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 #1

Sample processing (lines 172-173, lines 182-184, line 192) and Chemical analysis (lines 215-218): from the methods description given, I understand that the conditions of sample treatments (extraction of water-soluble fraction of aerosol samples and pre-concentration of these fractions and of precipitation/cloud water samples) was the same before speciation analyses of Se and S species. However, details of method development given in Supplement S2 (in particular species stability during extraction and pre-concentration) only target on Se species and no information about the stability of S species is provided. This may be due to the fact that such extraction and/or pre-concentration methods were previously validated for S species? In that case corresponding reference(s) should be added. Otherwise, the whole discussion around identified S species may be somewhat more complicated.

Thank you for pointing out that the pre-treatment of samples before S speciation analysis was unclear. S species were measured in precipitation samples without pre-concentration because their concentrations are high enough. The optimized pre-concentration method was developed to enable the quantification of Se species only. We have now clarified this in the method section on P10, L222-227 as follows:

"*Sub-samples used for Se speciation analysis were pre-concentrated by lyophilisation of frozen samples from an initial volume of 12 mL (for precipitation) or 9 mL (for water extract of aerosol filter) to a residual volume of 1.5 mL (pre-concentration factor of 8 or 6) to which ammonium citrate was added to increase ionic strength. The initial volume of cloud water samples was variable depending on sampled amounts. Further details on optimized protocol and stability of Se species during pre-concentration are given in Supplement S2. S speciation was analysed directly in all atmospheric samples (i.e., without the pre-concentration step).*"

Lines 236-245: the quantification method used for Se and S species must be specified in this section.

We agree with the reviewers. We have now clarified the quantification method used for Se and S species on P11, L252-255 as follows:

"*Quantification of Se and S species was done by external species-specific calibration (i.e., mixed Se or S species standards prepared in the corresponding LC eluent). Data treatment was performed using the MassHunter 4.6 (Agilent) software. $SeCys_2$ was used for the quantification of the "OrgSe" peak by anion exchange as further described in section 3.2.1."*

Line 351: as the indication of the range of values is given in previous sentence, the median value would be more meaningful here.

We agree with the reviewer and included both the average and median values on P15, L362-366:

"Total Se concentrations (after digestion using HNO_3 and H_2O_2) ranged from 2 to 221 pg·m^{-3} in the 2015-2020 aerosol time series (n=134; average: 58±57 pg·m^{-3}, median: 33 pg·m^{-3}; Fig. 2 and in Supplement S5, Fig. S4). We clearly see higher Se concentrations in summer (June-August; average:

114±50 pg·m^{-3}, median: 111 pg·m^{-3}) than during spring (March-May; average: 32±24 pg·m^{-3}, median: 30 pg·m^{-3}), autumn (September-November; average: 49±44 pg·m^{-3}, median: 27 pg·m^{-3}) and winter (December-February; average: 9±5 pg·m^{-3}, median: 9 pg·m^{-3})".

We thought it was important to keep the average value to enable (future) comparison with the literature since most previous studies solely reported average concentrations.

Lines 519-533 and corresponding supplements: Lines 519-533 and corresponding supplements: the comparison of example Se chromatograms illustrating the presence of a third Se-containing peak (fig S18a) to the standards one (supplement S3) seems to indicate a shift in retention times, although retention time units being different. It is not obvious to distinguish if the retention time of Org Se is different from the one of selenocystine standard? To facilitate readability, it would be helpful if chromatograms are plotted with same units (select min or s, and counts or counts per second for all layouts).

Thank you for pointing out this inconsistency in showing chromatograms. As proposed, the unit for retention time now made consistent in all chromatograms to seconds (sec). Please, see Figs. S3, S18 and S19 in the revised Supplement. The retention time of OrgSe is not different to the one of $SeCys_2$. For clarification, we added the following text in the caption of Fig. S18 (S9, P25):

"*Quantification of Se and S species was done by species-specific external calibration with mixed Se or S species prepared in the corresponding LC eluent. $SeCys_2$ was used for the quantification of OrgSe peak given that both had the same retention time (i.e., 50s).*"

The complementary use of cation exchange chromatography to try to understand the nature of Org Se peak is interesting. However, from Fig S19, the result of DMSeP addition is not quite clear as 2 peaks are increasing and one is decreasing. Then Se species recoveries are given (lines 524-525) but as indicated in previous comment, species quantification method was not indicated, which is important to know in particular in the case of Org Se peak, for which no commercial standard is available, to clarify recoveries and concentrations values (lines 530-533).

