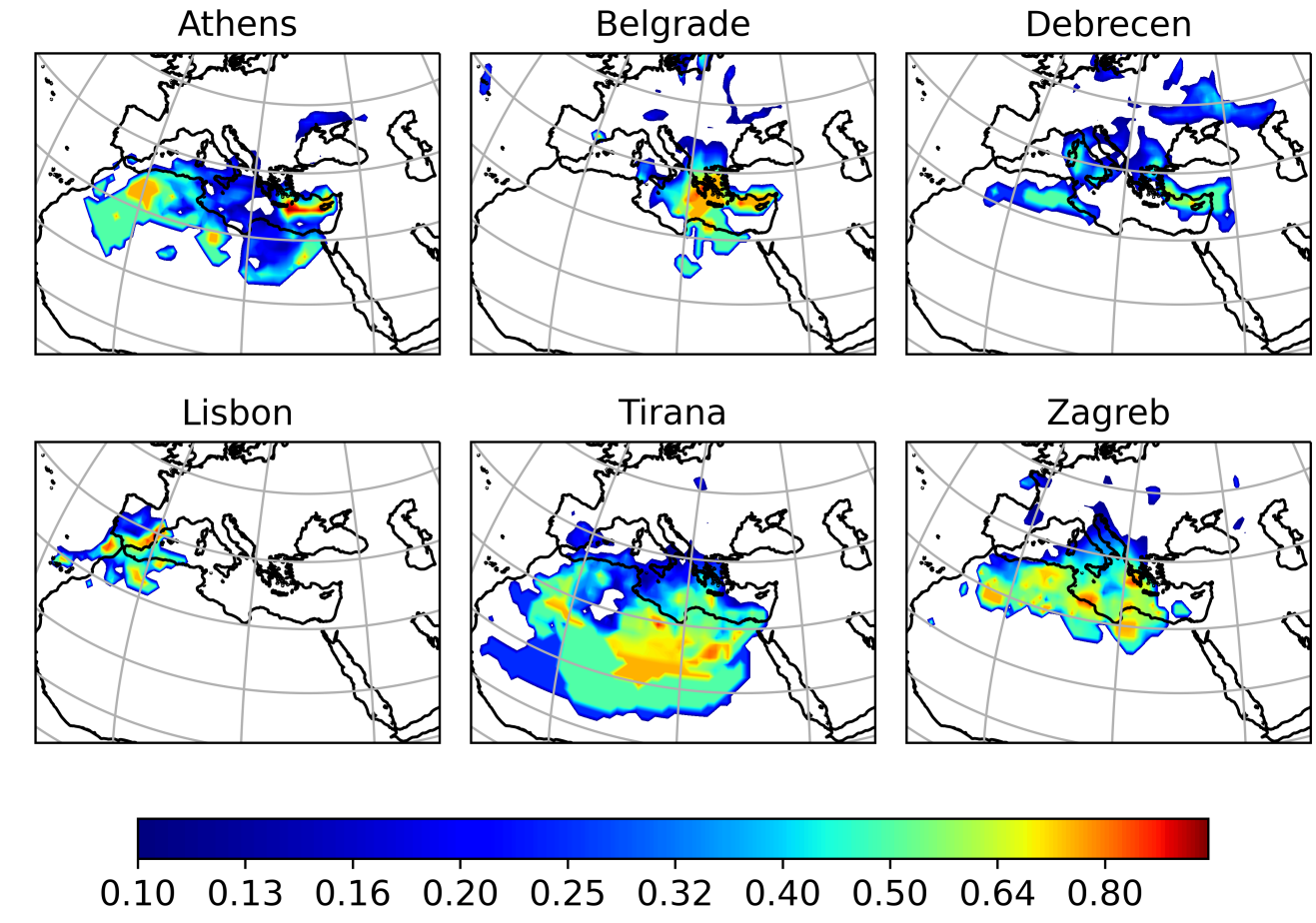
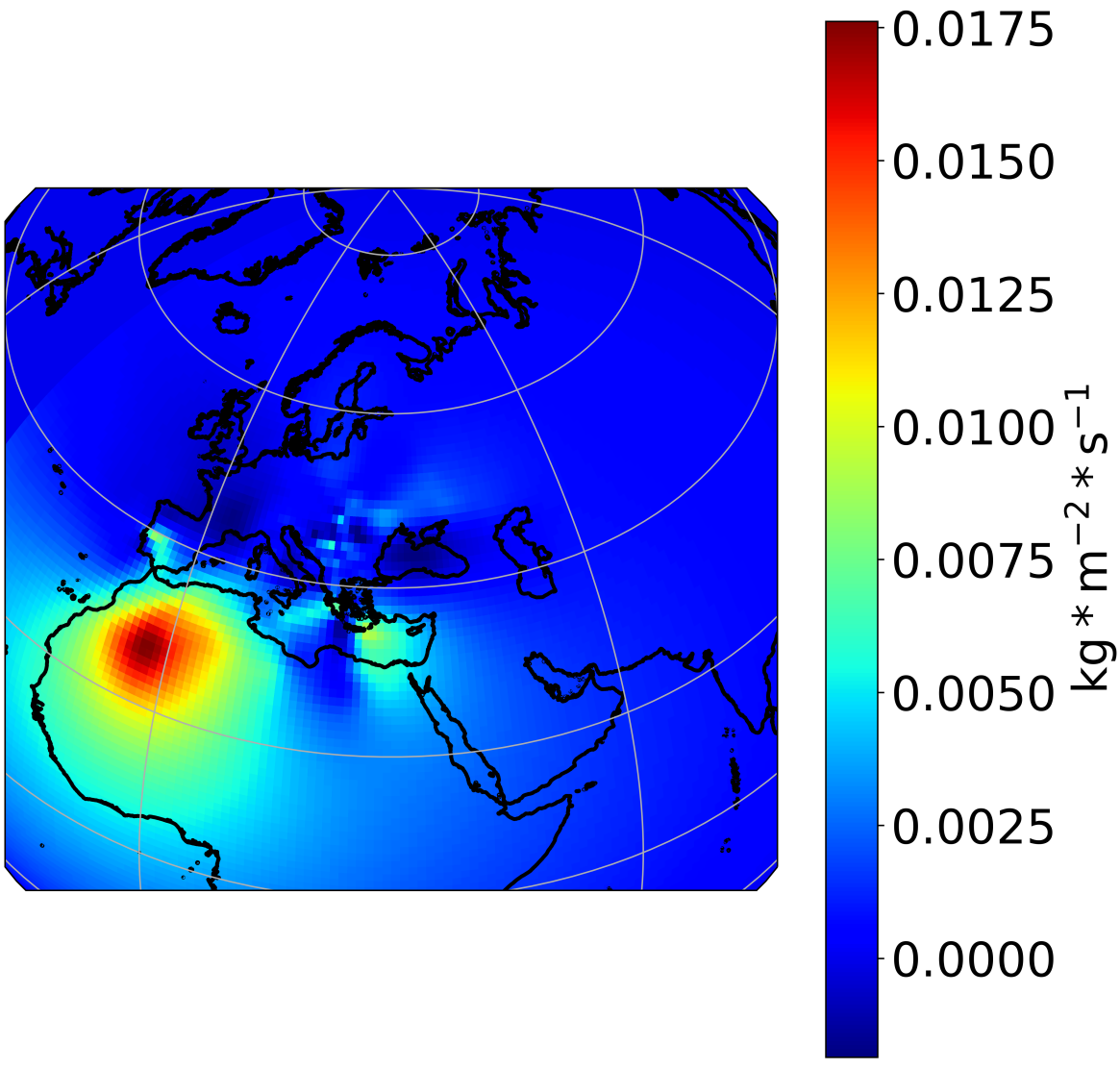




