We would like to thank the reviewer for their comments that helped to improve the manuscript. Hereafter, we have responded to the various comments. Some of the comments were directly answered within the text of the manuscript and the modified text is reproduced below in quotation marks.

Reviewer #2: Source Apportionment of PM2.5 in Montreal, Canada and Health Risk Assessment for Potentially Toxic Elements.

This work dealt with an analysis of PM2.5 collected in a sampling campaign that lasted roughly 3 months (actually 80 days) in Montreal, a populous city in Quebec, Canada. The analysis involved factor analytical source apportionment with positive matrix factorization, use of enrichment factors, a chemical transport modelling exercise with GEOS-CHEM and a health risk assessment of components of the sampled PM. The authors make some statements either implicitly or explicitly that can be considered as the main results/conclusions of the work:

1. Their chemical analyses are an exhaustive characterization of PM2.5. By contrast, the analyses done by Environment Canada within the National Air Pollution Surveillance (NAPS) framework is inadequate in fully characterizing the organic species in PM2.5.

2. The inclusion of their chosen tracers helps them identify and distinguish certain factors in their PMF analyses. Implying that these factor identifications would not have been possible/successful otherwise for the 11 factors found.

3. Certain factors with low mass are likely more critical from their health risk analyses perspective. Thus, implying that reductions in PM2.5 mass concentrations do not necessarily translate to healthier air quality.

4. Their GEOS-CHEM analyses results for SOA, ammonium sulphate and 'Dust in PM2.5' are said to show that SOA and ammonium sulphate have substantial origins in the US. 'Other' sources dominate the 'Dust in PM2.5'.

To start, the chemical analyses is not a complete characterization of particulate organic matter. Thus, to suggest that this study in some way improves on the NAPS method for organic PM is a stretch. There are entire compound classes of organic compounds that are missing in the proposed approach ranging the entire gamut of non-polar to polar compounds. Also, the practicality of perpetually running a chemical laboratory for exhaustive characterization of all organic compound

classes for air monitoring locations across an entire country is glossed over by the authors likely due to the fact that this study is an intensive 90-day sampling campaign, where it may be possible to analyze some more compounds than the standard NAPS protocol. There is always a trade-off between the frequency of analyses and how many components can be reliably analyzed. For long term monitoring, determining all organic particulate matter components is unrealistic for analytical laboratories, even if it is feasible for short-term campaigns such as this study of 80 near-consecutive days.

Answer: We agree with the reviewer that it is not feasible to perform an exhaustive chemical characterization of PM within the framework of a regular monitoring program. The aim of this study is to suggest adding one more instrument on top of the analyses already done by Environment Canada within the National Air Pollution Surveillance (NAPS) program, namely gas chromatography-mass spectrometry (GC-MS) to identify a small subset of organic tracers in $PM_{2.5}$. We are only proposing a few organic tracers that are particularly useful in source apportionment studies for better PMF results. Therefore, we entirely agree with the reviewer that for long term monitoring, determining all organic PM components is unrealistic for analytical laboratories, however, we are pushing towards determining some organic tracers.

Many articles in the literature are using PMF with little or no information on the organic composition of $PM_{2.5}$ (Alwadei et al., 2022; Lee et al., 2022; Han et al., 2022; Diao et al., 2022; Camilleri et al., 2022; Guo et al., 2021; Duan et al., 2021; Manousakas et al., 2020; Zhang et al., 2020; Park et al., 2019; Soleimanian et al., 2019; Galon-Negru et al., 2019; Luo et al., 2018). A smaller number of PMF studies have focused on organic molecular markers (Gadi et al., 2019; Shivani et al., 2019; Williams et al., 2010; Gupta et al., 2018) or combined both organic and inorganic tracers (Lu et al., 2018; Wong et al., 2019; Lv et al., 2021). In Canada, the NAPS program only provides data on organic compounds that can be measured by ion chromatography, which limits the available measurements to a small subset of polar organic compounds.

