

Interactive comment on “Comparison of primary and secondary particle formation from natural gas engine exhaust and of their volatility characteristics” by Jenni Alanen et al.

Anonymous Referee #1

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The authors simulated the effects of atmospheric aging of exhaust emissions from a natural gas engine with a PAM chamber and investigated the volatility of fresh and aged particles using a thermodenuder. The authors show that the engine tested produced significant secondary particulate matter with respect to the primary emission and that composition and volatility of the secondary aerosol was influenced by engine/ catalyst temperatures. The authors present a clear motivation for their work and the article is generally well written. However, there are major issues, which should preclude publication at this stage, outlined as follows:

Major comments

Scope of the paper: The authors are using a relatively new, hence unestablished, C1

technique to investigate emissions from one engine during conditions not shown to be relevant to real world driving. They then use their results to suggest that “the shift from traditional liquid fuels to natural gas can have a decreasing effect on total particle pollution in the atmosphere”. They also do not quantify the ‘shift’ to which they refer. Given these obvious limitations, I do not feel that such strong statements on the effect of natural gas engines on the atmosphere are justified. I would suggest they remove them from the manuscript.

Wall effects and sampling artefacts: There are issues relating to the measurement of ammonia and ammonium nitrate. In the PAM, ammonium nitrate will form in the presence of NO_x and ammonia. If sulfate is present, ammonium sulfate will form preferentially before ammonium nitrate. However ammonia is a very ‘sticky’ compound and difficult to measure see e.g. Suarez-Bertoa et al. It is thus clear that losses of gaseous ammonia and the walls of the sampling system and reactor will have a profound impact on the observed secondary inorganics, and potentially on subsequent experiments as the ammonia slowly desorbs. In turn, the effects observed in this paper may very well relate more to sampling conditions e.g. flow rates/ temperatures than to processes occurring in the atmosphere or in the engine. Ideally, the authors should determine how long it takes for ammonia concentrations reaching the PAM to match those emitted at the tailpipe and how long it takes for the PAM to become ammonia free after an experiment. Meanwhile, ammonium nitrate has been shown to influence measurement of the CO₂⁺ fragment in the AMS by Pieber et al. This influence on CO₂⁺ is small, 0.4-10% of the nitrate mass, but is instrument dependent, and becomes larger when the error is propagated through the AMS fragmentation table to m/z 28 and so on. The O/C ratio is also affected. This may go part way to explaining the observed difference between the EEPs and AMS. Fortunately, this may be corrected for retrospectively using the CO₂⁺ signal from the initial ammonium nitrate calibration, and is recommended for measurements such as these, with a high ammonium nitrate fraction. How do wall losses in the PAM effect the observed organic mass concentrations? This is of course not easy to answer, but some consideration of the effect of particle losses and vapour

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losses (organic/ inorganic secondary precursors) is required.

Minor Comments

Pg 1 Ln 8: What does low or moderate mean in this context? It seems to contradict Pg 1 Ln 10: "particle mass measured downstream the PAM chamber, was 6-184 times as high as the mass of the emitted primary exhaust particles." Presumably, the authors mean in absolute mass, but please clarify.

Pg 1 Ln 20: This last statement is too strong given the limited scope of the study (See major comments).

Pg 2, introduction: The recent review of SOA from vehicles by Gentner et al. should be cited somewhere here.

Pg 3 Ln 31: Jathar et al. found that SOA formation from raw LNG is higher than from gasoline. This result is relevant to this introduction and to the discussion sections of this work.

Pg 4 Ln 9: What was the remaining 3% of the fuel?

Pg 4 Ln 11: How relevant are these engine conditions to real world driving?

Pg 4 Ln 26: Was the sampling system heated in any way? If not, how did this effect losses of secondary precursors?

Pg 6 Ln 12: How was CO₂ gas interference at m/z 44 corrected for?

Pg 6 Ln 34: 'Representative' of what? What do the other cases look like? A figure similar to Figure 4 which shows 'non-representative' results should be shown in the SI.

Pg 11 Ln 5: "With a decreasing catalyst temperature, the mass concentration and fraction of sulfate in total aged particles decreased (Fig. 4). This was expected; at lower catalyst temperatures, the oxidation of SO₂ to SO₃ decreases and less sulfuric acid (sulfates) can form (Arnold et al., 2012). The mass fraction of nitrate in secondary par-

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ticles increased with a decreasing catalyst temperature. This could not be explained by catalyst performance improvement: gaseous NO_x levels remained similar in all catalyst temperatures or rose with an increasing catalyst temperature (see Lehtoranta et al., 2016). Sulfate concentrations, however, could explain the behaviour of nitrate concentrations: If enough gaseous sulfuric acid is available, ammonium sulfate forms, and if not, more ammonium nitrate can form instead." How large was the decrease in sulfate (absolute mass) shown in Figure 4? According to table 1 this decrease is small for the SP-AMS. In quantitative/ stoichiometric terms is the decrease in mass of sulfate sufficient to explain the increase in ammonium nitrate? If the change in sulfate mass is rather small, and since the authors are using catalysts with urea reduction, shown to result in increasing ammonia selectivity (vs. NO) at lower temperature, is it not more likely that an increase in ammonia emissions at low temperatures causes the observed effects?

Pg 11 Ln 22. Why was a collection efficiency of 0.5 used? This is clearly suspect given the discrepancy between EEPS and AMS. What, in quantitative terms, would be the time dependent collection efficiency using the parametrization by Middlebrook and how would this effect the magnitude of the SOA formation and SOA/POA ratios?

Pg 12 Ln 1. The authors extrapolate from one natural gas engine to natural engines in general (see major comments).

References

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Science & Technology (2016). 4 Jathar, S. H. et al. Secondary organic aerosol formation from photo-oxidation of unburned fuel: Experimental results and implications for aerosol formation from combustion emissions. *Environmental Science and Technology* 47, 12886-12893 (2013). 5 Heeb, N. V. et al. Three-way catalyst-induced formation of ammonia—velocity- and acceleration-dependent emission factors. *Atmospheric Environment* 40, 5986-5997 (2006). 6 Middlebrook, A. M., Bahreini, R., Jimenez, J. L. & Canagaratna, M. R. Evaluation of composition-dependent collection efficiencies for the aerodyne aerosol mass spectrometer using field data. *Aerosol Science and Technology* 46, 258-271 (2012).

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