**Figure 5.** PSCF analysis at the $90^{th}$ percentile for Dust aerosol, Athens, Belgrade, Debrecen, Lisbon, Tirana, Zagreb.

The main source area of Dust aerosol for Athens, Belgrade, Debrecen, Lisbon, Tirana and Zagreb was North-West Africa (Sahara dust). There was also evident contribution from the North-East Africa, but significantly lower. The maximum emission rate was as high as 17.5 $g * m^{-2} * s^{-1}$.

When the Tikhonov regularization solution for the Secondary Sulfates emissions was applied (all cities excluding Vilnius, Dushanbe, Kurchatov) to aerosol masses originating from Vilnius, a relatively good agreement was found between the modeled and the measured values. This indicates the robustness of the method, as we can acquire a useful approximation to the concentration of any station for an aerosol species that is mainly transported, based only on measurements conducted in the greater geographic area. That holds even for Secondary Sulfate, an aerosol component that is not emitted as such, but is produced in the atmosphere from precursor gases several hours after their release.

https://doi.org/10.5194/acp-2022-843
Preprint. Discussion started: 9 January 2023


(a) 1° x 1° solution for dust aerosol

**Figure 6.** Dust aerosol Tikhonov regularization, 1° x 1° emmission factors.

https://doi.org/10.5194/acp-2022-843
Preprint. Discussion started: 9 January 2023


Atmospheric Chemistry and Physics Discussions

Further work could include the application of the new method on other aerosol components, like Black Carbon, so as to estimate its emission rates from each geographic grid cell.