While performing PMF analysis with only organic species is valuable for understanding OA chemistry, it neglects important sources that largely contribute to the PM mass such as secondary sulfate, secondary nitrate, sea salt and crustal dust due to the absence of a specific organic tracer. On the other hand, performing PMF analysis without organic

species results, or only a few polar organics, not only in over- and underestimates some sources but also neglects some sources (Wang et al., 2019; Fakhri et al., 2023). This source apportionment study, which examined the main contributing sources to PM$_{2.5}$ using a larger suite of organic molecular markers than other Canadian studies, is the first of its sort in Canada. A focus of this study was on quantifying previously unresolved sources of PM$_{2.5}$ through the inclusion in the PMF analysis of additional organic molecular markers beyond those measured typically by the Canadian government's National Air Pollution Surveillance Program (NAPS). The organic species included in the PMF model from the GC-MS analyses were namely, 6 n-alkanes, 2 fatty acids, 1 dicarboxylic acid, 2 biogenic secondary organic aerosols (SOA) tracers and hopane. In this paper, we are demonstrating that having a small set of speciated organic tracers included in PMF input matrices would be beneficial for understanding the sources of PM$_{2.5}$ in Canada. We would kindly suggest that their identification by GC-MS within the NAPS program would not be an unreasonable expansion of the program. Even if GC-MS measurements were performed for a subset of NAPS stations and a subset of days (e.g., once in 6 days), which would lessen the burden on the NAPS program, such data could be included in future PMF analyses.

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Moreover, the determination of organic carbon is sufficient to account for about or more than half the mass of particulate organic matter. The prescribed remedy proposed by the authors wherein some organic compounds are individually determined is also flawed from a mass balance perspective since it leads to double-counting of organic carbon mass. Their remedy cannot be considered an exhaustive analysis of particulate organic matter but is neither insignificant enough to be harmless to an overestimation of organic mass.

Answer: In the literature, mass closure is a simple model that is also applied to identify source contributions (Taiwo, 2016; Mantas et al., 2014; Genga et al., 2017; Geng et al., 2013; Chow et al., 2015; Huang et al., 2014; Cesari et al., 2018). This method allocates PM mass to sources based on types of species. For example, the contribution of crustal matter is estimated by summing the concentrations of aluminum, silicon, calcium, iron, and titanium in their oxide forms (Huang et al., 2014). Another example is the contribution of sea salt that is calculated by summing the six major ions (Sciare et al., 2005; Fakhri et al., 2023). In PMF, source identification is based on the chemical profile (e.g., high percentages of speciated tracers, ratios of one species to another such as OC/EC or V/Ni) whereas in mass closure, the species are totally attributed to a specific source. Fe is for example attributed to crustal dust in mass closure. However, PMF can allocate Fe to different factors which emit Fe such as desert dust, resuspended dust or industries (Lv et al., 2021; Acciai et al., 2017; Galon-Negru et al., 2019; Ho et al., 2018; Saraga et al., 2019). All of this is based on the chemical profile of the source which is verified through comparison with the literature.

Source profiles or chemical fingerprints refer to the average relative chemical composition of the PM deriving from a pollution source (Pernigotti et al., 2016). Several source profile databases have been created across the globe and have been compiled in the United States Environmental Protection Agency (USEPA) SPECIATE database and a European database (SPECIEUROPE). To determine the chemical source profiles, the literature has focused on specific chemical fractions or species. Although the markers are not uniquely linked with emission sources, the chemical profiles play the major role of identifying the factors.

Not all the analyzed compounds (total number of 61) could be added in the PMF model given the recommended ratio of samples to tracers of 3-to-1 (Belis et al., 2019). Thus, only selected speciated organic and inorganic species were included. Moreover, not all organic species are source markers. To select the species included in the PMF analysis, it is important to have some initial knowledge of potential sources in the studied area. Then one can use the sources' chemical profiles that can be found in the European and

American databases as well as the literature to select appropriate tracers for the PMF analysis.

In this study, the potential sources identified qualitatively (e.g., via correlations of elements) guided us in the selection of tracers to include in the PMF analysis. Many recent articles in the literature include OC, EC and organic tracers as inputs in PMF, and there is no reason this practice would lead to an overestimation of organic mass (Lv et al., 2021; Galvao et al., 2019; Gupta et al., 2018; Wong et al., 2019; Kang et al., 2018; Lu et al., 2018; Fadel et al., 2023).