For the complementary analysis of DMSeP, we used an in-house standard synthesized by the protocol of W.-M. Fan et al. (1998) (DMSeP validated by Orbitrap and NMR analysis). The synthesis has several by-products of other organic Se compounds, which are visible in the spiked sample in Fig. S19, thus making the quantification of DMSeP difficult.

This is why we had detailed in the main manuscript that i) one peak "*co-elutes with an in-house synthesized standard of the metabolite dimethylselenonium propionate (DMSeP), which could indicate that this peak consists of small methylated Se compound(s)*" (P22, L539-541), and that ii) "*To achieve full identification of the organic Se species, high-resolution mass spectrometry may further be used given that sufficient pre-concentration can be reached*" (P22, L544-546).

Regarding the concentrations and recoveries for OrgSe, as described in the answer to the comment on L236-245, $SeCys_2$ was used for the quantification of the OrgSe peak by anion exchange chromatography because OrgSe had the same retention time than $SeCys_2$. The recoveries the reviewer is referring to were then calculated by the sum of identified species (i.e., OrgSe, Se^{IV}, and Se^{VI}) via anion exchange chromatography coupled to ICP-MS compared to total Se in the samples (i.e., precipitation, cloud water or aerosol water extracts).

Lines 539-541 and corresponding supplement: examples of S chromatograms of fig S18b indicate poor chromatographic separation of HMS (hydroxymethanesulfonate) and MSA (methanesulfonic acid)

peaks for which resolution does not allow accurate compounds quantification thus calling into question the following discussion and correlations using proportions or concentrations of these S compounds.

Indeed, these two S species are not perfectly separated. The LC-ICP-MS/MS method we used, which was developed by Müller et al. (2019), is the only available method to analyse S species at the low S concentrations encountered in atmospheric samples and further method optimizations did not help to improve the separation. To ensure correct quantification, all calibration standards were prepared with species-specific standard mixtures (including MSA and HMS). The Masshunter software allows consistent quantification, if the same peak integration conditions are kept for calibration standards and samples.

Furthermore, the quantified HMS and MSA species showed different links to other analysed and independent datasets, which is consistent with previous studies, i.e., HMS correlated with continental moisture sources, consistent with its expected anthropogenic origin, and MSA correlated with marine moisture sources, consistent with its expected marine origin.

As mentioned in our answer to a comment above, we have clarified the quantification method for S species on P11, L252-255: "*Quantification of Se and S species was done by external species-specific calibration (i.e., mixed Se or S species standards prepared in the corresponding LC eluent). Data treatment was performed using the MassHunter 4.6 (Agilent) software.*"

Furthermore, we added the following clarification in the discussion on P23, L558-560:

"To ensure correct quantification of MSA and HMS, which elute very close to each other, species-specific calibration standards (i.e., mixed S species standards) were used."

Lines 551-552: Se^{IV} proportion in aerosol water extracts appears to be significantly lower in summer than in autumn samples, does this difference remain if proportion is calculated as % of total Se in aerosol instead of its water-soluble extract?

Similar to the species proportions discussed on P23, L571-572 (calculated as % total Se in water soluble extract), the Se^{IV} proportions are significantly lower in summer (5±4%) than in autumn (9±7%), when the proportions in the aerosol water extracts are calculated as % of total Se in the total aerosol (i.e., in the acid digest). We specifically optimized the aerosol water extraction of Se for an extraction volume (15 mL) that is sufficient for both speciation analysis (after pre-concentration) and total analysis. If concentrations are compared between different extracts (i.e., water extract vs aerosol digest), there is a risk of introducing a certain bias that is caused by the general variability of Se over the entire aerosol filter.

Lines 558-562: as indicated in previous comments, without information about S species stability during extraction (and if so, preconcentration) and given the poor resolution between HMS and MSA peaks, the discussion involving HMS is very hypothetical.

See our answer to comment on Lines 539-541 & about method. Briefly, S speciation was analysed directly, i.e., without the pre-concentration step.

Lines 571-572: precipitation/cloud waters were collected in the period from end of August to October, comparison with aerosol water extracts of the same period (September to October) only indicates a difference between aerosol extracts and cloud waters, while Se^{IV} proportion in precipitation waters was not significantly different neither from cloud waters nor aerosol extracts (from letters indicated in fig 5).

We agree with the reviewer and have thus removed this sentence to avoid confusion.

Lines 622-624: same comment for discussion around MSA as previously indicated for discussion involving HMS.

