

We appreciate the thorough reviews and helpful comments. In the following, we present our answers and explain how we integrated changes in the final manuscript.

**Reviewer 2:**

General Comments:

This article reports on the design and application of a thiosulfate-impregnated honeycomb denuder to mitigate chemical losses from reaction with ozone in ultrafine particle sampling. This is important work, drawing attention to the unfortunately often overlooked interference from ozone in the sampling of atmospheric organic matter. I very much appreciate this study and its reporting and recommend the publication after consideration of a number my specific comments given below.

**It would be valuable to also have these experimental details provided: What fraction of ozone makes it through the sampling system without the sodium thiosulfate coating? Given that ozone is a rather reactive gas, a fair amount gets probably removed just by contact with the impactor and plumbing system?**

We thank the reviewer for this important point. In the absence of a sodium thiosulfate coating, ozone was measured at the sampling setup with an uncoated denuder installed and compared to the nearby governmental monitoring station (LfU) (Figure 4). The resulting regression slope of 1.04 ( $R^2 = 0.90$ ) indicates near-unity transmission within measurement uncertainty and does not suggest substantial systematic ozone loss in the inlet, impactor, or hose system.

We acknowledge that ozone losses on stainless-steel surfaces can occur and are known to be strongly conditioning-dependent. Initial ozone uptake may be substantial, but transmission efficiency increases with continued ozone exposure as surfaces become passivated (Altshuller and Wartburg, 1961). In our case, the 2.1 m stainless-steel inlet line and the MOUDI impactor were part of a routinely operated measurement setup and had been exposed to ambient ozone under continuous flow prior to the present campaign. Only the short Y-piece downstream of the impactor was newly installed (Figure S2).

Additionally, the ceramic denuder body is 50 mm in length, which is short compared with the 2.1 m stainless-steel inlet line. Given this limited additional flow-path length, the relatively short residence time in the inlet line ( $\approx 2\text{--}3$  s at  $30\text{ L min}^{-1}$ ), and the prior conditioning of the major stainless-steel components, ozone losses are expected to be limited.

**Given the multiple sampling and analysis steps, the chemical quantifications need a thorough experimental determination of the analytical reproducibility of the different chemical classes for the UFP determination. This should be done by deploying complete parallel samplers and not just by parallel sub-sampling of the fractionated aerosol or multiple chemical analyses of the extracts.**

We fully agree that reproducibility must reflect the complete sampling–extraction–analysis workflow. For this exact reason, we implemented a dual-channel sampling design in which two independent sampling lines operated in parallel to collect identical air masses simultaneously. Each channel utilized a separate filter, extraction procedure, and chemical analysis.

During reference operation, when both channels were equipped with uncoated ceramic bodies, this setup enabled an assessment of reproducibility under field conditions. The parallel two-channel design was selected to minimize variability resulting from UFP sampling methodologies, especially in regard of the dynamic nature of UFP. Consequently, differences observed during TSOD deployment can be attributed to ozone removal rather than to analytical variability.

Specific Comments:

**Line 21, 22: Instead of writing “ 0 ppb”, it would be more accurate to give the threshold of the ozone determination sensitivity, e.g. < 0.3 ppb, or whatever the detection limit of the utilized ozone sensor is.**

We thank the reviewer for this important comment. We agree that values close to the zero signal of the analyzer should not be reported as numerical ozone mixing ratios. We therefore determined the limit of detection of the instrument by separate zero-air measurements, which yielded  $4.6 \pm 0.5$  ppbV. In the revised manuscript, downstream ozone values in this range are no longer reported numerically but are described as indistinguishable from the zero-air baseline and therefore below the practical detection limit of the setup.

All instances of “0 ppb” have been replaced accordingly: L21, 23, 292, 337

**Line 28: Please give the uncertainty margins of the 15-46% determination.**

We agree that the magnitude of the reported ozone-induced changes should be accompanied by quantitative uncertainty estimates. We revised that accordingly for the PAH concentrations, as well as for the following comment regarding the 6PPD and 6PPDq concentration

*L28 Without upstream O<sub>3</sub> removal, the individual concentration of the PAHs were  $15 \pm 2.9 - 46 \pm 5.5$  % lower.*

**Line 30: Same here.**

*L29-31 (2) Secondly, for the tire and road wear marker, the antioxidant N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) and its oxidation product 6PPD-quinone (6PPDq), we observed in-situ ozonation of 6PPD to 6PPDq with transformation yields of about  $13 \pm 4.0$  to  $20 \pm 8.3$  %.*

**Line 49: Possibly also cite the WMO GAW Measurement Guidelines, GAW Report No. 281, Guidelines for Measurements of Non-Methane Hydrocarbons in the Troposphere, that emphasize the need to remove ozone in the sampling of volatile organic compounds.**

Thank you for the suggestion. We added the reference. L50

**Line 74. One could also consider [Helmig and Greenberg, 1995].**

Thank you for the suggestion. We added the reference. L72

**Line 144: Please mention that these are honeycomb structure channels and that CPSI stands for cells per square inch. How are these connected to your system plumbing? It might be nice to show a photograph of the denuder.**

Thank you for pointing this out. We named the CPSI accordingly and added pictures in the SI (Figure S1 and S2).