The reconstructed $PM_{2.5}$ mass (m_{chem}) using the mass closure method is defined as the sum of organic matter (OM), EC, crustal matter, sea salt, secondary inorganic aerosol (SIA), and other elements that are not taken into account as minerals (Chow et al., 2015). Thus, the mass closure analysis does not include the organic molecular tracers since that mass is already accounted for by the OC measurements (and Conversion Factor). Thus, we respectfully conclude that our approaches do not lead to overestimation of the organic mass, contrary to what is suggested in the comment above.

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Confidence in the PMF analysis itself is very low. The slope in Figure S2 shows that at any given time, their PMF analysis accounts for only 18% of observed PM2.5 mass. The authors have focused solely on the R2 metric but failed to realize that the sum of factors must account for 80 − 100 % of the measured mass (as seen from the slope) for the apportionment to be considered relevant. Based on this fact alone, this work should not be published.

Answer: We would like to thank the reviewer for pointing out the error we made by adding the incorrect figure to the text. We are aware that R^2 and slope are essential, and we have

revised the figure in the supplementary information. In this study, the R^2 between the reconstructed and measured PM2.5 mass was 0.87 and the slope was 0.90, which conforms to the requirements suggested by the reviewer.

To discuss the extra factor identities found in this work, it is always the case that the more disparate variables added in the input matrix, the more factors will be resolved. The challenge that arises though is establishing the linkage between 'factor' and 'source'. There is nothing in this work that goes the extra step to establish the actual sources of these novel factors that the authors claimed would not have been found without their analytical method. No attempts were made at showing temporal trends or spatial apportionments. How can it be conclusively shown that some of these new factors do not represent factor splits? Plant wax, biogenic SOA may in fact be an overextraction of the same factor that has now been split into two separate factors.

Answer: The authors understand the point of view of the reviewer regarding the number of factors identified by PMF. However, many recent articles that have included both inorganic and organic species in PMF have found similar results (Fakhri et al., 2023; Lv et al., 2021; Fadel et al., 2023). Generally, we think that the number of sources identified is reasonable based on three findings: (1) the number of sources identified in previous studies is consistent with the PMF analysis in the present manuscript, (2) the source profiles of the factors are similar to previously published profiles, (3) the mode results has little rotational ambiguity.

> *The number of sources identified in previous studies is consistent with the PMF analysis in the present manuscript.*

Many of the organic compounds we have selected for inclusion in the PMF model are well-known source tracers, and thus it is highly likely that they will improve the factor separation and therefore necessarily increase the number of identified sources. The literature usually presents source apportionment of PM2.5 with carbonaceous matter (EC and OC) and levoglucosan as the only input data for carbonaceous and organic matter (Achilleos et al., 2016; Hassan et al., 2021; Ikemori et al., 2021; Kim et al., 2018; Theodosi et al., 2018; Yu et al., 2019). The number of identified sources in these cases varies between 6 and 9 factors. Furthermore, papers found in the literature presenting source

apportionment studies using only organic compounds led to the identification of 5 to 7 sources (Esmaeilirad et al., 2020; Gadi et al., 2019; Gupta et al., 2018). Therefore, if it is possible to identify 6 to 9 factors using almost no data on the organic composition of PM and up to 5 to 7 factors using no data on the inorganic fraction of PM, it is this reasonable to expect that the sum of these ranges, 11 to 16 factors, would be achievable when including organic and inorganic tracers. This is a very rough estimation assuming that the organic and inorganic tracers provide orthogonal information on PM sources, but nonetheless, one can see that the 11-factor solution presented in this study is consistent with the number of factors identified in previous work. In other words, some sources can only be resolved by PMF by adding organic markers for sources such as cooking emissions, plant wax emissions, biogenic secondary organic compounds, diesel combustion, gasoline combustion, etc. In our case, the organic markers helped us resolve 5 additional factors in addition to 6 factors identified based on inorganic tracers, which is entirely consistent with number of factors in the studies cited above.

