

Interactive comment on “Real-time characterization of particle-bound polycyclic aromatic hydrocarbons in ambient aerosols and from motor-vehicle exhaust” by A. Polidori et al.

A. Polidori et al.

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Dear Reviewer #2,

We would like to thank you for your very constructive suggestions. We believe that the reviewer's comments have been properly addressed and that, as a result, the revised document has been substantially improved, and the Figures more accurately described. Our responses to the reviewer's specific observations follow.

Reviewer #2: This manuscript presents measurements of particles in Los Angeles and from dynamometer testing of diesel trucks. In the introduction, the authors make a good case for monitoring the temporal variation in polycyclic aromatic hydrocarbons (PAHs), which they are able to do with the photoelectric aerosol sensor. The work is

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comprehensive in its scope, spanning detailed size distributions and chemical composition to risk assessment. The particle characterization results contribute to knowledge about the relationship between size, black carbon, and PAHs as a function of time of day, in the case of ambient measurements, and engine load, in the case of dynamometer measurements. My one quibble is that there is no linkage between the ambient and dynamometer measurements; they seem randomly thrown together.

Authors: As described in the text, the sampling site was located between two major freeways (the I-110 and the I-710), and vehicle emissions (especially those from diesel-fuelled-vehicles) represent the most important source of p-PAHs in Wilmington. In the authors' view, it is evident that characterizing p-PAH emissions from diesel trucks by means of dynamometer tests (using an experimental set-up similar to that employed for ambient measurements) will help to improve our understanding of how vehicular traffic influences the p-PAH levels at the studied Wilmington site throughout the day.

Reviewer #2: The writing and figures are clearly presented, although the accuracy in describing the figures could be improved (see specific comments below). Probably as a result of the broad scope, the manuscript does not explore the dynamometer results as deeply as it could. Given that SCRT controls on diesel-powered vehicles are likely to become much more widespread in the future, the data associated with their testing are important. Greater emphasis could be placed on the magnitude of particulate reductions associated with the SCRT vehicles, whether Zeolite versus vanadium makes a difference, and the relationship of emissions to engine load.

Authors: The reviewer's observations about SCRT control technologies are important and correct. Because of space limitations we couldn't address the differences in particle reduction associated with using Zeolite-based or Vanadium-based catalytic converters. However, this and other important issues related to the use of SCRT technologies are the focus of another paper conducted at the same dynamometer facility (using the same test-vehicles and experimental set-up described in here) that has just been submitted for publication in "Atmospheric Environment" by our research group (the title is

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reported below)

"Physical Properties of Particulate Matter (PM) from Newer Heavy Duty Diesel Vehicles Operating with Advanced PM and NOx Emission Control Technologies"

1. Reviewer #2: (p. 17483, line 6) Table 1 seems un-necessary, given that most of the information in it is the same for all three vehicles. The only differences between vehicles are the control technology (already explained in the text) and the mileage, which could easily be mentioned in the text.

Authors: Although it is true that the truck mileage can easily be incorporated in the main text, Table 1 summarizes several important information (e.g. vehicle brand, engine size, dilution, GVWR, etc.) that someone interested in dynamometer studies might be happy to see.

2. Reviewer #2: (p. 17484, line 4) Was there any difference in weekday versus weekend concentrations?

Authors: The average diurnal variations of the PAS and NSAM signals and of the PN and BC concentrations were similar both on weekends and during weekdays, although the magnitude of the weekend concentrations was generally smaller, probably because of the reduced traffic activity around the port area on Saturdays and Sundays.

3. Reviewer #2: (p. 17484, line 7) A lower mixing height in the morning would also contribute to higher ambient concentrations. The importance of the mixing height is borne out by the observation stated in line 12 that concentrations were 4-8 times higher between 09:00-11:00 than between 17:00-18:00, even though we would expect heavy traffic during the evening rush hour, too.

Authors: We agree with the reviewer's comment, although we believe that the peak concentrations observed during rush hour traffic are mainly due to the close proximity of the Wilmington site to both the I-110 and the I-710 freeways. The predominant role of vehicle emissions in increasing the ambient concentrations of fine PM (and

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of its particle components) in the early morning has been demonstrated in several other works conducted in the same area by our research group (see, Ning, Z., Geller, M.D., Moore, K.F., Sheesley, R., Schauer, J.J., Sioutas, C. Daily variation in chemical characteristics of urban ultrafine aerosols and inference of their sources, *Environmental Science & Technology*, 41 (17): 6000-6006, 2007, for example).

4. Reviewer #2: (p. 17484, line 26) The statement that the Zeolite SCRT vehicle is not equipped with any kind of catalytic trap is confusing given that the Methods section already described the SCRT system as containing selective catalytic reduction and a continuously regenerating trap. So does this vehicle have SCR only and no particle removal system?

Authors: The reviewer's observation is correct and the text (starting from page 17484, line 23) was modified to "Figure 2 shows time series of the PAS and EAD (DC) signals for the "baseline" (2a) and the Zeolite-based SCRT vehicles (2b) operated in UDDS mode; both trucks are diesel-fuelled, although the former is not equipped with any type of catalytic trap."

5. Reviewer #2: (p. 17484, line 26) Figure 2b does not show an obvious inverse correlation between PAS and EAD signals. Rather, it appears that PAS seems to go with accelerations, and EAD pops up on three separate occasions. When EAD is high, it is not obvious from the figure that the PAS signal is lower than it would be otherwise.