**Line 148: I have a hard time believing that shaking of ta 400 CPSI honeycomb denuder will remove all the water? What is the actual diameter of the individual capillaries? This could possibly be checked by weighing a dry denuder and one that has been “shaken”. If residual water remains in the denuder, then that may actually affect the coating efficiency when the denuder is subjected to the sodium thiosulfate solution?**

We thank the reviewer for this careful comment. We agree that shaking alone does not remove all residual moisture from the honeycomb structure. The purpose of the shaking step is solely to remove bulk water from the honeycomb channels and to prevent individual capillaries from remaining completely water-filled.

The relevant section in the Methods has been revised for clarification:

*L139-148 Subsequently, the bodies were manually dried with vigorous shaking to remove bulk water from the honeycomb channels. Next, the bodies were placed in a 5.6 mol L<sup>-1</sup> solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>O, and ultrasonicated for an additional 10 minutes. After ultrasonic impregnation, excess solution was removed by vigorous shaking while holding the monolith vertically to allow drainage of bulk liquid from the honeycomb channels. Afterwards, bulk solution within the channels, which was not removed by shaking, was blow-dried with nitrogen (N<sub>2</sub>, 99.99%). This was a critical step to prevent the growth of crystals within the ceramic matrix and the subsequent occlusion of the channels. The drying process was finished by baking the TSODs at a temperature of 120°C for a duration of 60 minutes. For equilibration, the TSODs were placed in a sealed container with a separate water reservoir at the base to maintain a high humidity environment.*

The reviewer is right, that residual surface moisture after the shaking step cannot be fully excluded. However, any remaining thin water film would represent only a minor fraction compared to the volume of the subsequently applied 5.6 mol L<sup>-1</sup> sodium thiosulfate solution. During impregnation, the monoliths are fully immersed in excess thiosulfate solution and subjected to ultrasonic treatment for 10 minutes. This step promotes thorough exchange between the solution inside the capillaries and the bulk solution. Under these conditions, any residual moisture would at most slightly dilute the thiosulfate solution.

**Line 148. “5,6 mol L-1”? Please be consistent with using a decimal point for decimals.**

We changed it accordingly.

**Line 155: Please give complete details about the drying method.**

We thank the reviewer for this helpful comment. We have revised the Methods section to provide a clearer description of the drying procedure.

Specifically, we now clarify that the shaking step serves to remove bulk liquid from the honeycomb channels and to prevent individual capillaries from remaining fully flooded. Dehydration is not achieved mechanically but through subsequent nitrogen blow-drying followed by controlled thermal treatment at 120 °C for 60 minutes. We explicitly describe the sequence of shaking, nitrogen drying, and oven treatment, as well as their respective purposes.

Please see the revised version according to the previous comment regarding line 148.

**Line 187: Round site coordinates to a reasonable number.**

The site coordinates have been rounded to an appropriate level of precision (48.358° N, 10.907° E) in the revised manuscript.

*L180-183 To evaluate the performance of the TSOD under real environmental conditions, a novel setup was installed in a measurement container at an urban field site of the University of Applied Sciences in Augsburg, Germany (48.358° N, 10.907° E) in September 2023.*

**Line 254: Are the error margins 1-sigma standard deviations?**

Yes, the reported uncertainties represent  $1\sigma$  standard deviations (SD) derived from triplicate recovery experiments ( $n = 3$ ). We have clarified this in the revised manuscript.

*L250 Uncertainties represent  $1\sigma$  standard deviations (SD) obtained from triplicate spiking experiments.*

**Line 264: Give numeric results and stated uncertainty comparison.**

We thank the reviewer for this suggestion. We have revised the manuscript to include explicit numerical validation results for SRM 2786. The measured concentrations are now reported relative to the certified values.