*Code availability.* Code will be available upon request

*Data availability.* Data will be available upon request.

## Appendix A: Results

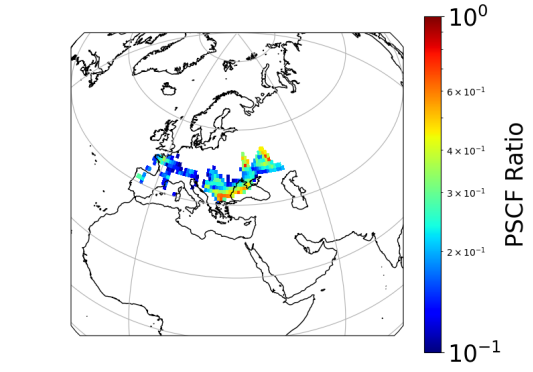
### A1 Secondary Sulfate PSCF, all cities

Banja Luka Secondary Sulfate main origin is the Volga region and Eastern Balkans. Belgrade Secondary Sulfate mainly stems from the Eastern Mediterranean. Chisinau indicates as source the South Balkans and Poland. It also indicates the area in the North-East of the Caspian Sea. Debrecen Secondary Sulfate also stems from the Eastern Mediterranean. Vilnius Secondary Sulfate comes from Ukraine and the Balkans, but we have to keep in mind that we have only 50 measurements. We only have 50 measurements also from Niksic and its PSCF results are not considered statistically significant. Skopje Secondary Sulfate stems from the North of the Balkans and Northern Italy. A source area appears in Africa, but this might be connected to the boundary layer lowering when we have a Sahara dust event. From Sofia we only have 50 measurements, clearly not enough for PSCF analysis. Tirana indicates a transport path from Ukraine and Central Europe. Kurchatov indicates Secondary Sulfate source areas in Siberia, probably related to gas flaring.

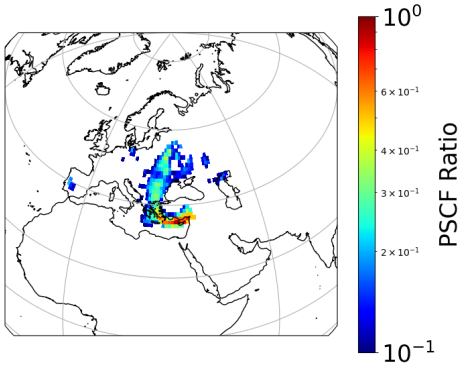
*Author contributions.* SV analysed data, interpreted results, prepared the figures and wrote the text of the manuscript. LD, MM, MA, IB, ZK, LS provided the PMF analysis data and contributed in interpreting results. KE contributed in interpreting results. All authors reviewed the final manuscript.

*Competing interests.* The authors declare that they have no conflict of interest.

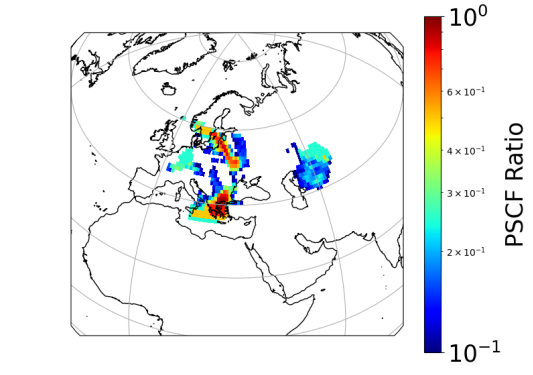
https://doi.org/10.5194/acp-2022-843
Preprint. Discussion started: 9 January 2023

