Author response to all referees' comments on "Influences of sources and weather dynamics on atmospheric deposition of Se species and other trace elements"

We would like to thank the three reviewers for their time reviewing our manuscript and their valuable comments, which significantly enhanced the clarity of the paper. We have considered all comments carefully and present our point-by-point responses below (reviewer comments are in blue and author responses are in black). In the manuscript and supplementary information, the changes are shown using the track changes feature of word processor.

Response to Referee #2

I recommend the authors write a shorter abstract. Please, introduce a more summarized writing where you highlight the main findings of the article. I think this paper presents a very complete analysis, but if the authors abbreviate this section, it makes it more appealing to the reader.

Thank you for your feedback. We revised the abstract to make it shorter.

Line 37: The authors state that trace elements and isotopes in water are decoupled from clouds during precipitation. Can the authors indicate the specific result where this effect is observed?

The potential links between trace elements and water isotopes are discussed in details in section 3.1.2, on P17-18, L431-445. For clarification, we adapted the sentence in the abstract on P2, L34-36:

"Correlations between cloud water isotopes and trace elements indicate that the water and trace element cycles are coupled from the source to the formation of clouds, with possible decoupling during precipitation in relation to below cloud scavenging."

This is a very long article, as it presents different subsections. I recommend introducing a table of contents at the beginning of the manuscript.

Thank you for your proposition. We asked the editor from ACP and having a table of contents is very uncommon for research articles in ACP. Therefore, after introducing the research questions in the introduction, we indicated now explicitly in what sections they are addressed:

"*The research questions (1), (2) and (3) are discussed in Sect. 3.1, while Sect. 3.2 is focused on the last research question (4).*" (see P6, L131-132)

Methods section: the reviewer strongly recommends the authors extend the description of the study region, specifically to detail the Pic du Midi Observatory monitoring station site. It would be interesting to know the height of the mixing layer in the region. Since this study deals with a synoptic transport of Se, it would be interesting to know if the authors discarded the local influence (convective transport in the mixed layer).

Pic du Midi Observatory is an established long-term monitoring site of different chemical compounds (e.g. ozone, mercury, carbon monoxide, formaldehyde), which included detailed descriptions of the monitoring station (Marenco et al., 1994; Chevalier et al., 2007; Fu et al., 2016; Chevalier et al., 2008; Prados-Roman et al., 2020). Furthermore, extensive research has been conducted to investigate specific influences to the measurements at the monitoring station from the boundary layer (e.g. Gheusi et al. (2011); Hulin et al. (2019)). The typical summer afternoon mixing layer height is 2km (Gheusi et al.,

2011). We did not discard the local influence, because aerosol sampling included these hours. We discuss on P15, L373-374 how higher summertime aerosol Se is likely caused by boundary layer sources and upslope winds.

We agree with the reviewer and included references to previous studies that included a detailed description on the monitoring station on P7, L139-142:

"This high-altitude monitoring station is only occasionally influenced by the boundary layer through convection or by anabatic (i.e. upslope or valley) wind systems (Gheusi et al., 2011; Hulin et al., 2019), making it particularly suitable to investigate long-range transport as it is mostly exposed to free tropospheric air (Marenco et al., 1994; Henne et al., 2010; Fu et al., 2016)."

Local influences on Se are described in more detail in the last questions of Referee #2 on Line 365.

From your results: it is possible to assess if Se concentrations decline with precipitation amount?

Se concentrations did not significantly decrease with increasing precipitation amount. The effect of precipitation amount on the concentrations of Se and other elements were explored using principal component analysis (PCA), for which the output is described in detail in the Supplement, S8 (Fig. S11, P20).

For clarification, we added the following sentence on P18, L456-458:

"*While many major and trace elements (e.g. Na, K, P, Fe, Cu, Zn, As, Pb) showed a significant negative correlation with precipitation ($p<0.05$), Se concentrations did not significantly decrease with increasing precipitation amount."*

What about the solubility of Se species: your study, only measures dilute Se species?

Our study focuses on dissolved species in both wet deposition (dissolved fraction filtered with 0.2 µm) and in the water-soluble fraction of aerosols.

The investigation of other Se species, which are not soluble in water, would require specific extraction methods and/or direct solid phase speciation techniques, which have not been developed or are not suitable for low Se concentrations in aerosols collected in remote areas (e.g. synchrotron-based X-ray spectroscopy: detection limits in the $mg \cdot kg^{-1}$ range). From what is known from other matrices (e.g., soils, sediments), it is however likely that Se^{VI} is more water-soluble than Se^{IV}, because Se^{IV} is known to be more strongly bound to minerals such as Fe (oxy)hydroxides (Tolu et al., 2014).

In the conclusions, you state that: "for the first time we were able to identify an organic Se species as a biomarker of marine biogenic sources". Could you describe the specific result that allows you to conclude this?

This point was brought up by Referee #1 as well, we replaced the sentence "*for the first time we could identify an organic Se species as a biomarker for marine biogenic sources*" as follows: "*for the first time we could detected a new Se fraction likely of organic nature, which appears to be a biomarker for marine biogenic sources. Further work is required to investigate the molecular composition of this Se fraction and its role in atmospheric Se cycling.*" on P28, L683-685.

