

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 Nadine Borduas-Dedekind & team

This paper represents a large undertaking by the team of authors of method development, monitoring data, reporting of unique Se concentration datasets, hypothesis-generating analysis related to the role of thunderstorm clouds AND climate modeling. It's a super paper. The reported data is of the highest quality, the methods are accurate, and the details included in this paper are remarkable. This manuscript also includes a highly detailed SI.

Creation of their aerosol sample (n=134) at weekly resolution over 5 years is impressive.

The figures in this paper are remarkable! Some of the best made figures we've seen. The TOC figure is clean, clear, precise, and really compelling. Figure 1 is so clean and clear and yet has a ton of information portrayed. The use of symbols is particularly clever. Figure 6b also allows an unusually large amount of information to be presented clearly.

The results presented in Figure 4 are particularly compelling. The enhancement due to thunderstorms is clear (and unexpected to us).

(section 3.2.1) The measurement of the "third peak" as organo-selenium compound was particularly exciting for our group (since we are working on atmospheric methylated selenium compounds and their atmospheric fate). And the authors present convincing evidence of the presence of reduced Se species.

We would like to thank Nadine Borduas-Dedekind and her team for taking the time to read our article in detail and for providing constructive feedback. Thank you for acknowledging the broad and high-quality datasets we acquired as well as appreciating the quality of the figures.

We felt there were two stories in this paper: Se concentrations over 5 years (Fig 2), and trace elements in atmospheric deposition/role of thunderstorms (Fig 3). It makes for a super paper; but it wasn't clear to us, the readers, why these stories needed to be present in one super paper. If the authors could connect the two storylines better, it would be beneficial for the future reader.

In this study, our overarching goal was to bring significant contribution to an improved understanding of atmospheric Se deposition as stated in the introduction, P6, L124-125.

"Our objective in this study is to comprehensively investigate the role of different source factors and weather dynamics on the observed variability in trace element concentrations and Se speciation in atmospheric deposition."

We used different datasets (weekly aerosol series, high-resolution campaign of precipitation and cloud water samples) to address this overarching objective. The high-resolution campaign offered the investigation of unique source and process factors within individual precipitation events, whereas the aerosol series offered more long-term insights, however at lower temporal resolution. The effects of local cloud dynamics of specific weather events on total element deposition as well as the effect of source and process factors on Se speciation in atmospheric deposition samples are two linked research gaps, which significantly contribute to an improved understanding of atmospheric Se deposition. Splitting the material in two papers would, in our view, weaken the paper(s) substantially. Furthermore,

it was important to not only analyse Se and its specific source signatures (Fig. 2), but also other (trace) elements (Fig. 3) to highlight process factors (i.e., as identified for deep convective activity during thunderstorms) that affect multiple elements.

For clarification, we added the following sentence on P18, L448-451:

“Even though our study focuses on Se, we also investigated other (trace) elements in wet deposition which have been used as source indicators in previous studies, e.g., mineral dust (e.g., Fe and Mn) or anthropogenic activities (e.g., Pb).”

References to further support lines 60-62 discussing oxidation of volatile selenium should include (Atkinson et al., 1990) and could also include our very recently accepted work: <https://doi.org/10.1021/acs.est.3c01586> (in press, Heine & Borduas-D., ES&T, 2023). We observed selenic acid and dimethyl selenoxide as products. Same references are also relevant for discussion in lines 646-649.

Thank you for the suggestion to include these references on oxidation of volatile selenium. We included these references on P4, L64-65 and on P28, L667-668.

The discussion about variability of Se over the 5 years dataset in section 3.1.1. is likely location-dependent. We saw in (Lao et al., 2023) that the seasonal trends were drastically different and could be categorized in 6 distinct profiles related to geographical location in the US. Did the authors consider normalized their Se data with PM total mass? That analysis would help identify times of Se depletion or enhancement events (Lao et al., 2023).

We wanted to do so, but the aerosol mass on our collected filters could not be determined gravimetrically due to low aerosol loading and relatively large filter size (i.e., aerosol mass within the balance error of the filter mass). The aerosol loading under free tropospheric conditions is very low in contrast to most sampling sites of monitoring networks, which are generally located at low altitude sites (as is the case for the IMPROVE network in Lao et al. (2023)). No online measurements of the particle mass were available at the monitoring station.

