Reviewer #2:

The authors presented a very comprehensive characterization of molecular composition in aerosol particles from controlled tailpipe and tunnel samples, using high-resolution mass spectrometry. The key finding is that tunnel samples contained more complex organics, especially sulfur-containing ones, as compared to tailpipe samples. Multiple parameters were used to demonstrate the differences, and interpretations and implications were also given. The study was well designed and manuscript clearly written. I therefore recommend Minor Revision with comments as below.

Response: We thank Reviewer #2 for the positive assessment and constructive comments. Each comment is addressed individually.

Comments

1. One main drawback, as the authors noted somewhere in the manuscript, of this study is that the electrospray ionization (ESI) method is preferable for more polar components, while it might miss some non-polar compounds. Please make a note or two on this limitation somewhere in the Summary and implication section.

Response: The revised Section 4 limits the formula-level comparison to the organic fraction extracted and ionized by this method and states what this means for the interpretation of formula occurrence and TCR. The GC×GC-MS measurements already proposed in this section address the non-polar fraction. The vehicle and operating-condition scope is specified in the Section 4 passage quoted in our response to Reviewer #1, Major Comment 1. The analytical-scope text in Section 4 now reads as follows:

"**Both profiles are limited to the organic fraction extracted with acetonitrile and ionized by ESI; non-polar hydrocarbons from lubricating oil, which dominates primary organic aerosol emissions from motor vehicles (Worton et al., 2014), are weakly ionized, so TCR describes coverage within this analytical window.**"
(Section 4, Lines 434–436)

2. For the ESI+ and ESI- modes, there might be some overlapping components. Please specify how they were treated in counting the number of compounds, as well as estimation of concentration (or intensity).

Response: A neutral formula detected in both modes (294 in the tunnel samples; Section 3.2) is counted once in each mode; the same counting rule applies to formulas selected for HCA. Counts are mode-specific and refer to formulas, not identified compounds. Peak areas from ESI+ and ESI− were processed and normalized separately and are never summed or averaged, because ionization efficiency differs between the modes. The areas are relative responses, and no concentrations were estimated. The counting rule is stated in Section 2.4 (see our response to Reviewer #1, Major Comment 4), and the peak-area treatment in Section 2.4 now reads as follows: "**Peak areas from ESI+ and ESI− were processed and normalized separately and were not summed or averaged across modes. Areas are relative responses.**" (Section 2.4, Lines 136–137)

3. There are a few places where the authors used many parallel/possible sources to describe certain compound classes, e.g., in L225. These are not very informative. Please use more specific possible sources, backed by evidence.

Response: We agree. The list of six possible sources at L225 has been replaced by the one statement that our data support, consistency with vehicle exhaust, because the persistent-core formulas were also retained in all three CD samples. The published evidence for the possible sources of the sulfur-containing formulas is consolidated in Section 3.4, where tire inputs are linked to benzothiazole measurements and lubricant inputs to measured additives and primary aerosol contributions, and these source hypotheses are kept separate from the MS/MS evidence for individual formulas, as detailed in our response to Reviewer #3, Major Comment 5. The revised text now reads as follows:

"**Because these formulas were also retained in all three CD samples, they are consistent with a contribution from vehicle exhaust, including lubricant-derived organics (Worton et al., 2014).**" (Section 3.2, Lines 252–254)

"**Published measurements of tire wear, road dust and lubricating oil provide specific source hypotheses for the sulfur-containing formulas. Benzothiazoles occur in tire wear and road dust (Zhang et al., 2018) and in leachates of tire crumb rubber and road dust (Seiwert et al., 2020), sulfonate detergents are standard additives in formulated lubricating oils (Rudnick, 2017), and lubricating oil contributes to vehicle primary organic aerosol (Sonntag et al., 2012; Worton et al., 2014).** Together with the low tailpipe coverage ratios of CHOS and CHONS, these results identify C2 as a molecular **group** rich in sulfur-containing formulas and characteristic of tunnel aerosol." (Section 3.4, Lines 384–389)

Additional manuscript references are listed in the following paragraphs.

Seiwert, B., Klöckner, P., Wagner, S., and Reemtsma, T.: Source-related smart suspect screening in the aqueous environment: search for tire-derived persistent and mobile trace organic contaminants in surface waters, Anal. Bioanal. Chem., 412, 4909–4919, https://doi.org/10.1007/s00216-020-02653-1, 2020.

Zhang, J., Zhang, X., Wu, L., Wang, T., Zhao, J., Zhang, Y., Men, Z., and Mao, H.: Occurrence of benzothiazole and its derivates in tire wear, road dust, and roadside soil, Chemosphere, 201, 310–317, https://doi.org/10.1016/j.chemosphere.2018.03.007, 2018.

4. L229: how is the NOx condition affecting the "tunnel processing" of organic components? More N-containing species? In fact, this term of "tunnel processing" is not very clear. Is it prompt oxidation? Or other physical or chemical processes? Please specify.

