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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A study on the relationship between mass concentrations, chemistry and number size distribution of urban fine aerosols in Milan, Barcelona and London" *by* S. Rodríguez et al.

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First of all, we would like to thank to the anonymous referee #1 for his constructive comments, which definitively help to improve the manuscript. The replies to the referee's questions are listed below. Most of the suggestions have been introduced in the manuscript and will appear in the final version of the manuscript after the discussion period.

Comments are addressed following the order of the referee's questions.

-p. 611, lines 9-14. About the factors. The factors (slope including the r2 linked to

the linear regression) have been added to the text. Different techniques were used at each site, so these factors will not be comparable owing to they have different physical meanings (gravimetric versus DMA-volume at Milan; gravimetric versus OPC-volume at Barcelona; gravimetric versus TEOM-mass at London).

-p. 612, lines 23-25. Meaning of "The difference PM2.5 (MILAN) minus PM2.5 (BARCELONA or LONDON): 15ugPM2.5/m3 = 7.0ugNO3-/m3 +5.5ugOM/m3 +2.5ugNH4+/m3". Actually, the sentence is not very clear in the text. This has been rewritten as:

The difference of the concentrations of PM2.5, NO3-, OM and NH4+ 'Milan minus Barcelona' (D) and 'Milan minus London' (D) fit very well to this equation: "15ugDPM2.5/m3 = 7.0ugDNO3-/m3 +5.5ugDOM/m3 +2.5ugDNH4+/m3" (for each of these differences: 'Milan-Barcelona' and 'Milan-London'). This indicates that the PM2.5 concentrations at Milan are 15ug/m3 higher than in Barcelona and London because a mean contribution of 7.0ugNO3-/m3 +5.5ugOM/m3 +2.5ugNH4+/m3.

-p. 613, lines 15-17. About the concentration ratio. We agree with the referee, a ratio do not mean necessarily that the concentrations are higher. We tried to express here that the concentrations of ultrafine particles experiences a higher "night-to-morning rush hours" increase than that experienced by the number of particles$>$0.1μm. This night-to-morning increase is quantified by the ratio shown in Figure 4. Because it may be that the sentence is not definitively clear, we have rewritten it as follow:

"Road traffic emissions result in a higher night-to-morning increase in the concentrations of ultrafine ($<$100nm) than in the coarser particles (Figure 4)".

-p. 614, lines 6-9. About the contribution of coagulation to the high "morning / night" concentrations ratio. We agree with the referee, the effects of coagulation and the subsequent explanations can not be concluded from Figure 4. This figure is cited just to reference to the concentrations ratio. The effects of coagulation are deduced from this analysis: "at night a significant increase in the particles diameter is observed (see

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in Figure 3C the size distribution modes). This can be explained by two possible microphysical processes: 1) condensation, and 2) coagulation. Condensation prompts a simultaneous increase in the particles size and in the particles PM2.5 mass concentrations, but does not decrease the number concentration. Coagulation decreases the number concentration. In order to let clear in the text why this Figure is cited, we have changed the site where the Figure 4 is cited in the sentence referred by the referee:

“Particle growth by coagulation in short time scales (˜hours) is the origin of the low residence time of particles <50nm that we have observed, and contributes to the above cited (Figure 4) high ‘morning-rush hours’ and ‘daylight’ to ‘nocturnal-background’ concentrations ratios”.

-p. 614, lines 18-19. About the concentration of particle N10-100 in Figure 3A1-B1. This has been introduced in the Figure.

-p. 614, lines 22-23. About the concentration of particle N>100(nm) in Figure 3. This has been introduced in the Figure.

-p. 618, lines 18-21. About the correlation between PM2.5 and N>100(nm) in Figure 7. Yes, no correlation coefficient is shown in Figure 7. We tried to express that PM2.5 and N>100(nm) exhibits correlated temporal variations, and this can be observed in Figure 7. We have rewritten this sentence in order to express this properly:

“the degree of correlation between PM2.5 and the number concentration changes significantly depending on the particle size. Observe, in the examples shown in Fig. 7, how: 1) N>100(nm) and PM2.5 tend to exhibit correlated temporal variations, 2) Ĕ..”

-About the amount of data shown in Figures 3 and 6. These Figures have been modified in order to provide only the necessary data (i.e. those included in the discussion) and improve the caption.