See our answer to comment on Lines 539-541 & about method**.**

Line 662: Org Se was detected and not identified, the presence of single species in this chromatographic peak eluting at or close to the void volume of the column was not proven here

We agree with the reviewer. Therefore, we modified 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.

Supplement S2:

Line 59: partial transformation of SeMet is indicated to explain its lower recovery following extraction of water-soluble fraction of aerosols. It would be interesting to learn more (chromatographic detection of other Se-containing compound(s) and if so, which retention time(s)?).

Yes, the initial spiked SeMet was transformed into a Se species that eluted close to the void volume of the anion exchange column and so close to the retention time of $SeCys_2$ (retention time: 50s). Since we did not identify SeMet in analysed atmospheric deposition samples, we did not investigate specific transformation products of SeMet further. These transformation products are assumable very specific to SeMet (e.g. selenomethionine-oxide, SeOMet) and thus should not have an impact on our results. Nevertheless, we agree that it is a very interesting question that could be further investigated by high-resolution mass spectrometry given that sufficient pre-concentration can be reached.

Lines 87-88: lyophilisation to dryness led to losses of organic Se species for which the authors indicated a possible "transformation to other organic Se species that are not retained by anion exchange". This is a very important point as compounds not retained by anion exchange should elute at or close to the void volume of the column, as it is the case for the unknown organic Se compound/pool later detected in samples.

This is correct. However, this observed transformation was very specific to the lyophilisation to dryness in low ionic strength matrices (ultrapure water and rainwater) and was not observed in the optimized matrix (ammonium citrate) later applied to collected samples as described in Supplement S2, P5-7. For clarification, we have now added a sub-section giving the optimal conditions applied to the samples (see section 2.3).

Lines 97-104: the second set of tests compared different containers using lyophilisation to a residual volume < 1,5 mL. In this part, it is not clear in which aqueous medium (or media) the test was done? In the same way, tested media (lines 74-78) were ultrapure water, ammonium citrate solution and rainwater, but water-soluble fraction of aerosols does not seem to have been considered, is that right?

These specific tests were done in ammonium citrate solution as indicated in the caption of Fig. S2 ("*Lyophilisation was done with addition of 2 mmol L^{-1} ammonium citrate solution (eluent of LC-method*"). For clarification, we have now added this information in the text, S2, P6, L102-103 as follows:

"*Compared to when using lyophilisation of sample to complete dryness, all Se species in 2 mmol L^{-1} ammonium citrate solution were entirely recovered with lyophilisation to a residual volume of <1.5 mL, and this was true for all tested containers*".

The stability of different Se species during the extraction from aerosol filter samples are described in Supplement S2.1. For the following lyophilisation experiments, the water-soluble fraction of aerosols was not considered since rainwater samples and aerosol water extracts are expected to have very similar matrices. Furthermore, the performed lyophilisation tests showed that ionic strength was the major cause of species transformation. Since all collected aerosol samples were pre-concentrated with the addition of ammonium citrate, no significant differences in stability are expected between tested rainwater samples and the water-soluble aerosol fraction.

Supplement S10: add in the table caption, the number of samples considered for calculated correlations. It is important information as although statistically significant with p-values < 0.01 or <0.05, the strength of correlations is weak to moderate.

We have added the number of samples considered for the calculated correlations in the caption of Table S10.

Technical corrections

- Abstract line 19: check for duration of aerosol sampling 2015-2019 or 2015-2020? done
- Line 167: "53.6 ± 2.8" round to the number of significant figures. done
- Line 205: revise "equipped with and SPS4…" done
- Line 321: revise "in order to minimized…" done
- Lines 352-354, 530-532 and 536-538: round to the number of significant figures done
- Fig 5: aerosol time series is 2015-2019 in the figure, 2015-2020 in figure caption done
- Supplement S3 line 127: revise "an anion exchanges…" done
- Table S3: round to the number of significant figures (recoveries column) done

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References

Müller, E., von Gunten, U., Bouchet, S., Droz, B., and Winkel, L. H. E.: Hypobromous Acid as an Unaccounted Sink for Marine Dimethyl Sulfide?, Environmental Science & Technology, 53, 13146-13157, 10.1021/acs.est.9b04310, 2019.
W.-M. Fan, T., N. Lane, A., Martens, D., and M. Higashi, R.: Synthesis and structure characterization of selenium metabolites†, Analyst, 123, 875-884, 10.1039/A707597I, 1998.