Anonymous referee #2

General comments

The paper "A new method for the quantification of ambient particulate matter emissions" by Vratolis et al. investigates an inverse method based on receptor and back trajectory models to identify and quantify the distribution and intensity of dust and sulfate emission sources.

The paper is well written, with concise and clear statements, and it does not require any substantial review of syntax and language.

The paper content fits the scope of ACP, however at this stage is not suitable for publication due to several major issues that need to be addressed.

The authors are grateful for all the reviewer's comments and suggestions.

The corresponding author would like to state the following:

There was an error in the units of the emission fluxes from each grid cell.

We will correct this in the manuscript and the deducted emission maps.

Our answers on your questions follow in italics:

In particular:

1. The authors introduce an optimization function they apply to define the matrix of emission density (called "x"), but the discussion about the choice and the robustness of the solution is totally missing

A very similar optimization function has been used in Stohl et al, (2009) paper with the title: "An analytical inversion method for determining regional and global emissions of greenhouse gases: Sensitivity studies and application to halocarbons".

The robustness of the method is displayed when we examine Figures 3a and 3b: When we use data from Kurhatov, Dushanbe and Vilnius stations, the result for the European area is almost identical to the result when we include all cities. The only difference is the area East of the Caspian Sea, which is quite distant from the cities in Europe. Since the residence time of Secondary Sulfate in the atmosphere according to Seinfeld and Pandis (1998) is 80 hours and usually the prevailing winds are westerlies, the European cities in the study cannot identify these emissions. In Figure 3c where the

result for Zagreb is displayed, similarities to Figure 3b are apparent (area in NE Europe, West and Central Balkans), but due to the fact that we have less measurements and only one station the result lacks specificity.

We will also add the Tikhonov regularization emission fluxes maps for Secondary Sulfate for 14 cities during winter and summer. In summer the hotspot east of the Caspian Sea almost disappears, indating that these emissions probably relate to heating. In South Poland the hotspot is significantly reduced. Hotspots on Western and Central Balkans appear to have similar values in winter and summer, indicating that they possibly originate from power plants.

We will also add the comparison between Tikhonov regularization modeled Secondary Sulfate concentrations in relation to measured ones.

2. The optimization formula seems reasonable for non-reactive pollutants, but it is not clear if the simple approach A*x = b can be applied also for reactive pollutants like SO$_2$ producing sulphate through chemical reactions

In this method we follow the Secondary Sulfate aerosol species concentration at each station backward in time and try to locate the area that it originated from. In the mid latitudes, Seinfeld and Pandis (1998), page 66, report a residence time for Secondary Sulfate of 80 hours and a residence time for SO$_2$ of 25 hours. That means that our approach is on average correct for most of the travel time of the emitted Sulfur that is within the SO$_2$ at the beginning and Secondary Sulfate aerosol later.

We will add in the manuscript in the FLEXPART description, line 83:

In the case of Secondary Sulfate, we have to keep in mind that SO$_2$ is the primary emitted species and Secondary Sulfate is produced in the atmosphere through chemical reactions in gas and liquid phase. In order to calculate the uncertainty that this error induces to the calculated footprint, we refer to residence times in the atmosphere reported by Seinfeld and Pandis (1998), page 66. The SO$_2$ mean residence time reported due to dry deposition is 60 hours, its residence time due to wet deposition is 100 hours, and its residence time due to transformation to Secondary Sulfate is 80 hours. The resulting SO$_2$ residence time due to wet and dry deposition is 37.5 hours, while if we also include the transformation to Sulfate the overall mean residence time is 25 hours. The corresponding wet and dry deposition residence time indicated for Secondary Sulfate is 80 hours. Therefore, in such a case, SO$_2$ deposits (wet and dry deposition) twice as fast as Secondary Sulfate. These calculations correspond to the mid-latitudes (45°-65° North) according to Rodhe et al. FLEXPART model is provided with a Secondary Sulfate aerosol particle size distribution and it compensates for wet and dry deposition as it follows the species backward in time. The error in the calculation of the residence time in each geographic grid cell is mainly due to not accounting for the enhanced deposition of SO$_2$ for 1-2 days just after emission. But this enhanced wet and dry deposition for SO$_2$ should be applied only for a small fraction of the travel time. The mean error in residence time due to this discrepancy is expected to be close to 10%.

We also have to keep in mind that we do not present emission fluxes of the SO$_2$ emissions, but the origin of Secondary Sulfate aerosol measured at each station, if it was produced as such in the emitting grid cell. Therefore we report the combined effect of SO$_2$ emissions, air mass transport and environmental conditions that produce the Secondary Sulfate aerosol measured in the stations participating in the study. That is why the authors believe that we cannot apply the fluxes derived to

very distant measurement stations, whose environmental conditions might be very different from the stations in the study. Also, the estimated error is calculated based on values derived for the mid-latitudes.