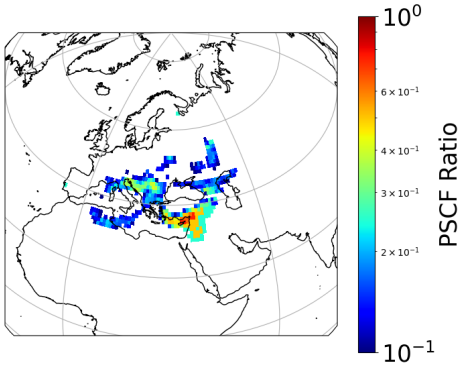

(a) Banja Luka PSCF at the $90^{th}$ percentile for Secondary Sulfate aerosol



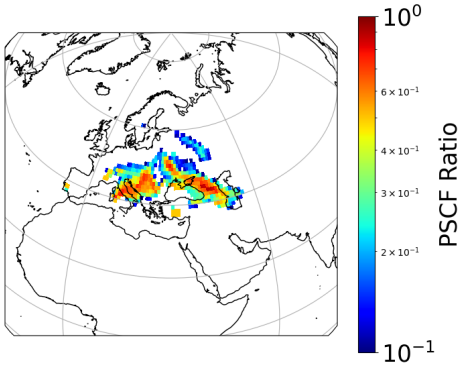

(b) Belgrade PSCF at the $90^{th}$ percentile for Secondary Sulfate aerosol




(c) Chisinau PSCF at the $90^{th}$ percentile for Secondary Sulfate aerosol




(d) Debrecen PSCF at the $90^{th}$ percentile for Secondary Sulfate aerosol



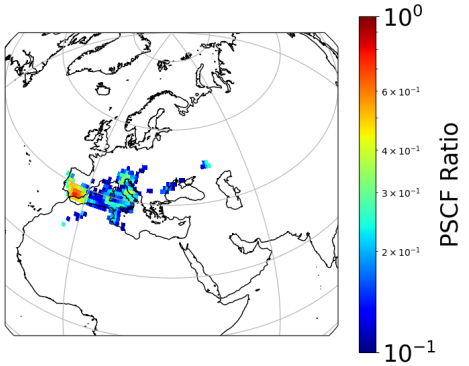

(e) Vilnius PSCF at the $90^{th}$ percentile for Secondary Sulfate aerosol



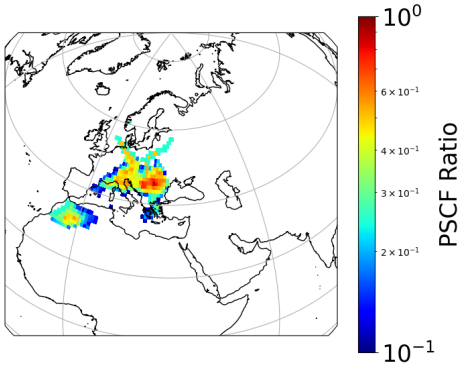
**Figure A1.** PSCF for Secondary Sulfate source, all cities

https://doi.org/10.5194/acp-2022-843
Preprint. Discussion started: 9 January 2023

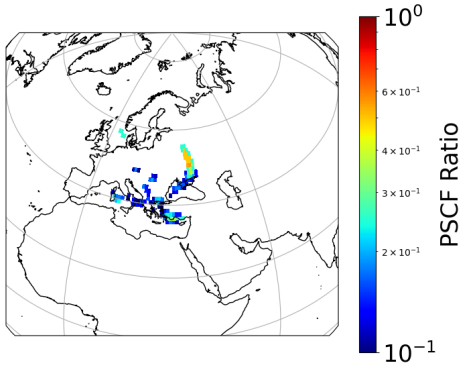

Atmospheric Chemistry and Physics Discussions



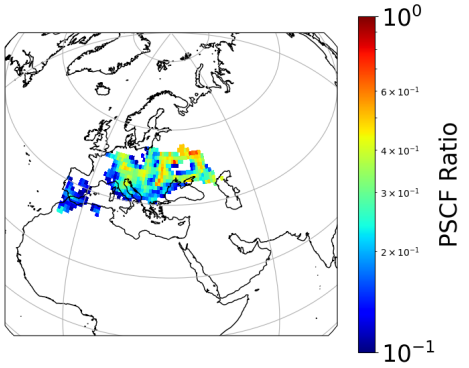

(a) Niksic PSCF at the $90^{th}$ percentile for Secondary Sulfate aerosol



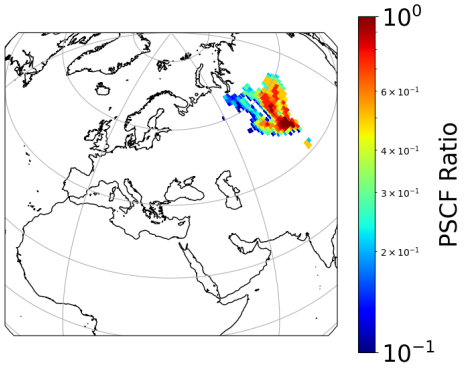

(b) Skopje PSCF at the $90^{th}$ percentile for Secondary Sulfate aerosol




(c) Sofia PSCF at the $90^{th}$ percentile for Secondary Sulfate aerosol




(d) Tirana PSCF at the $90^{th}$ percentile for Secondary Sulfate aerosol




(e) Kurchatov

**Figure A2.** PSCF for Secondary Sulfate source, all cities

https://doi.org/10.5194/acp-2022-843
Preprint. Discussion started: 9 January 2023


