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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Effect of organic compounds on nanoparticle formation in diluted diesel exhaust" *by* U. Mathis et al.

U. Mathis et al.

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We thank the reviewer for his comments.

Comment 1a:

Nucleation particle formation is very sensitive to experimental conditions and authors have taken this already into account. However it would be rather useful to show how reproducible the formation of nucleation particles throughout the test series was. It needs to be shown that ageing effects of instrumentation or vehicle are responsible for observed effects.

Response:

The repeatability of the nucleation mode particles throughout the same test series is shown in Figure 5 for the four alcohols methanol, 2-propanol, 1-butanol, and 1-hexanol.

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All alcohols were tested on the same day without turning off the engine. The test was started with condition B. As soon as stable sampling conditions were achieved, the concentration of the first alcohol was varied. Before the next alcohol was tested, SMPS scans were recorded without adding any alcoholic vapor. As illustrated in Figure 5, the mode ratio of nucleation to soot particles was repeated each time before testing the next alcohol when no alcoholic vapor (saturation ratio = 0) was added. The test procedure was analogue for the conditions A and C. The mode ratio of nucleation to soot particles varied without alcoholic vapor (saturation ratio = 0) in a small range under these conditions. Therefore, the nucleation mode particles were found to be stable under all conditions (A, B and, C) within a time period of at least one hour.

Comment 1b:

The data points at 0% saturation ratio in figure 5 scatter from 0.02 to 0.25 for condition A, 0.2 to 0.63 at condition B and 2.2 to 3.6 at condition C, which already shows some instability occurring during these experiments. Data points at higher saturation ratios need to be addressed more carefully with respect to scatter, especially if effects are weak in cases of toluene, aniline, acetone and MTBE. I.e. effects observed might be only test-to-test variation!

Response:

Only a weak effect on the nucleation mode particles was found for toluene, aniline, and acetone. Since we observed a stable nucleation mode and a trend in the same direction under all three sampling conditions (A, B, and C), we conclude a clear but small effect on the volatile nanoparticles. Aniline is discussed below.

Because we conducted the measurement campaign within a week, the engine was restarted several times and a variation from test-to-test was unavoidable. We consider the test-to-test variation as uncritical since the interpretation of this data is based on relative changes within a test series. The differences of volatile nanoparticles observed from restarting the vehicle may be explained by the operation temperature of the oxi-

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dation catalyst. A small exhaust temperature variation can be responsible to alter the conversion rate from SO2 to SO3 by the oxidation catalyst.

Comment 1c:

Soot mode maxima presented in figures 3, 7, 8 and 9 vary between 1.0e8 and 1.6e8 cm-3 which is much larger than uncertainty in dilution ratio given in table 3. Please explain!

Response:

The speed was controlled within a very narrow range (+/- 0.1 km h-1), but a possible reason was the vehicle load variation of +/- 3 % at this very sensitive vehicle operation point. We totally conducted five series and thus, the engine was started five times. The variations of the accumulation mode particles during the test series without turning off the engine were in an acceptable range. We found increased soot particles in the series 5. The series 5 differed from the other test series with a higher particle mode concentration accompanied by slightly enhanced exhaust temperature and decreased CO2 concentration:

Series 1 to 4: 1.04e8 to 1.41e8 cm-3; 149.3 to 155.1 °C; 5.90 to 6.15 % CO2

Series 5: 1.54e8 to 1.75e8 cm-3; 157.7 to 159.7 °C; 5.85 % CO2

What are the implications on the nucleation mode particles? Within the series 5 hexane, cyclohexane, toluene, aniline, and acetone were investigated under the test condition C. As illustrated in Figure 5, there was only a weak effect on the nucleation mode particles under condition C: Without adding any organic compounds (saturation ratio = 0), the mode ratio of volatile to soot particles ranged from 2.9 to 3.6 for the series 5 (hexane, cyclohexane, toluene, aniline, and acetone) compared to a variation between 2.2 to 3.2 for the other series (MTBE and alcohols).

We totally conducted 30 different tests (10 compounds and 3 conditions). Within a single test series the variation of accumulation mode particles were small. We found a

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variation of less than 2 % for 37 % of the test series, between 2 % and 3 % for 43 % of the test series, and between 3 % and 7.5 % for 20 % of the test series.

Comment 1d:

Data on sulphate content particles would be very useful to show stable exhaust concentrations of this important nucleation precursor.

Response:

Since the mass of the nucleation mode particles is on such a low level, we were not able to conduct any chemical analysis.

Comment 2:

The introduction states very widely why nucleation particle formation might be important for ambient atmosphere, however the conclusions leave this point open. The observed effects need to be put in context with atmospheric conditions and if they would have implications for ambient air.

Response:

We mainly refer to the nucleation process that occurs during dilution of exhaust from internal combustion engines in the introduction chapter. The objective of our study is to gain a better understanding of the functional groups involved in the nucleation process of diluted exhaust. Therefore, we restricted our discussions and conclusions on parameters that directly affected this nucleation process without considering other nucleation processes in the atmosphere.

Comment 3:

Experimental, second paragraph: 99% rel. Hum. at dilution point raises the question about the possible effects within the residence time volume due to cooling, increase in rel. humidity or condensation. Has the residence volume been kept at respective sample temperature or how has this been accounted for with respect to data evaluation?

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Response:

A relative sample humidity of 99 % was only applied to investigate the humidity effect on volatile nanoparticles as shown in Figure 3 (top panel). When organic compounds were added into the dilution air, a relative sample humidity of maximum 81.2 +/- 3.8% (condition B) was used.

The relative sample humidity was calculated at ambient temperature because a fast cooling of the diluted exhaust was achieved.

Comment 4:

Results and discussions, chapter 3.2.2: The possible explanation for aniline effect given implies a removal process involving ionic reactions in gas phase, which are unlikely, since this typically requires a solvent (e.g. water). Further it is stated this would form particles in the size range of accumulation mode particles, which is also unlikely, because reactions of gas-phase compounds would form very small new particles might grow and appear in the nucleation mode.

Response:

We agree with the reviewer that our interpretation is speculative. A reduction of volatile nanoparticles was found under condition A and B (see Figure 5) and was not clearly supported by the condition C. We will revise this chapter according to the reviewer's comment.

Comment 5:

Results and discussions, chapter 3.2.5: The authors introduce the idea of a surface tension effect changed by different alcohols in conjunction with water solubility, water miscibility and concentrations (saturation ratios). This needs to be baked by solid data. I.e. it needs to be shown that the surface tension is lowered according to above parameters in the same order as nucleation is increased, otherwise the explanation should only be stated as "possibly".

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Response:

We agree with the reviewer that our statement "increasing water solubility and decreasing surface tension led to stronger nucleation" cannot be generalized. Since the effect on the nucleation mode particles was similar for methanol and 1-butanol, no clear conclusion can be drawn for these compounds. We will revise this chapter according to the reviewer's comment

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Interactive comment on Atmos. Chem. Phys. Discuss., 4, 227, 2004.

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