- About SO2 in the Figures 3 and 5. The role of SO2 is not described explicitly, but included in p614 lines 27-28. Because SO2 has strong contributions from other sources

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different to road traffic (industrial ones), its daily evolution does not correlate with that of number concentration as strongly as the “number concentrations and road traffic derived gaseous pollutants (NOx and CO) correlates”. This is important owing to the fact vehicles using sulphured fuels emit SO2 which may contribute to N by relatively fast nucleation processes. The sentence cited by the referee has been reworded as (p614, following line 28):

“3) the daily evolution of CO and NOx (main road traffic derived gas pollutants) correlates better with the number concentration N than with PM2.5 (Figs. 5a2-d2)”.

This sentence was added:

“4) only at London the number concentration and SO2 exhibits a significant correlation. This is probably due to the influence of other processes and sources contributing to the SO2 daily cycle at Barcelona and Milan, probably industrial emissions and subsequent fumigations within the conurbation (power plants and other industrial activities). This is important owing to the fact that vehicles using sulphured fuels are important potential contributors to the ambient air particles number concentration (Wåhlin et al., 2001).

Wåhlin, P., Palmgren, F., Van Dingenen, R., Raes, F., 2001. Pronounced decrease of ambient particle number emissions from diesel traffic in Denmark after reduction of the sulphur content in diesel fuel. Atmospheric Environment 35 3549-3552.

- About Fig 4 A2 and 4B2. This Figure includes the concentrations ratio for PM2.5 and the total number concentration, which are not included in Figure A1 and B1. Moreover, the ratios for the number concentrations of particles $<$0.1um (as a whole) and $>$0.1um (as a whole) are included to be compared with those of PM2.5 and N. We think that comparing the values of the N$>$10(nm) and PM2.5 ratios with those of N10-100 and N$>$100(nm) as a whole is important. Among other points, it shows how the ratio: 1) for the total number concentration is very close to that of the ultrafine particle, and 2) for PM2.5 is very close to that of N$>$100(nm). This is important for understating with the relationship between size distribution and the total number concentration (mostly

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weighted by ultrafine particles) and PM2.5 (mostly weighted by particles >0.1um).

- Are the Fig 5 A3, B3, C3, D3 necessary? We considered that the Fig 5, A3, B3, C3, D3 are important for the same reasons provided above for the Figures 4 A2 and B2. It shows how the total number concentration N>10(nm) tend to exhibit a behaviour very close to that of the ultrafine particles (because these are the min contributor to N>10 (nm), whereas N>100(nm) tend to exhibit a behaviour close to that of PM2.5.

- Why Fig 6A and 6E (both showing PM2.5) are so much different? This is due to the fact that Figure 6A shows daily mean PM2.5 concentrations based in 1 sampling day every 4 days, whereas Figure 6E shows the continuous hourly mean concentrations of PM2.5. So, Figures 6A and 6E are complementary.

- Fig 9A: Why correlation coefficient is much better in Milan than in London or Barcelona? With our data base we can not provide a definitive explanation for this. In Figure 9, can be observed how the much higher correlation at Milan (with respect to the other sites) is enhanced in the particles size >100nm. We speculate that this may be the result of the confluence of several facts: 1) the number concentration of particles >100nm is much higher in Milan than in the other site, 2) mineral dust concentrations are much higher in Barcelona than in the other sites, and this mineral dust significantly contributes to the mass but not to the number concentration (because of the much high density of mineral dust when compared to that of other aerosol compounds).

- Fig 9B: This figure contains additional information compared to Fig. 9A? The reason to add Figure 9 is the same than for adding Figures 4A2, 4B2, 5A3, 5B3, 5C3, 5D3, 10B1, 10B2 and 10B3. All these Figures showing the number concentration N10-100 and N>100(nm) as a whole (together with the discussions in the text) shows how the behaviour and properties of PM2.5 are mainly weighted by the particles with a diameter >100nm and the microphysical processes occurring in this range, i.e. in the particles within the “accumulation mode”. In contrast, the total number concentration is mainly weighted by the ultrafine mode and the microphysical processes occurring in this range.

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We understand that it may be possible that this has not been highlighted properly in the text of the manuscript, but will be done in the final version after the discussions period.

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