3. The validation of the obtained results is limited to one species and one site, while it should be extended to both pollutants and a significant number of sites

Sulfate or Dust concentration at each measurement station is due to local production and long range transport. With Tikhonov regularization we aim not to perfectly reconstruct the concentrations measured at each station, but find x in the equation b = A x, where b is the concentration measured at each station (local and long range transport aerosol), A is the residence time matrix for each grid cell and x the emissions map. A corresponds to the part of the concentration that is transported to the site from other grid cells. Therefore, we expect that during the Tikhonov regularization procedure, while we search for b_{exact}, local aerosol will be attributed as noise and we will recover the correct x (emission map). We also have the problem of different uncertainty levels at each station due to the variations to the methodologies and materials used.

We have plotted the regularization solution predicted to measured values for all sites participating in the study. For secondary sulfate R^2 is low, the slope is approximately 0.3 and the intercept is approximately 3 μg/m^3.

For Dust aerosol the slope is 0.3, the intercept is approximately 0.5 μg/m^3 and R^2 is 0.33.

We will add in the manuscript in the Results sections for Secondary Sulfate and Dust:

When we compare the result of the regularized solution for Secondary Sulfate using data from 14 cities to measured values at each station (Figure 5b), the agreement is not good. This could be partly due to the fact that air mass transport cannot account for the locally produced aerosol (i.e. Secondary Sulfate aerosol produced within the same grid cell and very close to the measurement station will have short residence time in the cell and high impact on the measured value)

4. Beyond these major concerns, authors should also:

Better clarify the relationship *between PSCF and matrix A, in terms of both definition and use*

We will add in the manuscript (section 2.3, Tikhonov regularization):

In our particular case, each row of A matrix corresponds to FLEXPART model sensitivity (residence time in each grid cell) for each filter measurement, and each column of A matrix corresponds to a specific geographic grid cell sensitivity for all filter measurements. b corresponds to the actual species mass concentration for each filter, while x is the emission flux from each geographic grid cell. In other words we try to extract information associated to residence time in each grid cell for each filter measurement.

We will also add in the manuscript (section 2.5, Potential source contribution function (PSCF)):

We apply the PSCF analysis for each measurement station and each aerosol species. The information that we use is the overall residence time for all filters in each station (n_{ij}) and the overall residence times in each grid cell for the filter measurements with the highest Secondary Sulfate or Dust aerosol concentrations (m_{ij}). In other words we extract information from the sum of residence times of all filters and the sum of residence times for filters with the highest concentration (90th percentile).

Check the terminology, particularly when referring to "source" and "concentration"

We will add in the manuscript at the end of the Introduction section:

From now on, we refer to "source apportioned concentration by PMF" as "concentration" and to "geographic grid cell source areas emission fluxes" as "emission fluxes".

There are also a several specific comments that should be addressed, that are listed below.

Specific comments and Technical corrections

P2 R48 - Does the concept of "smooth solution" require additional details?

We will add in the Tikhonov regularization section:

A smooth solution is obtained when the L matrix requires that the difference between two neighboring cells is minimum. In other words, when the regularization matrix L is the first-order discrete derivative operator, it imposes smoothness on the solution (M. Donatelli et al, 2013).

P2 R50 - To which grid do authors refer at this point of the article?

The grid for Dust and Secondary Sulfate aerosol is 1° x 1°.

P3 R70 – Is the "residence time" a property of each cell particle? Does it represent the time elapsed by each air parcel over each grid cell?

Yes, they represent the time spent by the air parcels over each grid cell. Each 3 hours 40000 air parcels are released from each measurement station and are followed backward in time for 20 days. The residence time for each of these air parcels over each grid cell is calculated. Then the average is taken for all air parcels for each grid cell. This is the sensitivity for each 3 hours. We then sum these 3-hour sensitivities so as to correspond exactly to each filter sampling time.

We will add in the manuscript, in section 2.2 Flexible Particle Dispersion Model (FLEXPART):

The residence time for each of these air parcels over each grid cell is calculated. Then the average is taken for all air parcels for each grid cell. This is the sensitivity for each 3 hours. We then sum these 3-hour sensitivities so as to correspond exactly to each filter sampling time.

P3 R75 – How is the pollution concentration associated to each air parcel?

The sum for all grid cells of the {residence time in each grid cell (seconds) multiplied by the emissions in the grid cell (kg/(m^2*seconds)) divided by 500 m (this is the height up to which we sum the residence time of each air parcel)}= concentration measured at station (kg/m^3)

The pollution concentration in each air parcel is linearly related to residence times and emissions

This is the forward problem.

We will add this in the manuscript in section 3.1 (Secondary Sulfate aerosol) as equation 5, in order to calculate model concentrations based on emission fluxes derived by Tikhonov regularization.

P3-Figure 1 - What are the urban and suburban stations?

Ankara and Belgrade stations are reported as suburban background by Almeida et al, 2020. Ankara station data are not used in the study, while Belgrade station data are used in both Secondary Sulfate and Dust aerosol analysis.