We were therefore curious about the “similar patterns” referred to on lines 356-358. Could the authors show these similarities in their SI for example?

The similar patterns you referred to are already illustrated in Supplement 5, Fig. S5 (P15). For this figure, we selected three elements (S, Fe, and Pb) because of their likely contrasting source origins. Reference to Fig. S5 was given in the sentence following the one you referred to:

“This is interesting as it is likely that these elements are derived from different sources, e.g., mineral dust (e.g., Fe and Mn) or anthropogenic activities (e.g., Pb, Supplement S5, Fig. S5)”.

In order that future readers do not miss Fig. S5, we modified the text on P15, L369-373 as follows:

“In our study, we compared Se concentrations to many other (trace) elements and most of them show a similar pattern with higher concentrations in summer (see data for S, Fe and Pb in Fig. S5). This is interesting as it is likely that these elements are derived from different sources, e.g., mineral dust (e.g., Fe and Mn) or anthropogenic activities (e.g., Pb), which would indicate that elemental concentration patterns are not only driven by sources but also other (physical) processes”.

Lines 400-405. We thought it would be worth tabulating this information from the literature. It would be a great resource to point to and build upon for the authors, but also for the community.

The papers of Feinberg et al. (2020b); (2020a), which we cited on P4, L66-72, already tabulated Se concentrations in precipitation and aerosols from previous studies in their supplementary information. We did not want to duplicate this effort. We have however gathered and presented published Se speciation in precipitation in Fig. 7 as this has not been done in a previous study.

(section 3.2.2) lines 551-552 and subsequent paragraph: do the authors have an idea why there was no clear seasonal difference for Se(VI)? We thought that correlations with aromatics and aliphatics which likely oxidize quickly was surprising. What role of aerosol partitioning, aerosol viscosity could play here? Se can also undergo fast redox, and could Se(IV) and Se(VI) undergo redox chemistry in the atmosphere? See for example: (Reich and Hondal, 2016)

We think that there is no clear seasonal difference for Se^{VI} because Se^{VI} is the oxidation product of various emitted Se species. Regarding the correlation of Se^{VI} with aromatics and aliphatics, it is important to keep in mind that the aromatic and aliphatic compounds detected by Py-GC-MS are not necessarily aromatic and aliphatic compounds present in the aerosols, but rather pyrolytic products of specific compounds. Indeed, Py-GC-MS allows identifying pyrolytic products of organic matter, which are specific for biochemical classes of organic matter, such as carbohydrates, proteins (detailed list in Supplement, S4), and/or have been previously related to certain compounds, sources or conditions. For example, (poly)aromatic and aliphatic compounds detected by Py-GC-MS have been related to anthropogenic sources (Zhao et al., 2009; Subbalakshmi et al., 2000) and organic compounds that do not oxidize quickly (e.g., lipids, black carbon (Zhao et al., 2009; Zhao et al., 2012)). Therefore, the correlations of Se^{VI} with Py-GC-MS-obtained aromatics and aliphatics do not contradict with the fact that Se^{VI} is the oxidation product of various emitted Se species. Indeed, Se^{IV} and Se^{VI} are expected to undergo redox reactions in the atmosphere as indicated in the relationship between inorganic Se species and pH in precipitation and cloud water (Fig. 6a, P25). We further highlighted this in the conclusions on P28, L687-690:

“Nevertheless, it should be noted that inorganic Se species (Se^{IV} or Se^{VI}) are also affected by atmospheric processing, such as atmospheric oxidative transformations and pH changes, thereby losing their source information with increasing distance to emission sources. Therefore, it is likely that Se^{IV} indicates more local sources, whereas Se^{VI} could also be transported over longer distances.”

Figure 6a: could the relationship be due to chemical transformations or/and to partitioning?

The relationship between inorganic Se species and pH is most likely affected by contributing air masses and their associated chemical signatures and conditions, which may include chemical transformations (e.g., redox reactions) and partitioning to aerosol phases. However, our study cannot conclusively identify the contribution of specific processes as we focused on the end products of atmospheric transport, i.e., deposition.

Technical corrections

Line 204: “Se” is missing in the list just before Br. done

References

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