Reply to comments from referee #2

Thank you very much for your positive observations on our paper. We also thank you very much for your critical comments and suggestions that we are taking into account in the revised version and that improved the quality of our manuscript.

General comments

1.   First of all, the MS is very difficult to read and follow in detail. According to the present reviewer, it should be somewhat shortened and clarified, some figures are unnecessary over-sophisticated, and many variables are handled at a time. It should be more emphasized that the results for S-L9 station concern two different ventilation regimes, which - as the authors demonstrated nicely - has a huge impact on the concentration levels. Strictly speaking, these two periods are only comparable with limitations.
        OUR REPLY: Yes, referee #1 also pointed to this problem. We have reduced the number of figures from 11 to 9, and tables from 7 to 5, as suggested and moved them to supplementary information. We have shortened text from sections 4.2. and 4.3. We also added recent results to support this important effect of the ventilation system.

2. Air flow within the tunnels and in the platforms can be substantial. This leads to wind erosion which is not included into the list of main emission sources (Page 6658, lines 18-26), and it is not discussed at later stages. This should be adopted.
        OUR REPLY: Done, added and discussed in the revised version.

3. The authors should revise their rounding off strategy at many places in the text and tables. Here is an example from page 6666, line 4: 1.442±0.2. The number of significant
digits - as it is for the former value - often suggests that the relative precision
is better than 1%. This is generally questionable and it requires additional discussion and explanation.
        OUR REPLY: Done, revised across text and tables.

4. The author's statement on page 6671, lines 21-23, and 6680, lines 4-5 that they were the first to identify the major Fe species is not fully correct. There were indeed only few papers dealing with the chemical speciation of elements, mainly transition metals in metros published earlier. Nevertheless, there are some, which are missing from the MS. Their list definitely includes the following articles 1) Karlsson et al., Subway particles are more genotoxic than street particles and include oxidative stress in cultured human lung cells. Chemical Research in Toxicology 18, 19-23, 2005, 2) Karlsson et al., Mechanisms related to the genotoxicity of particles in the subway and from other sources. Chemical Research in Toxicology 21, 726-731, 2008, and 3) Salma et al., Properties and sources of individual particles and some chemical species in the aerosol of a metropolitan underground railway station, Atmospheric Environment 43, 3460-3466, 2009. These papers and the important and relevant information contained therein should also be included into the present MS, and the discussion on the speciation of Fe should be modified accordingly, and should be put into an international frame.
        OUR REPLY: Indeed we changed this text to : The high proportion of atmospheric iron present in underground steel wheel metro systems has been documented previously (Seaton et al., 2005, Adams et al., 2001a and b, Aarnio et al., 2005). Here we show that the dominant iron species is hematite (as deduced from XRD analysis). Salma et al. (2009) showed by means of Mössbauer spectroscopy, microscopy and XRD analysis that the particles in the Budapest' metro were dominantly made up of Fe-rich particles in the PM2.0 size fraction typically consisted of

aggregates of nano-sized hematite crystals that were randomly oriented, had round shapes and diameters of 5–15 nm). In addition to hematite they found, a minor fraction of the iron oxide particles also contained magnetite. Further constituents, such as ferrite, carbides and FeOOH were also identified. Magnetite was also found by Karlsson et al. (2008 and 2005) in the Stockholm subway system by XRD.
We also added the 2 new references (one of them we had already in the list) and and additional comment: …….Karlsson et al. (2005 and 2008) found that the subway particles were approximately four times more likely to cause oxidative stress in the lung cells than outdoor urban PM in Stockholm, and this may be due to the high metal load.

5. The authors also measured the ambient atmospheric concentrations for several aerosol constituents near the stations. This would allow them to calculate crustal enrichment factors (EFs) for both the metro aerosol and aerosol in the ambient urban air. The ratio of these two EFs represents an enrichment of an element relative to the urban air. This quantity could help in further identifying or confirming some emission sources. It is advised that this characteristics is calculated at least for selected elements such as Fe, Cr, Ba, Mn, As and Cu.