Atmospheric Chemistry and Physics Discussions

*Acknowledgements.* This research has been funded by the program “RER/1/015 - Apportioning air pollution sources on a regional scale”, 2016 - 2017. We also acknowledge support of this work by the project “PANhellenic infrastructure for Atmospheric Composition and climatE change” (MIS 5021516), which is implemented under the Action “Reinforcement of the Research and Innovation Infrastructure”, funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund).

https://doi.org/10.5194/acp-2022-843
Preprint. Discussion started: 9 January 2023


Atmospheric Chemistry and Physics Discussions

## References

Almeida, S., Manousakas, M., Diapouli, E., Kertesz, Z., Samek, L., Hristova, E., Šega, K., Alvarez, R. P., Belis, C., and Eleftheriadis, K.: Ambient particulate matter source apportionment using receptor modelling in European and Central Asia urban areas, Environmental Pollution, 266, 115 199, https://doi.org/10.1016/j.envpol.2020.115199, 2020.

Cavalli, F., Alastuey, A., Areskoug, H., Ceburnis, D., Čech, J., Genberg, J., Harrison, R., Jaffrezo, J., Kiss, G., Laj, P., Mihalopoulos, N., Perez, N., Quincey, P., Schwarz, J., Sellegri, K., Spindler, G., Swietlicki, E., Theodosi, C., Yttri, K., Aas, W., and Putaud, J.: A European aerosol phenomenology -4: Harmonized concentrations of carbonaceous aerosol at 10 regional background sites across Europe, Atmospheric Environment, 144, 133–145, https://doi.org/10.1016/j.atmosenv.2016.07.050, 2016.

Chen, P., Kang, S., Zhang, L., Abdullaev, S. F., Wan, X., Zheng, H., Maslov, V. A., Abdyzhapar uulu, S., Safarov, M. S., Tripathee, L., and Li, C.: Organic aerosol compositions and source estimation by molecular tracers in Dushanbe, Tajikistan, Environmental Pollution, 302, 119 055, https://doi.org/10.1016/j.envpol.2022.119055, 2022.

Eleftheriadis, K., Vratolis, S., and Nyeki, S.: Aerosol black carbon in the European Arctic: Measurements at Zeppelin station, Ny-Ålesund, Svalbard from 1998-2007, GEOPHYS RES LETT, 36, 2009.

Gini, M., Manousakas, M., Karydas, A., and Eleftheriadis, K.: Mass size distributions, composition and dose estimates of particulate matter in Saharan dust outbreaks, Environmental Pollution, 298, 118 768, https://doi.org/10.1016/j.envpol.2021.118768, 2022.

Hansen, P. C.: Analysis of Discrete Ill-Posed Problems by Means of the L-Curve, SIAM Review, 34, 561–580, https://doi.org/10.1137/1034115, 1992.

Laden, F., Schwartz, J., Speizer, F. E., and Dockery, D. W.: Reduction in Fine Particulate Air Pollution and Mortality: Extended Follow-up of the Harvard Six Cities Study, Am. J. Respir. Crit. Care Med., 173, 667–672, https://doi.org/10.1164/rccm.200503-443OC, 2006.

Lohmann, U. and Feichter, J.: Global indirect aerosol effects: a review, Atmos. Chem. Phys., 5, 715–737, https://doi.org/10.5194/acp-5-715-2005, 2005.

Manousakas, M., Diapouli, E., Papaefthymiou, H., Kantarelou, V., Zarkadas, C., Kalogridis, A.-C., A.-G., K., and Eleftheriadis, K.: XRF characterization and source apportionment of PM10 samples collected in a coastal city, X-Ray Spectrometry, p. 1–11, https://doi.org/10.1002/xrs.2817, 2017.