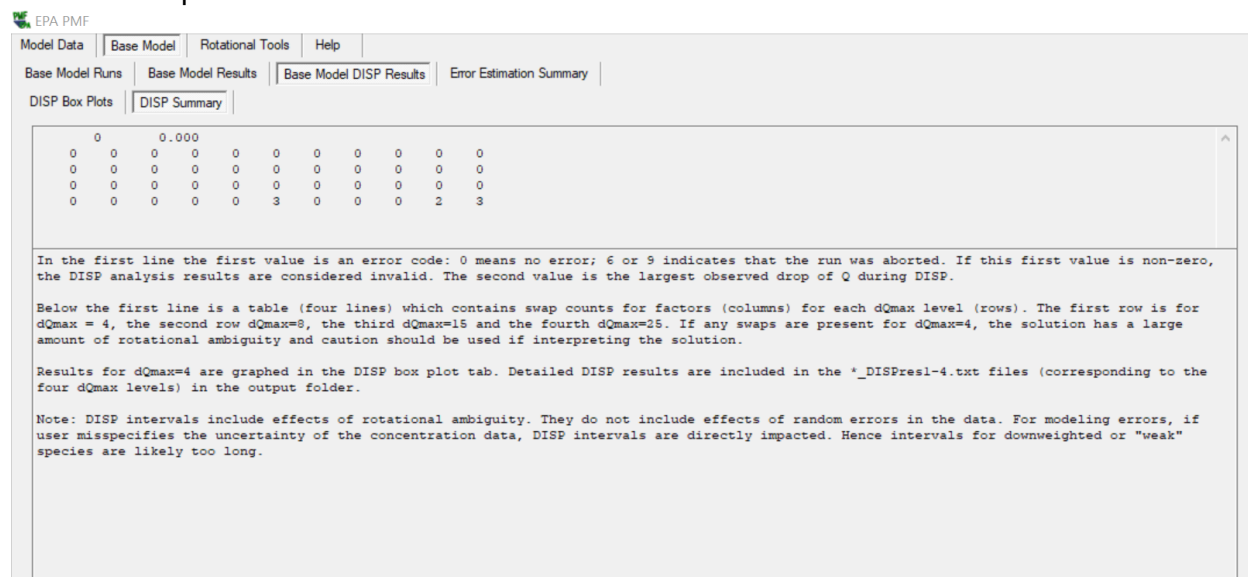> ### *The source profiles of the factors are similar to previously published profiles.*

We acknowledge that the assignment of specific sources to the obtained PMF factors is performed mainly through the factor chemical profiles and the presence of well-known tracers. In particular, factor identification was confirmed by comparison with source profiles available in the literature and in the SPECIEUROPE European database (Pernigotti et al., 2016). The cooking emissions factor for example was identified based on the contribution of hexadecanoic and octadecanoic acids. These carboxylic acids have been used in source apportionment studies to distinguish cooking activities (Gadi et al., 2019; Lv et al., 2021; Fadel et al., 2023) (line 460-463). Another example is the marine factor which was characterized by the ions Na^+, Cl^- and NO_3^-, as well as a Cl^-/Na^+ ratio below 1.8, a profile comparable to Petit et al. (2019) (line 449-451). The plant wax profile was identified by high loading of C27 and C20; which is similar to Fadel et al. (2023). The SOA factor was distinguished with high loading of oxalic acid, similar to Petit et al. (2019). Biomass burning was identified by high loadings of levoglucosan and an OC/EC ratio consistent with biomass burning (Fadel et al., 2023). Thus, the comment of the reviewer

was taking into consideration and these references to a similar profiles from the literature were added in the manuscript.

