Response to Anonymous Referee #1

Review of "How much is particulate matter near the ground influenced by upper level processes within and above the PBL? A summertime case study in Milan (Italy)" by Curci et al.

This study uses field data in Milan, Italy in 2007 along with WRF/CHEM modeling to investigate what the composition is of aerosol layers formed at the top of the boundary layer during the day, how much of the surface aerosol layer is from entrainment of aerosols aloft, and how much these layers aloft contribute to surface concentrations on the following day. The topic is of interest to this journal. This topic has not received that much attention and this paper adds to the growing body of knowledge about how aerosol layers above the PBL can influence the surface layer. The authors focus on one case event and treat it in depth and reach interesting conclusions that are worthy of publication. The paper requires minor English editing. Prior to publication, the authors should address the issues below.

The authors thank the reviewer for careful reading and valuable comments which improved the clarity of the manuscript. The paper was revised following reviewer's suggestions as detailed below. Moreover, English was edited in the revised version of the manuscript.

Specific Comments:

Page 26405, Line 2: I suggest changing "yield" to "lead"

Done.

Page 26405, Line 11: change "evidences" to "evidence"

Done.

Pg 26406, Line 2: remove "the" before "atmospheric"

Done.

Page 26407, Line 26: Could another reason for why winter PM is high is low-level residential combustion for heating purposes?

There are certainly more emissions for heating in winter. Actually, biomass burning was reported as a dominant winter PM source, at least for the organic fraction (Gelencser et al., 2007; Gilardoni et al., 2011). This source includes wood burning for domestic heating. However, in summer there are likely enhanced biogenic and soil erosion sources, with respect to winter. Thus changed primary emissions were not listed among the driving factors of winter/summer PM differences in the Po Valley in the studies we refer to, in that part of the manuscript (Barnaba et al.). We thus preferred to leave the sentence unchanged in the revised manuscript.

Gelencser, A., B. May, D. Simpson, A. Sanchez-Ochoa, A. Kasper-Giebl, H. Puxbaum, A. Caseiro, C. Pio, and M. Legrand (2007), Source apportionment of PM2.5 organic aerosol over Europe: Primary/secondary, natural/anthropogenic, and fossil/biogenic origin, J. Geophys. Res., 112, D23S04, doi:10.1029/2006JD008094.

Gilardoni, S., Vignati, E., Cavalli, F., Putaud, J. P., Larsen, B. R., Karl, M., Stenström, K., Genberg, J., Henne, S., and Dentener, F.: Better constraints on sources of carbonaceous aerosols using a combined 14C – macro tracer analysis in a European rural background site, Atmos. Chem. Phys., 11, 5685-5700, doi:10.5194/acp-11-5685-2011, 2011.

Page 26408, Line 1-6: The authors should improve the balance of this paragraph's discussion to also mention other airborne data that have shown that secondarily produced species can be higher aloft than at the surface. Such studies shown below have pointed to the importance of clouds and relative humidity in leading to higher mass concentrations of aerosol species aloft. Duong et al. (2011). Water-soluble organic aerosol in the Los Angeles Basin and outflow regions: Airborne and ground measurements during the 2010 CalNex field campaign, J. Geophys. Res., 116, D00V04, doi:10.1029/2011JD016674.

Wonaschuetz et al. (2012). Aerosol and gas re-distribution by shallow cumulus clouds: an investigation using airborne measurements, J. Geophys. Res., 117, D17202, doi:10.1029/2012JD018089.

Heald et al. (2006), Concentrations and sources of organic carbon aerosols in the free troposphere over North America, J. Geophys. Res., 111, D23S47, doi:10.1029/2006JD007705.

Novakov et al. (1997), Airborne measurements of carbonaceous aerosols on the East Coast of the United States, J. Geophys. Res., 102(D25), 30,023–30,030, doi:10.1029/97JD02793.

We thank the reviewer for bringing to our attention those interesting studies, which add further observational evidence of the presence of enhanced aerosol layers above the surface. We added a related sentence at the end of the paragraph: "Moreover, the presence of aerosol layers enriched with sulfate and water-soluble carbonaceous matter was observed above the boundary layer or in convective clouds during several aircraft campaigns over North America (Novakov et al., 1997; Heald et al., 2006; Duong et al., 2011; Wonaschuetz et al., 2012), and attributed to biomass burning plumes or aqueous-chemistry processes."

Page 26410, last line and into next page: this sentence confuses me about why nitrate is in the coarse fraction due to ammonium being neutralized by sulfate. If sulfate is fully neutralized by ammonium it would seem that if there is any more ammonia present that it can then interact with nitric acid to produce ammonium nitrate, which typically is in the fine mode. Based on literature (see for instance: Lee et al. (2008), Observations of fine and coarse particle nitrate at several rural locations in the United States, Atmos. Environ., 42, 2720–2732, doi:10.1016/j.atmosenv.2007.05.016.), coarse mode nitrate originate from interactions of nitric acid with coarse particle types such as mineral dust and sea salt. This sentence should be revised as it currently confuses this reviewer.