Mantas, E., Remoundaki, E., Halari, I., Kassomenos, P., Theodosi, C., Hatzikioseyian, A., and Mihalopoulos, N.: Mass closure and source apportionment of $PM_{2.5}$ by Positive Matrix Factorization analysis in urban Mediterranean environment, Atmos. Environ., 94, 154–163, 2014.

Panteliadis, P., Hafkenscheid, T., Cary, B., Diapouli, E., Fischer, A., Favez, O., Quincey, P., Viana, M., Hitzenberger, R., Vecchi, R., Saraga, D., Sciare, J., Jaffrezo, J. L., John, A., Schwarz, J., Giannoni, M., Novak, J., Karanasiou, A., Fermo, P., and Maenhaut, W.: ECOC comparison exercise with identical thermal protocols after temperature offsets correction – instrument diagnostics by in-depth evaluation of operational parameters., Atmos. Meas. Tech., 8(2), 779–792, 2015.

Park, Y., Reichel, L., Rodriguez, G., and Yu, X.: Parameter determination for Tikhonov regularization problems in general form, Journal of Computational and Applied Mathematics, 343, 12–25, https://doi.org/10.1016/j.cam.2018.04.049, 2018.

Perrone, M. G., Vratolis, S., Georgieva, E., Torok, S., Sega, K., Veleva, B., Osan, J., Beslic, I., Kertesz, Z., Pernigotti, D., Eleftheriadis, K., and Bellis, C. A.: Sources and geographic origin of particulate matter in urban areas of the Danube macro-region: the cases of Zagreb (Croatia), Budapest (Hungary) and Sofia (Bulgaria), Sci. Total Environ., 619-620, 1515–1529, 2018.

https://doi.org/10.5194/acp-2022-843
Preprint. Discussion started: 9 January 2023




Pope, C. A. I. and Dockery, D. W.: Health Effects of Fine Particulate Air Pollution: Lines that Connect, JAPCA J. Air Waste Ma., 56, 709–742, 2006.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, Wiley Interscience, 1998.

Stohl, A., Forster, C., Frank, A., Seibert, P., and Wotawa, G.: Technical Note: The Lagrangian particle dispersion model FLEXPART version 6.2, Atmos. Chem. Phys, 5, 2461–2474, 2005.

Stohl, A., Seibert, P., Arduini, J., Eckhardt, S., Fraser, P., Greally, B. R., Lunder, C., Maione, M., Mühle, J., O'Doherty, S., Prinn, R. G., Reimann, S., Saito, T., Schmidbauer, N., Simmonds, P. G., Vollmer, M. K., Weiss, R. F., and Yokouchi, Y.: An analytical inversion method for determining regional and global emissions of greenhouse gases: Sensitivity studies and application to halocarbons, Atmospheric Chemistry and Physics, 9, 1597–1620, https://doi.org/10.5194/acp-9-1597-2009, 2009.

Tikhonov, A. N., Goncharsky, A. V., Stepanov, V. V., and Yagola, A. G.: Numerical Methods for the Solution of Ill-Posed Problems, https://doi.org/10.1007/978-94-015-8480-7, 1995.

Valentine, A. P. and Sambridge, M.: Optimal regularization for a class of linear inverse problem, Geophysical Journal International, 215, 1003–1021, https://doi.org/10.1093/gji/ggy303, 2018.

Viana, M., Chi, X., Maenhaut, W., Cafmeyer, J., Querol, X., Alastuey, A., Mikuška, P., and Večeřa, Z.: Influence of Sampling Artefacts on Measured PM, OC, and EC Levels in Carbonaceous Aerosols in an Urban Area, Aerosol Science and Technology, 40, 107–117, https://doi.org/10.1080/02786820500484388, 2006.

Vratolis, S., Fetfatzis, P., Argyrouli, A., Papayannis, A., Muller, D., Veselovskii, I., Bougiatioti, A., Nenes, A., Remoundaki, E., Diapouli, E., Manousakas, M., Mylonaki, M., and Eleftheriadis, K.: A new method to retrieve the real part of the equivalent refractive index of atmospheric aerosols, Journal of Aerosol Science, 117, 54–62, 2018.

Wesseling, J., Pisoni, E., Guevara, M., Janssen, S., Tarrason, L., Clappier, A., Thunis, P., Guerreiro, C., Pirovano, G., González Ortiz, A., Monteiro, A., and Belis, C.: Recommendations regarding modelling applications within the scope of the ambient air quality directives, European Commission Joint Research Centre, https://doi.org/10.2760/819240, 2019.

WMO: World Weather Information Service-Vilnius, Wikipedia, 2013.