*L258-259 Specifically,  $107 \pm 4\%$  of the certified BaP concentration was recovered. BbF, BkF,  $\Sigma(\text{Chry} + \text{BaA})$ , and IcdP showed recoveries of  $96 \pm 5\%$ ,  $94 \pm 7\%$ ,  $89 \pm 5\%$ , and  $99 \pm 7\%$ , respectively.*

**Line 287: How do you conclude that the sodium thiosulfate efficiency is dependent on relative humidity rather than specific humidity?**

We thank the reviewer for this important clarification. We agree that the fundamental controlling parameter for thiosulfate reactivity is water availability at the surface. In our laboratory experiments, temperature was kept approximately constant, such that RH served as a practical proxy for water availability. In the intended atmospheric field application, RH is the routinely monitored and reported parameter and thus represents the operationally relevant descriptor of ambient moisture conditions.

We have revised the manuscript to avoid implying that the process depends uniquely on RH as a thermodynamic variable and instead refer more generally to “water availability,” while retaining RH as the reported parameter under atmospheric conditions.

*L287-291 We therefore intentionally conducted our laboratory experiments under distinctly drier conditions (reported as  $\text{RH} = 52.4\text{--}53.3\%$ ), in order to test TSOD performance near the lower end of the humidity range expected during field operation. Previous studies indicate that thiosulfate-based ozone removal decreases under drier conditions, consistent with reduced water availability at the denuder surface (Ernle et al., 2023; Rynek et al., 2025)*

**Line 298: The ozone monitor that was used really isn't suited for measuring levels below 1 ppb, and the lowest detectable ozone will be quite sensitive to the zero offset that is applied in the monitor. Therefore, the reliably measurable lowest ozone level needs to be carefully determined in a set of zero ozone measurements and only numerical values above the determined ozone detection limit should be reported as numerical data. All other recordings need to be reported as below the detection limit ( $< x.x$  ppb) of the measurement.**

We thank the reviewer for this important comment and agree that ozone values close to the zero signal of the analyzer should not be reported as numerical concentrations. We initially performed zero-air measurements to determine the practical baseline of the instrument under ozone-free conditions. These measurements yielded an analyzer response of  $4.6 \pm 0.5$  ppbV.

During the denuder experiments, the downstream ozone signals ranged from 4.4 to 5.0 ppbV and were therefore indistinguishable from the zero-air baseline. We have revised the manuscript accordingly and no longer report these values as numerical ozone concentrations. Instead, we now state that ozone downstream of the TSOD was below the practical detection limit of the measurement setup / indistinguishable from the zero-air baseline.

*L156-159 To assess the practical zero-level response of the instrument, separate zero-air measurements were performed, yielding an analyzer signal of  $4.6 \pm 0.5$  ppbV under  $\text{O}_3$ -free conditions.*

L295-297 As depicted in Figure 2, the outlet  $O_3$  mixing ratio (4.4–5.0 ppbV) were indistinguishable from this zero-air baseline, indicating that ozone downstream of the denuder was below the practical detection limit of the measurement setup.

**Figure 4 caption: Replace ‘concentration’ with ‘mixing ratio’ here and elsewhere.**

Thank you for pointing this out. We changed the caption accordingly.

*Figure 4 (A) Correlation between hourly averaged  $O_3$  mixing ratios from the sampling site and the LfU monitoring station. A linear regression through the origin (red line) yields a slope of 1.04 and  $R^2 = 0.90$ . (B) Time line of ambient  $O_3$  mixing ratios before and during the field campaign in Augsburg. Measurements before the campaign were taken from a setup without a TSOD, allowing comparison with reference data from the LfU monitoring station. After the start of UFP sampling, measurements were taken downstream of the TSOD (blue, “Sampling site”) and compared to the LfU reference data (orange, “LfU”).*

**Table 1: Explain in table caption what the reference data are.**

Thank you for pointing the unclarity. We changed the table caption accordingly.

*Table 1 Linear regression slopes of marker compound concentrations between the two sampling channels during operation with ozone removal (TSOD installed in Channel A). For comparison, slopes obtained during reference operation, when both channels were equipped with uncoated ceramic bodies, are also shown (Reference). Slopes were derived from linear regressions constrained through the origin. Values greater or smaller than unity indicate enhancement or loss of the respective compound in the presence of  $O_3$  removal.*

**Line 458: Most journals these days do not accept this data availability statement. Data should be shared with readers readily within the Supplemental Materials or through a public archive.**

The study was conducted within a project funded by the Bavarian State Ministry of the Environment and Consumer Protection (StMUV). Therefore, the release of the underlying project data requires prior approval by the funding authority.

We are happy to provide the data used to generate the figures upon reasonable request. Should public deposition of the figure data or a dedicated dataset be required by the editor or the journal, we will submit a corresponding request to the StMUV. We kindly note that obtaining this approval may require additional time.

Helmig, D., and J. Greenberg (1995), Artifact formation from the use of potassium-iodide based ozone traps during atmospheric sampling of trace organic gases, *Journal of High Resolution Chromatography*, 18, 15-18.