Related sentence from the original submission "This pattern is consistent with the preferential ESI+ detection of protonatable nitrogen containing organics and may reflect contributions from primary traffic emissions together with in tunnel processing of emitted organics under NO_x rich conditions (Wang et al., 2019; Cai et al., 2022)." (Section 3.2)

Response: The intended process was possible secondary formation of some CHON constituents through oxidation chemistry involving NO_x. Organic peroxy radicals can form organic nitrates through a branch of their reaction with NO, and studies of benzene and naphthalene oxidation show NO_x-dependent formation of nitrogen-containing products (Priestley et al., 2021; Edwards et al., 2022), as do observations of nitroaromatic formation in polluted urban air (Wang et al., 2019; Cai et al., 2022). The NO_x enrichment reported for road tunnels (Zhou et al., 2014) provides environmental context and not evidence of prompt oxidation within the tunnel. Our data cannot show whether, where or how fast this pathway occurs in the sampled tunnel, so the sentence at original Line 229 now names the pathway in place of the term "tunnel processing" and presents it as a possible contribution beside direct vehicular emissions. The prominence of nitrogen-containing formulas in ESI+ is likewise not taken as evidence for this pathway. Section 3.2 now reads as follows: "**The dominance of nitrogen-containing formulas in ESI+** is consistent with preferential detection of protonatable organics**,** and **their sources** may **include direct vehicular** emissions **and secondary chemistry involving VOCs and** NO_x (Wang et al., 2019; Cai et al., 2022). **Traffic-related NO_x enrichment has been observed**

inside road tunnels (Zhou et al., 2014), and elevated NO_x can favor the formation of some nitrogen-containing products (Priestley et al., 2021; Edwards et al., 2022)." (Section 3.2, Lines 255–259)

Additional manuscript references are listed in the following paragraphs.

Edwards, K. C., Klodt, A. L., Galeazzo, T., Schervish, M., Wei, J., Fang, T., Donahue, N. M., Aumont, B., Nizkorodov, S. A., and Shiraiwa, M.: Effects of Nitrogen Oxides on the Production of Reactive Oxygen Species and Environmentally Persistent Free Radicals from α-Pinene and Naphthalene Secondary Organic Aerosols, The Journal of Physical Chemistry A, 126, 7361–7372, https://doi.org/10.1021/acs.jpca.2c05532, 2022.

Priestley, M., Bannan, T. J., Le Breton, M., Worrall, S. D., Kang, S., Pullinen, I., Schmitt, S., Tillmann, R., Kleist, E., Zhao, D., Wildt, J., Garmash, O., Mehra, A., Bacak, A., Shallcross, D. E., Kiendler-Scharr, A., Hallquist, Å. M., Ehn, M., Coe, H., Percival, C. J., Hallquist, M., Mentel, T. F., and McFiggans, G.: Chemical characterisation of benzene oxidation products under high- and low-NOx conditions using chemical ionisation mass spectrometry, Atmospheric Chemistry and Physics, 21, 3473–3490, https://doi.org/10.5194/acp-21-3473-2021, 2021.

Zhou, R., Wang, S., Shi, C., Wang, W., Zhao, H., Liu, R., Chen, L., and Zhou, B.: Study on the Traffic Air Pollution inside and outside a Road Tunnel in Shanghai, China, PLoS ONE, 9, e112195, https://doi.org/10.1371/journal.pone.0112195, 2014.

5. It would be good to have more discussion on where do those sulfur-containing species come from in tunnel samples, and how will they affect aerosol properties such as volatility, hygroscopicity, toxicity etc.

Response: The possible origins of the sulfur-containing formulas are discussed in our responses to Reviewer #2, Comment 3 and Reviewer #1, Major Comment 5. Sulfur-containing constituents may influence particle water uptake depending on molecular structure; laboratory measurements show substantial differences even among confirmed organosulfates (Peng et al., 2021). The two C2 sulfur formulas detected in ESI−, $C_9H_{19}NOS$ and C_7H_5NOS, each contain only one oxygen atom and cannot represent sulfate esters or sulfonates. Organosulfate hygroscopicity therefore cannot be applied directly to these formulas. Volatility and hygroscopicity were not measured here, so no directional change is inferred from the sulfur-containing formula fraction. The four tentative annotations in Table S16 provide candidates for structural confirmation and subsequent property and exposure-relevant toxicity measurements. Section 4 now reads as follows:

"**The tentatively annotated 6PPD, 6PPD-quinone, 2-aminobenzothiazole (ABT) and 2-(4-morpholinyl)benzothiazole (Table S16 and Figure S8), together with the formulas differing from ABT by CH_2 increments ($C_{11}H_{14}N_2S$, $C_{13}H_{18}N_2S$ and $C_{15}H_{22}N_2S$; the Supplementary Data file), provide candidates for structural confirmation and subsequent assessment of volatility, hygroscopicity and exposure-relevant toxicity.**" (Section 4, Lines 450–453)

Reference cited only in this response.

Peng, C., Razafindrambinina, P. N., Malek, K. A., Chen, L., Wang, W., Huang, R.-J., Zhang, Y., Ding, X., Ge, M., Wang, X., Asa-Awuku, A. A., and Tang, M.: Interactions of organosulfates with water vapor under sub- and supersaturated conditions, Atmos. Chem. Phys., 21, 7135–7148, https://doi.org/10.5194/acp-21-7135-2021, 2021.

Table S16**. Selected** retention-time-specific **MS/MS annotations.**

Neutral formula	Tentative annotation	Observed MS/MS RT (min)	Eligible scans	Median library cosine	HCA group
$C_{18}H_{24}N_2$	6PPD	10.074–10.133	19	0.803	Outside HCA set
$C_{18}H_{22}N_2O_2$	6PPD-quinone	14.994–15.041	25	0.884	C1
$C_7H_6N_2S$	ABT	9.393	1	0.826	C1
$C_{11}H_{12}N_2OS$	24MoBT	9.515–9.696	10	0.830	C2

Annotations are tentative and apply to the specified RT-resolved features.