➢ **The model result has little rotational ambiguity**

The robustness of the PMF solution was tested by the two-error estimation method (bootstrap and displacement) as instructed in the PMF manual to ensure the solution was stable (USEPA, 2014). Of particular relevance to the reviewer's comment above, displacement (DISP) is an analysis method that helps the user understand the effects of rotational ambiguity and explores the rotational ambiguity of the solution by assessing the range of source profiles with a given increase in the Q-value (USEPA, 2014; Paatero et al., 2014). As also presented in the supplement, Table 1 below contains swap counts for the 11 factors (columns in Table 1) for several dQmax levels (rows) where dQmax is the maximum increase in Q. The second row is for dQmax = 4, the third row dQmax=8, the fourth dQmax=15 and the fifth dQmax=25. The swap counts indicate when two factors exchange identities in the PMF solution and are a key indicator of the stability of a PMF solution. Factor swaps result in the same physical model as the original solution, but the presence of factor swaps means that all intermediate solutions (i.e., mixing of two factors) must be considered as alternative solutions. Thus, swaps occurring at dQmax = 4 indicate that there is significant rotational ambiguity and that the solution is not sufficiently robust to be used (USEPA, 2014).DISP results for our results show that there are no swaps between the factors except at the highest dQmax level., indicating a solution with little rotationally ambiguity. In contrast, if factors where "split" as suggested by the reviewer one would expect a high degree of rotational ambiguity since the split factors would not be distinct and the elements in the source profiles could be exchanged with little change in Q.

Table 1: Displacement error estimation

EPA PMF

Model Data | Base Model | Rotational Tools | Help

Base Model Runs | Base Model Results | Base Model DISP Results | Error Estimation Summary

DISP Box Plots | DISP Summary

```
     0       0.000
  0    0    0    0    0    0    0    0    0    0
  0    0    0    0    0    0    0    0    0    0
  0    0    0    0    0    0    0    0    0    0
  0    0    0    0    0    3    0    0    0    2    3
```

In the first line the first value is an error code: 0 means no error; 6 or 9 indicates that the run was aborted. If this first value is non-zero, the DISP analysis results are considered invalid. The second value is the largest observed drop of Q during DISP.

Below the first line is a table (four lines) which contains swap counts for factors (columns) for each dQmax level (rows). The first row is for dQmax = 4, the second row dQmax=8, the third dQmax=15 and the fourth dQmax=25. If any swaps are present for dQmax=4, the solution has a large amount of rotational ambiguity and caution should be used if interpreting the solution.

Results for dQmax=4 are graphed in the DISP box plot tab. Detailed DISP results are included in the *_DISPres1-4.txt files (corresponding to the four dQmax levels) in the output folder.

Note: DISP intervals include effects of rotational ambiguity. They do not include effects of random errors in the data. For modeling errors, if user misspecifies the uncertainty of the concentration data, DISP intervals are directly impacted. Hence intervals for downweighted or "weak" species are likely too long.

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While the GEOS-CHEM analysis is to be lauded, its value accrues when it is used in a framework that exhaustively analyzes the receptor modelling data first before a comparison can be done. PMF factor contribution results themselves are usually subjected to spatial analyses in the form of polar meteorological plots as well as air mass back trajectory analyses for both local and regional apportionments. If these were done then compared with GEOS-CHEM, more support could have been said to derive from the latter. Thus, it is hard to believe that Quebec, a province with no coal-fired power generation, is a source of more particulate secondary sulphate than the US or the rest of Canada, as seen just by relying on the GEOS-CHEM results alone. The authors are enjoined to study the use of conditional probability plots for both local (CPF) and regional (PSCF) spatial apportionments at the very minimum. For a more thorough analyses on local and regional scales, CBPF and CWT are respectively recommended.

Answer: Regarding the sources of sulphate in Québec, it would be more accurate to describe the contributions from the province and the US as the same within modeling uncertainty (35% vs. 33%). Nonetheless, the reviewer's comment that this is somewhat surprising is a valid point given the lack of coal-fire power generation in Quebec. However, it is important to consider other sources of sulphate that are important regionally. Specifically, aluminum production is a major industry in Quebec that emits large amounts of SO_2 (NPRID, 2022). Nearly, 70% of North American aluminum is produced in Québec. In addition, other industries involving smelting and metallurgy in Québec emit SO_2. When also considering the recent decreased use of coal in the US (USEIA, 2022), the equal contributions of US and Quebec emissions to sulphate is reasonable.