Authors: In the authors' view the EAD signal doesn't "pop" randomly, but an increase in the EAD signal (given to the production of particles with a high surface area) is accompanied by a correspondent decrease in the PAS signal (Figure 2). As observed in the analysis of our ambient data (and in previous publications), the presence of large particles in the analyzed aerosol (especially if coated with condensable species with weak photo-emitting properties) tends to suppress the PAS signal.

6. Reviewer #2: (p. 17486, line 1) Figure 3a certainly shows considerable spread in the PAS/NSAM ratio, but it does not appear to have "two branches." If there were

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two separate branches, I would expect to see an obvious separation between them. Instead, the data points seem to be continuously distributed between two boundaries.

Authors: We agree with the reviewer's comment and the text was modified to "As shown in Figure 3a, the PAS versus NSAM plot obtained in Wilmington is characterized by measurements that are continuously distributed between two boundaries. This indicates the presence of both nucleation/aged accumulation mode (lower boundary) and fresh accumulation mode (upper boundary) particles; the majority of data-points was scattered in between."

7. Reviewer #2: (p. 17487, line 20) Same comment as above about the existence of "two branches."

Authors: Also in this case the text was changed to "Similarly to what was observed in Wilmington, the PAS versus NSAM plot consists of data-points that are uniformly distributed between two boundaries (Figure 5a). However, when measurements were segregated based..."

8. Reviewer #2: (p. 17487, line 27) In Figures 5c and 5d, a shift from the nucleation to accumulation mode is not obvious. Does the line in the figure indicate the arithmetic mean or the median? The evidence for a shift should be quantified.

Authors: The authors replaced Figure 5d with a different example, and added 2 footnotes to clarify a few points (please see re-submitted manuscript)

9. Reviewer #2: (p. 17488, line 5) The meaning of "bimodal bursts of the PAS signal" is unclear.

Authors: This part of the text was modified to "Very different results were observed for the PAS versus EAD plots of vehicles equipped with SCRT emission control technologies and operating in the UDDS cycle. Distinct spikes in the PAS signal were clearly detected when plotting all data-points collected while testing the catalyst-equipped vehicles (data not shown)." Here, the authors' intention was to avoid adding 2 more Fig-

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ures and save some space.

10. Reviewer #2: (p. 17488, line 11) The authors defined accumulation mode particles as those with diameters of 50-60 nm. Here, they claim that higher numbers of accumulation mode particles were observed at start-up, but in Figure 6b, it appears that the numbers are higher during acceleration compared to start-up. The explanation that follows about the catalyst not being warm enough to convert SO₂ to particulate sulfate seems to contradict the claim. If the catalyst is supposed to convert SO₂ to particulate sulfate and were not warm enough during start-up, then we would expect lower particle numbers (as suggested by the figure) during start-up.

Authors: The reviewer's observation is correct and, thus, we modified the text to "Also, a lower relative contribution of nucleation mode particles to the measured particle number concentration was observed at start-up (Figure 6b), probably because the engine temperature was not high enough to activate the catalyst (Vanadium or Zeolite) and, thus, to convert gaseous SO₂ to particulate sulfate."

11. Reviewer #2: (p. 17489, line 6) Provide units on the regression slope between the PAS signal and total PAHs. If the units are ng per cubic meter per fA, then the value of 17.5 is considerably higher than the manufacturer's range of 0.3-1, Arnott et al.(2005,EST, 39:5398-5406) finding of 0.11, and Wilson et al. (1994, Polycyclic Aromatic Compounds, 5: 167-174) finding of 1. Please look into this.

Authors: Right before this study began, the PAS was sent back to the manufacturer (EcoChem Analytics; <http://www.ecochem.biz/>) for calibration. The EcoChem technicians we spoke to told us that the signal of our instruments is reported in fA, and that its magnitude was within the expected range. We are not exactly sure why a PAS-pPAH (y-axes) vs Sum-of-PAHs (x-axes) plot would produce such a different in the magnitude of the regression slope, but it is possible that a higher than normal value (17.5) is due to the relatively low pPAH concentrations (ng/m³) detected at our sampling site (in this types of plots the higher the pPAH concentration, the lower the regression slope). In

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addition, the magnitude of our PAS signal (fA) is well comparable with that reported in similar ambient measurements by Bukowiecki et al. (Aerosol Science 33, 1139-1154, 2002).

Technical corrections 12. Reviewer #2: (p. 17476, line 12) "catalytic converted" should be "catalytic converter"

Authors: The change was made

13. Reviewer #2: (p. 17477, lines 18-21) As written, the sentence makes it sound like the Pope study looked at PAHs, when in reality, it looked at fine particles.

Authors: We agree with the reviewer's comments and modified this sentence to "Fine and ultrafine particles (and, thus, the PAHs bound to them) can penetrate deeply into the bronchial and pulmonary part of the human respiratory system, where their deposit and accumulation has been associated with short and long term health effects (Pope et al., 2002; 2004)."

14. Reviewer #2: (p. 17479, line 12) "Air Resource Board" should be "Air Resources Board"

Authors: The change was made

15. Reviewer #2: (p. 17480, line 2) "Souvain" should be "Sauvain"

Authors: The change was made

16. Reviewer #2: (p. 17491, line 8) The slope for methylanthalene is incorrect.

Authors: The slope was changed to the correct value (188.3)

17. Reviewer #2: (p. 17497) Marr et al. (1999) is missing from the references.

Authors: The missing reference was added to the main text

18. Reviewer #2: (p. 17497) All Riddle et al. (2007a) authors should be listed.

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Authors: All authors were listed

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 17475, 2007.

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