OUR REPLY: We preceded to EFs calculations and we added the following paragraphs to the discussion section on this issue: "If the Enrichment Factors (EF) with respect to the mean upper crust contents of major and trace elements (Rudnick and Gao, 2003) are calculated for the elements analyzed in the S-L9 and F-L3 platforms and the outdoor PM2.5 concentrations the following evidences were obtained:
•   A number of elements are depleted compared with the crustal concentrations. These are the typical crustal components, with EFs <0.1: Al2O3, TiO2, Na K, Rb, Y; and EFs in the range 0.1-0.5: Mg, Th, V, REEs, Nb, Ga, Li and Ba at S_L9.
•   Elements with similar concentrations to the upper crust: EFs in the range 0.5-2.0 Ca, Co, Ni, Zr, U
•   Elements enriched with different degree in the subway PM compared with the crust: EFs in the range 2.0-5.0: Mn, Cr, Ge, As at S-L9, Pb and Bi; EFs reaching 5-15: W, Fe2O3 and Cd; EFs in the range of 15-60: Zn, Ba and As at F-L3, Sn and Mo and Cu at S-L9, EFs reaching 60-225: Cu and Mo at F-L3, and 300-800: Sb.

When the EF are calculated for the outdoor PM2.5 a similar enrichment/depletion degrees were obtained for a number of elements, but not for the following ones:
•   Elements enriched in the subway PM but depleted in outdoor PM2.5 with respect the crust: Mn, Cr, Co, and Fe 2O3.
•   Elements enriched and not depleted (as in the subway PM) with respect the crust: V.
•   Elements enriched in the subway PM but much less enriched in the outdoor PM2.5: Cu (EF of 17 instead of 30-146), As (3 instead 3-17), W (3 instead of 6-9), Sb (119 instead of 444-800).
•   Elements with much higher EFs in outdoor PM2.5 compared with subway PM: Cd (53 instead 10), Pb (22 instead of 1-4) and Bi (59 instead of 4-6)."

Detailed comments

6. Page 6656, line 13 and many other places in the text I would suggest that the unit expressed as "µg PM_x mˆ(-3)" is avoided, and the correct unit for PM_x mass concentration of "µg mˆ(-3)" is used instead.
OUR REPLY: Done, revised across text.

7. Page 6658, line 7. The authors may want to write passenger car instead of private car.
OUR REPLY: Changed.
8. Page 6662, line 8. Replace: opened 2009 by opened in 2009.

OUR REPLY: Changed.

9. Page 6664, lines. 25-27 Explanation needed for "the coarse fraction retained in the PM2.5 cut of inlets". Does this mean that the particles from the pre-selection device were further investigated?
OUR REPLY: Yes, as stated in the text these were used for SEM and XRD analyses.

10. Page 6666, line 23 Full stop needed.
OUR REPLY: Text is changed now.

11. Page 6666, line 25 Rewording is advices for "extraction well is extracting".
OUR REPLY: This text is changed now.

12. Page 6669, line 11 Correct wording to "by buses or cars".
OUR REPLY: Changed.

13. Page 6673, line 19 Put a space between 1.5µg.
OUR REPLY: Changed.

14. Page 6679, lines 20-21 It is not completely clear what the next sentence means: "In the Barcelona's Metro, levels of Fe ranged from 144 and 55 µgm−3 in PM10 and PM2.5 respectively, for F-L3 to 9 µgm−3 in PM10 for the first 8 days at S-L9...". Rewording is required.
OUR REPLY: Changed.

15. Page 6705, Fig. 3 The axis label and scale for the abscissa is missing.
OUR REPLY: Added.

16. Page 6706, Fig. 4 It is extremely difficult to differentiate between the curves for PM2.5 and PM1 in Fig. 4. Another solution for this would be appreciated.
OUR REPLY: We leaved as it was. PM2.5 levels are clear. PM1 levels were very similar but we could not correct the optical values vs a gravimetric high vol sampler for PM1. We are less sure on the accuracy of PM1. We would like to show that PM1 and PM2.5 levels are very close.

17. Some other smaller typing errors should also be corrected.
OUR REPLY: Changed when detected.