We agree with the reviewer that the original sentence may be confusing, and acknowledge that the reviewer correctly guessed the real intended meaning. We reformulated the sentence as follows: "In summer, nitrate can exhibit a broader size distribution as a larger fraction may also form in the coarse mode. Higher temperatures, lower humidity, higher load of sulphate competing for the uptake of ammonia, are less favourable to ammonium nitrate accumulation in the fine mode. As a consequence, more nitric acid is available to react with soil dust or sea salt leading to the formation of mineral nitrate on coarse particles.". We also added the suggested reference Lee et al., 2008.

Page 26414, Line 9: A period is missing after "measurements"

Done.

Page 26424, Line 1: Can the authors be more clear when they say it is "visible e.g. on 16-17 July in both observations and models". Are readers supposed to know this clearly from looking at specific figures? If so, what figures and be specific as to how readers will know that this is visible.

First of all we corrected a wrong reference to Hodzic et al. (2006) to Hodzic et al. (2004) at the beginning of the same paragraph. We agree with the reviewer that the sentence is obscure and ambiguous. We now revised the last part of the paragraph for a more clear and sharp guidance to the features we would like to bring to reader's eyes. We now focus on days 14-16 July, in place of 16-17 July, because they better illustrate those features. Here is the revised part of the paragraph: "Then, in the afternoon, the mountain-valley breeze cleans the lower PBL (note the abrupt abatement of both the Lidar and the model aerosol signals in the second part of the day), often leaving an upper air aerosol residual layer above. Model simulations also reproduce such residual layers (note the afternoon increase of PM2.5 values in the upper levels, particularly visible on July 15-16). When such residual layers persists overnight, the Lidar shows these to entrain into the developing PBL the day after (note the merging of the upper level aerosol layers with the growing, aerosol-traced PBL in Figure 6a, particularly evident in the morning of July 14 and 15). There are hints of the same features also in model simulations."

Page 26427, Lines 4-8 and subsequent text: It is argued that nitrate is produce at higher altitudes due to more favorable RH values that allow for aqueous conversion of nitric acid to nitrate. But one major aspect of this argument that requires discussion is that if such aerosols aloft are then brought down to the surface, wouldn't the aerosols get dried at lower RHs and then the nitrate evaporates back out? For the case of cloud droplets for instance, it has been shown in past studies that evaporation of drops leads to losses of nitrate back to the gas phase. Also, in the discussion in this same section, I was hoping the authors could discuss whether the ambient multicomponent particles would be expected to deliquesce at the DRH point of ammonium nitrate or at a different RH. Past work has shown that the DRH varies from the pure salt form when there are other components included, and it can be argued that it is more practical to assume that the aerosols in the region will deliquesce at a point other than the DRH of ammonium nitrate.

The nitrate layer formed in the upper PBL during the day indeed forms because nitrate re-evaporates back to the gas phase when brought back near the ground by vertical turbulent motions. It's exactly the reason why the nitrate profile is not homogeneous, as it is the case for sulfate. Thus the contribution to surface nitrate from this upper layer is expected to be very small, if not negative, during daytime. This point is indeed highlighted for days 13 and 16 July in the subsequent paragraph of the manuscript, regarding the budget analysis of ground PM as contributed from different layers of the lower atmosphere (lower PBL, upper PBL, and above PBL). As also mentioned in that paragraph, if enough aerosol (including nitrate) survives the night in the layer above the PBL, it may entrain into the PBL the following morning and then effectively contribute to surface PM levels. However, we haven't pushed the latter budget to the detail of single species, since we feel that more observational constraints on the aerosol vertical profile should be available (which is not the case here) to support the modelling results.

Regarding the multicomponent DRH point we are aware that it is different from that of pure nitrate. However, it is known that multicomponent DRH point is always lower than that of single components (e.g. Seinfeld and Pandis, 2006), thus a more accurate calculation of the DRH would just make a broader layer for the potential aqueous formation of nitrate, but it will not change the substance of the discussion, i.e. that nitrate preferentially forms in the upper PBL and in aqueous form. The thickness of the layer favourable to nitrate formation deducible from Figure 12 may thus be regarded as a conservative lower estimate.

In order to improve clarity on these points, we added the following sentences at the end of the paragraph: "Although the real multicomponent DRH point will differ from that of pure nitrate, it is known that the DRH of mixtures is always lower than that of pure salts (Seinfeld and Pandis, 2006). The thickness of the layer favourable to aqueous nitrate formation deducible from Figure 12 may thus be regarded as a conservative lower estimate. During daytime, the nitrate formed in the upper boundary layer re-evaporates back to the gas phase when brought to the ground by vertical motions, and that's the origin of the

inhomogeneous vertical profile of nitrate. For further discussion on how much the upper aerosol layer contributes to ground PM we point the reader to the next paragraph.”

Figure 2 caption: should say “. . .shown in inset are. . .”

Figure 2 caption: should say “. . .shown in inset to. . .”

We believe the reviewer here refers to Figures 3 and 4. We added the sentence “Shown inset are statistical indices defined in Appendix A.” in the caption of both figures.

Figure S5 caption: “Rolf” is mis-spelled and should be “Rolph”

Done.

Figure 12: I recommend moving the text box off of the data curves as it is distracting.

Done.