This conclusion is based on: i) the detection of an unknown Se peak ("OrgSe) at the same retention time than $SeCys_2$ (described in section 3.2.1, P22, L536-341); and ii) the significant correlations between OrgSe in different atmospheric samples and independent data sets, including the S species $DMSO_2$ and MSA (oxidation production of DMS), the quantitative contribution of Atlantic moisture sources and Chl-*a* exposure, and the proportions of pyrolytic products that are specifically derived from proteins and amino acids. These correlations are discussed in detail in section 3.2.3 (P26-28).

Line 365: Se can be released to the atmosphere from a variety of sources (e.g., natural sources such as soil, water, and vegetation, as well as anthropogenic sources). Are the terrestrial contributions of Se at Pic du Midi only due to synoptic transport or to local sources?

The different applied chemical analyses and modelling techniques include all potential source signatures (including terrestrial contribution) of both long-range and local emission. Specifically, the moisture source analysis included different pre-defined regions, including contribution over e.g., all European countries, North Africa, but also "local" moisture uptakes (in a 0.5° radius around Pic du Midi Observatory). None of the Se species or chemical source signatures correlated significantly to local moisture uptakes (sources), thus suggesting longer-range sources. Although there is no significant correlation between Se species and local moisture uptakes, local sources e.g., due to wet scavenging cannot be fully excluded.

References

Chevalier, A., Gheusi, F., Attié, J. L., Delmas, R., Zbinden, R., Athier, G., and Cousin, J. M.: Carbon monoxide observations from ground stations in France and Europe and long trends in the free troposphere, Atmos. Chem. Phys. Discuss., 2008, 3313-3356, 10.5194/acpd-8-3313-2008, 2008.

Chevalier, A., Gheusi, F., Delmas, R., Ordóñez, C., Sarrat, C., Zbinden, R., Thouret, V., Athier, G., and Cousin, J. M.: Influence of altitude on ozone levels and variability in the lower troposphere: a ground-based study for western Europe over the period 2001–2004, Atmos. Chem. Phys., 7, 4311-4326, 10.5194/acp-7-4311-2007, 2007.

Fu, X., Marusczak, N., Wang, X., Gheusi, F., and Sonke, J. E.: Isotopic Composition of Gaseous Elemental Mercury in the Free Troposphere of the Pic du Midi Observatory, France, Environmental Science & Technology, 50, 5641-5650, 10.1021/acs.est.6b00033, 2016.

Gheusi, F., Ravetta, F., Delbarre, H., Tsamalis, C., Chevalier-Rosso, A., Leroy, C., Augustin, P., Delmas, R., Ancellet, G., Athier, G., Bouchou, P., Campistron, B., Cousin, J. M., Fourmentin, M., and Meyerfeld, Y.: Pic 2005, a field campaign to investigate low-tropospheric ozone variability in the Pyrenees, Atmospheric Research, 101, 640-665, https://doi.org/10.1016/j.atmosres.2011.04.014, 2011.

Henne, S., Brunner, D., Folini, D., Solberg, S., Klausen, J., and Buchmann, B.: Assessment of parameters describing representativeness of air quality in-situ measurement sites, Atmos. Chem. Phys., 10, 3561-3581, 10.5194/acp-10-3561-2010, 2010.

Hulin, M., Gheusi, F., Lothon, M., Pont, V., Lohou, F., Ramonet, M., Delmotte, M., Derrien, S., Athier, G., Meyerfeld, Y., Bezombes, Y., Augustin, P., and Ravetta, F.: Observations of Thermally Driven Circulations in the Pyrenees: Comparison of Detection Methods and Impact on Atmospheric Composition Measured at a Mountaintop, Journal of Applied Meteorology and Climatology, 58, 717-740, 10.1175/jamc-d-17-0268.1, 2019.

Marenco, A., Gouget, H., Nédélec, P., Pagés, J.-P., and Karcher, F.: Evidence of a long-term increase in tropospheric ozone from Pic du Midi data series: Consequences: Positive radiative forcing, Journal of Geophysical Research: Atmospheres, 99, 16617-16632, https://doi.org/10.1029/94JD00021, 1994.

Prados-Roman, C., Fernández, M., Gómez-Martín, L., Cuevas, E., Gil-Ojeda, M., Marusczak, N., Puentedura, O., Sonke, J. E., and Saiz-Lopez, A.: Atmospheric formaldehyde at El Teide and Pic du Midi remote high-altitude sites, Atmospheric Environment, 234, 117618, https://doi.org/10.1016/j.atmosenv.2020.117618, 2020.

Tolu, J., Thiry, Y., Bueno, M., Jolivet, C., Potin-Gautier, M., and Le Hécho, I.: Distribution and speciation of ambient selenium in contrasted soils, from mineral to organic rich, Science of The Total Environment, 479-480, 93-101, https://doi.org/10.1016/j.scitotenv.2014.01.079, 2014.