We will add in the manuscript in section 2.1 PM sampling stations and filter analysis:

Ankara and Belgrade stations are reported as suburban background by Almeida et al, 2020, while all other stations are reported as urban background.

P5 R105-7 - What do "m" and "n" refer in this application?

In lines 129-130 we write:

m_{ij} is the sum of residence times (sensitivity) in a cell for concentrations higher than the 90th percentile and n_{ij} is the sum of residence times for all measurements.

P6 R128 – are i and j the grid cell indexes?

Yes, indexes corresponding to latitude and longitude of a grid cell.

We will add in the manuscript in section 2.5, Potential source contribution function (PSCF):

Indexes i,j correspond to latitude and longitude of each grid cell.

P6 R129 – When the authors state: "for concentrations higher than the 90th percentile" do they refer to air parcels generated in days with observed concentrations at the receptor higher than the 90th percentile?

We will add in the manuscript, in section 2.5 Potential source contribution function (PSCF):

where m_{ij} is the sum of residence times (sensitivity) in a cell with observed concentrations at the receptor higher than the 90th percentile

P6 R130-133 – The role and the use of the weight matrix is not clear

Polissar et al, 2001 report:

Since the PSCF is computed as a ratio of the counts of selected events (m_{ij}) to the counts of all events (n_{ij}), it is likely that relatively small mi_j ($<ni_j$), which are often related to sparse trajectory coverage of the more distant grid cells, may result in PSCF$_{ij}$ with high uncertainty in the apparent high value. For large values of n, there is more statistical stability in the calculated value. Thus, to reduce the effect of small values of n_{ij}, an arbitrary weight function $W(n_{ij})$ is multiplied into the PSCF value to better reflect the uncertainty in the values for these cells.

We will add in the manuscript in section 2.5 Potential source contribution function (PSCF):

Grid cells with very small residence time may result in PSCF with high uncertainty in the apparent high value. For large values of n_{ij}, there is more statistical stability in the calculated value. Thus, to reduce the effect of small values of n_{ij}, an empirically determined weight matrix is multiplied into the PSCF value to better reflect the uncertainty in the values for these cells (Polissar et al, 2001).

P6 R143 – The term "source" referred to Secondary sulfate detected with PMF analysis is misleading because it refers to a concentration not to a source. Maybe it could be referred as "source contribution to secondary sulfate concentration"

We will add in the manuscript at the end of the Introduction section:

From now on, we refer to "source apportioned concentration by PMF" as "concentration" and to "geographic grid cell source areas emission fluxes" as "emission fluxes".

P6 R151-152 – The term "source" is used again to indicate a contribution to concentration, I would suggest to thoroughly check the terminology

Same as previous point.

P7 R160 – The comparison between Figure 1 (a) and (d) should be expressed with harmonized units

We added OMI-HTAP (EMISSIONS 2015 for SO$_2$) as suggested by referee #1. We will display in the manuscript the OMI-HTAP emission map in kgm^2*s^{-1} in Figure 3.*

P9 R176 – How is computed the modeled concentration? applying the FLEXPART model forward in time?

Model concentration(kg/m^3) = residence time in each grid cell (seconds) * emission map deducted by Tikhonov regularization (kg/m^2*s^{-1}) divided by 500 m (height we consider relevant for emissions to take place)

We will add in the manuscript how this is produced (equation 5).

We state in lines 78-79:

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.

P10 R190 – why do authors state that dust is mainly of local origin? PSCF results in figure 5 seem to indicate a relevant role of long range transport (i.e. from Sahara)

We state in line 191: The PSCF results for the rest of the stations indicated that their Dust aerosol was mainly of local origin (Dust re-suspension). We refer to stations (Ankara, Dushanbe, Vilnius, Krakow, Kurchatov, Banja-Luka, Chisinau, Niksic, Skopje, Sofia) whose PSCF analysis was not presented in the manuscript and does not indicate origin from a known Dust aerosol source.

We will add the names of the cities to the manuscript in section 3.2 Dust aerosol (Ankara, Dushanbe, Vilnius, Krakow, Kurchatov, Banja-Luka, Chisinau, Niksic, Skopje, Sofia). We will add the PSCF analysis for these cities as appendix A.4

P10 R198-201 This statement is rather surprising considering that dust is non-reactive, therefore it is difficult to accept that "negative emissions" could be considered an acceptable solution

Negative emissions could represent deposition velocity that is underestimated - especially in the beginning - by the FLEXPART deposition scheme. Also, this is due to inaccuracies in model and data

We will add in section 3.2 (Dust aerosol):

Stohl et al. (2009), referring to halocarbons, state that inaccuracies in model and data will in general cause their method to find solutions containing unrealistic negative emissions that are larger than expected. In the linear framework this cannot be prevented directly as positive definiteness is a nonlinear constraint. 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 * 10^{-12} kg*m^{-2}*s^{-1}) representing higher deposition velocities than calculated by the FLEXPART deposition scheme.

References:

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