With respect to the suggested spatial analysis of the PMF factors in the form of polar meteorological plots, we have provided below (Figure 1) pollution roses displaying the frequency of a given concentration of a factor as a function of wind direction. The wind data was taken from a nearby meteorological station at Montréal-Pierre Elliott Trudeau Airport. In general, the pollution rose plots are consistent with the identification of the

factors proposed in the manuscript. These figures will be added to the supporting information of the manuscript along with the following text.

"Pollution rose plots (Figure 1) can be used analyze the correlations between wind direction and factor concentrations by plotting in a polar graph the frequency of different concentrations of a factor as a function of wind direction. Such analyses provide information on the potential local origin of the factors.

The traffic exhaust and road dust factors show similar polar plots with the highest concentrations of these factor being observed when the wind is from the southern and western directions. The observations of high factor concentrations with winds from these directions is expected given that major highways (Autoroutes 15 and 40) are located to the west and the south of the measurement site, and winds from the south and west tend to have higher speeds facilitating transport. The road dust factor also exhibits some periods of very high concentrations when the wind is from the northeast, possibly due to the greater influence of very local emissions and surface streets.

In contrast, the biomass burning and crustal dust factors dust showed higher concentrations when winds were from the northeast. No major highways are in this direction. The biomass burning factor showed no trend with date during the campaign period. It is possible that this factor is related to certain food preparation activities such pizzerias and bagel bakeries that traditionally use wood ovens. Similarly, the crustal dust factor may be attributable to local construction activities, although further studies of the sources of these factors is needed. Interestingly, the cooking factor, unlike the biomass burning factor, shows little dependence on wind direction, which is reasonable given the measurements site is surrounded by residential neighborhoods and many restaurants.

