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Comment on acp-2022-130

Anonymous Referee #1

Referee comment on "Oxygenated volatile organic compounds (VOCs) as significant but varied contributors to VOC emissions from vehicles" by Sihang Wang et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-130-RC1, 2022

Oxygenated VOCs as significant but varied contributors to VOC emissions from vehicles. *Preprint acp-2022-130*

Overview

This manuscript characterizes gaseous emissions from a number of vehicles meeting a wide range of Chinese emissions standards, to include gasoline, diesel, and liquified petroleum gas (LPG), as measured using a chassis dynamometer setup. Measurements are primarily presented for those using a PTR-ToF-MS, and included canister sampling with GC-MS/FID analysis and a few species by Iodide CIMS, along with common measurements (CO_2, etc.) using a portable emissions measurement system. Oxygenated VOC's (OVOC) are indicated to be molecules with less than 18 carbons.

This work shows the strong influence of OVOC in diesel exhaust (>50% by mass) compared to a much smaller influence in gasoline vehicles (~15%). Clear differences between cold-start and hot-start emissions are also observed, notably they are much more significant for gasoline vehicles than for diesel vehicles, and aromatics and OVOC had similar temporal profiles. Some ratios of emissions (e.g. toluene to larger aromatics) are unique between gasoline and diesel vehicles, and are suggested as potentially useful for emissions attribution.

Overall the work as presented is quite thorough, and the intended goals of the work are clearly made. The insights from the work are a good contribution to the field. There are a few details that should be addressed, however prior to suitability for publication, notably quality control.

General Comments

It is concerning that the agreement between canister with GC-MS/FID and PTR-ToF measurements for toluene are so disparate in more than 20% of the tested vehicles, as shown in Figure S6c. These discrepancies are essentially ignored in the manuscript. How can canister measurements be near-zero while PTR-ToF measurements are 250 mg/km, and vice versa? Perhaps this might cold occur for more exotic species, but for toluene I would expect agreement at least within a factor of 2 in all cases, as it is a high volatility species that is easily ionized in PTR and observed with GC-MS/FID. Perhaps in some cases one or the other measurement was not made and simply reported as zero? This issue should be clarified. Furthermore, agreement between generally accepted canister measurements and PTR-ToF measurements must be reported for a wider variety of species, to include oxygenated species and larger aromatics.

The mileage of the vehicles tested is quite variable, are there any correlations in your data with mileage, are these different for gasoline vs. diesel?

Was any analysis of the fuels done? To make clear sense of the emissions, the compositions of each fuel type, in terms of saturates (linear and cyclic), aromatics (BTEX and others), and oxygenates should be given. This is especially important for the diesel fuel, which can vary significantly in terms of aromatic content. Were the fuels summer or winter blends? The results presented have much narrower significance without clearer information on the fuel composition. Did the gasoline fuel have any ethanol content, as might be expected for gasoline in China after 2017? Ethanol content will have significant effects on small OVOC emissions. The discussion beginning on line 377 is well explained by the difference in aromatic content of the two fuels.

When considering the usefulness of ratios between emitted species as diagnostic for diesel vs. gasoline species, you should also consider their atmospheric lifetimes for oxidation.

Specific Comments

Figure 9. The fits to your data are poorly presented this way, either for predicting the

values through the whole range or for giving physical insight. Perhaps you should make the axes linear rather than logarithmic. At the very least, you should explain that the strange curves to these linear fits in log-log space are due to the y-intercept, or perhaps only plot these fits in the region where they appear linear (where the intercept is small compared to the fit value) and note that you plot only in the region of reasonable fit.

Please review again thoroughly for grammar. A few corrections are:

Line 224 “species emitted by vehicles”

Line 377 “Comparing gasoline and diesel vehicles,”

Line 445. “can be determined”

Line 486. “Substantially larger”