The SIA and SOA factor both have similar dependences on wind direction with the highest concentrations tending to be observed when the wind is from the south and southeast. As already mentioned for the traffic-related factors above, winds from this direction can potentially transport aerosol and aerosol-precursors to the measurement site from major highways located to the south and southwest of the site. Alternatively, as discussed in the main text, GEOS-Chem modeling shows large transboundary contributions from the USA to these components. Thus, the wind blowing from the south may also correspond to large
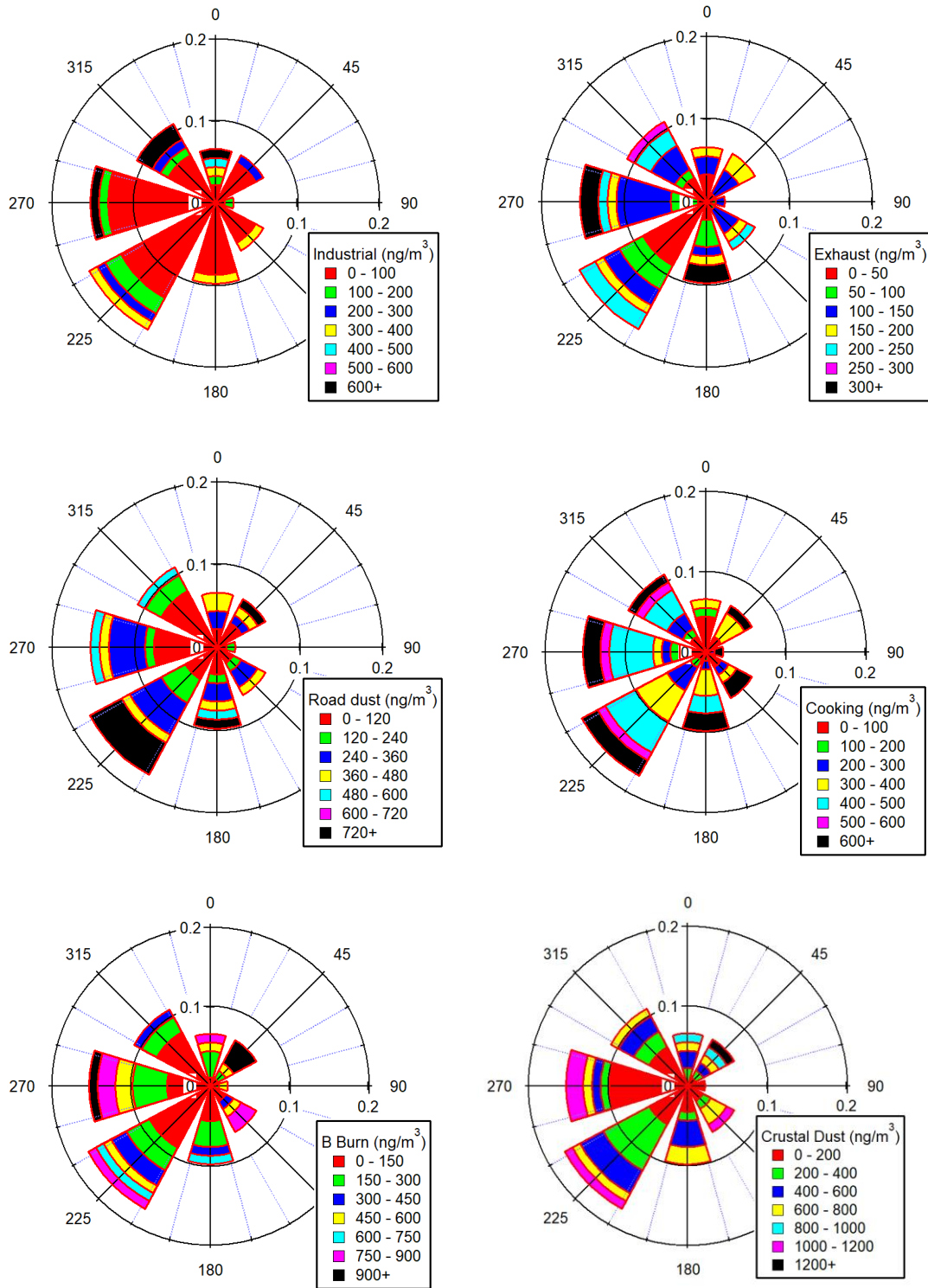
scale transport from south to north that increases the transboundary contribution to the SIA and SOA factors.
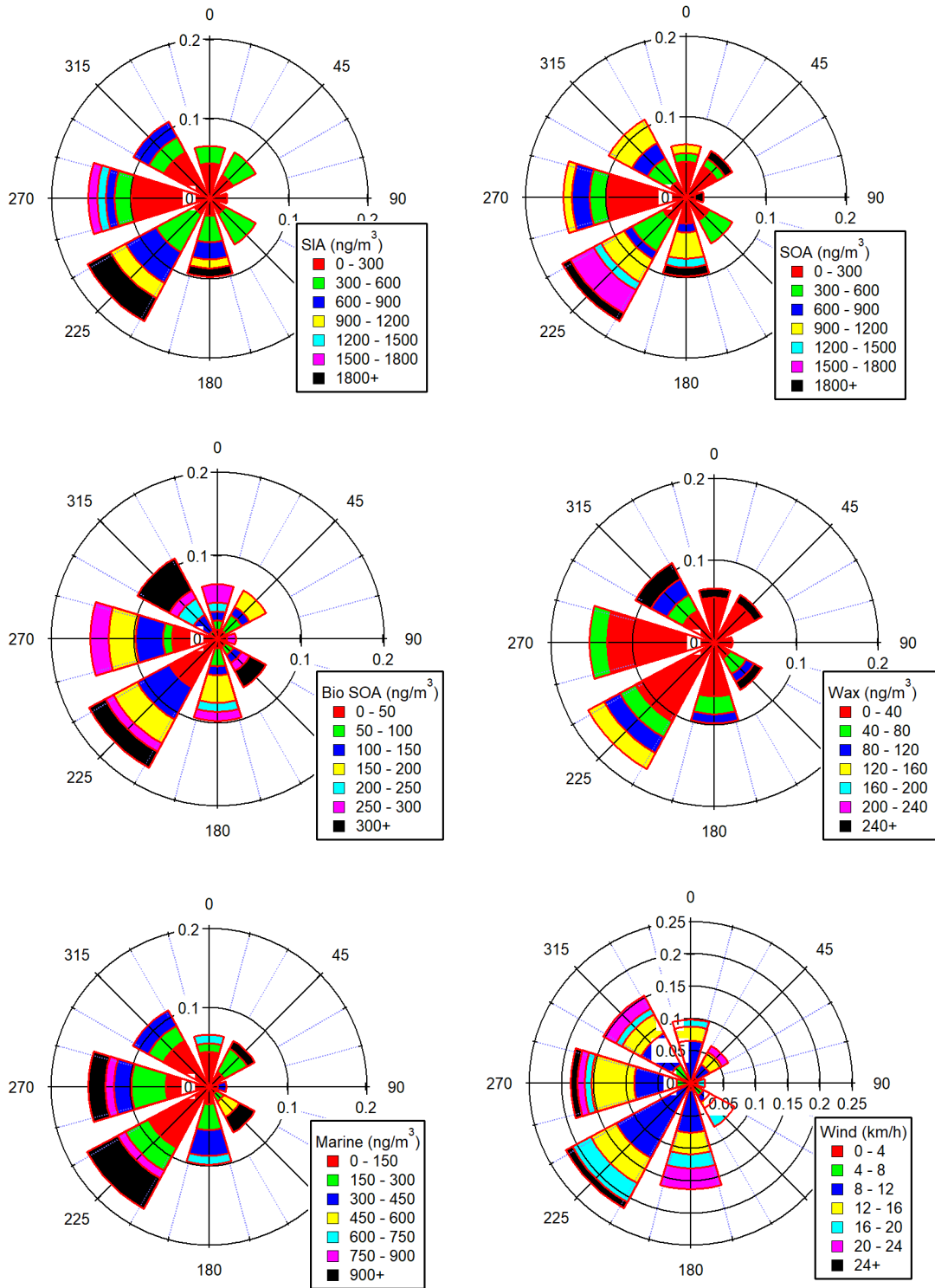
Both the biogenic SOA and plant wax factors exhibit high concentrations when winds are blowing from the northwest. In this direction is a major suburb of Montréal, Town of Mont-Royal, which contains a high density of trees relative to the rest of the metropolitan area. At the same time, we note that the biogenic SOA factor reaches moderately high concentrations for almost all wind directions, suggesting the importance of regional formation, which is expected to be important for this factor.

The marine factor exhibits relatively high concentrations for multiple wind directions including from the west and southwest. Thus, the marine factor pollution rose resembles to some extent that of road dust. It is also notable that the marine factor exhibits its highest concentrations in November when minimum temperatures were below freezing, and some snowfall occurred. Thus, it is possible that is factor originates from road salt, although further work is needed to evaluate the contribution of road salt to $PM_{2.5}$ in Montréal.

Lastly, the industrial factor exhibits its highest concentration when winds are blowing from the west and north. Many major industries on the Island of Montreal are located to the northeast of the site (e.g., the Suncor Energy Refinery). Thus, the pollution rose for the industrial factor does not correspond to the location of these sources. This discrepancy may be explained by changes in wind direction upwind of the site, especially given that the distances to some of the largest potential emitters is approximately 10 km."

Figure 1: Pollution rose plots for the PMF factors showing the frequency of a given concentration as function of wind direction.

Figure 1 (continued): Pollution rose plots for the PMF factors showing the frequency of a given concentration as function of wind direction. Wind rose is shown in lower right panel.

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Finally, the use of enrichment factors does not belong in contemporay source apportionment studies. Enrichment factors are flawed for incontrovertible scientific reasons, e.g., see Reimann and De Caritat. Environ. Sci. Technol. 2000, 34, 5084-5091.

Answer: Enrichment factor (EF) are still used in the literature before proceeding to PMF (Esmaeilirad et al., 2020; Acciai et al., 2017; Cesari et al., 2018; Li et al., 2018; Nayebare et al., 2016). These previous studies have used EF analysis along with the correlations between elements to provide qualitative details regarding the potential sources before proceeding to a more quantitative source apportionment using PMF. Nonetheless, we share the concerns of the reviewer and while our EF analysis is largely consistent with both the observed elemental correlations and our PMF analysis the section concerning the enrichment factors was removed from the manuscript.

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