

Responses to interactive comment on “Spatial variation of chemical composition and sources of submicron aerosol in Zurich: factor analysis of mobile aerosol mass spectrometer data” by Referee #2

This paper describes submicron refractory and black carbon particle composition measurements conducted from a mobile laboratory in Zurich for periods during two winters. The focus is on the deconvolution of the organic mass, measured by AMS, into PMF-derived source components and the estimation of the absolute and relative contributions of the different PM1 components in on-road location relative to “urban background” concentrations. PMF factors found were secondary oxidized organic aerosol (OOA), wood burning organic aerosol (WBOA), and hydrocarbon-like organic aerosol (HOA), largely consistent with other studies. One of the primary conclusions seems to be that HOA, BC and particle number concentration are significantly enhanced in the on-road measurement locations and secondary components such as OOA and inorganics in addition to WBOA are not.

As part of the basis for this analysis, it is shown that the off-road regions in this urban area show relatively uniform distribution of the components of interest. Strengths of the paper are the measurements and data analysis, including PMF, which required considerable expertise and were generally explained well. The results are important because they represent a relatively unique dataset of mobile measurements of aerosol composition in a European urban area.

However, much of the scientific interpretation and explanation of the observations is poorly written with many statements made with little to no justification. I suspect in many cases there are good arguments the authors can make to support their claims, thus I recommend that it be published after significant revisions are made to the text.

We thank Referee #2 for his/her comments and the detailed review of our manuscript. We will first respond to the main points and then address the specific comments further below.

Main Points:

There needs to be a clear discussion of and justification for use of the inorganic sulfate as a normalization factor for accounting for small scale variation in the PM1 concentrations. This is pitched as a “new method” in the abstract; however, the introduction/rational for this method states only that “the oxidation rate of gaseous SO₂ by OH being lower by a factor of ~10 compared to NO₂”. What is the significance of that comparison? Typically in most studies secondary products are normalized to primary components in order to account for dilution. It think many readers will think that is the rational for this normalization, but I’m pretty sure that is not the authors’ intention. This confusion is clear from the comments of referee #1. The authors seem to be using sulfate as a secondary component that forms more slowly than other secondary components (and of course primary components), and thus normalizing out effects of broader inhomogeneities in pollutant concentration, not effects from fresh emissions (in which case CO, BC, NO_x would be more appropriate).

Referee #2 is right, it was not our intention to normalize secondary products to primary components to account for dilution. This approach is usually used for the characterization of city plumes, to investigate what happens with emissions and pollutants downwind of a city, when no further primary emissions occur (see e.g. DeCarlo et al., 2010). This approach is not possible in our case, where the primary emissions vary strongly with location. As stated by Referee #2, we are using sulfate,

which is formed more slowly than other secondary components, to normalize out inhomogeneities due to small-scale meteorological effects, such that primary emissions and chemistry are the only two reasons left for differences in background pollution and “local” pollution. Lenschow et al. (2001) and Querol et al. (2004) showed that in a city area, the background PM concentration is elevated compared to the regional background PM concentration (“urban background”). This enhancement is more pronounced for primary components (like BC) than for secondary components like sulfate (Baltensperger et al., 2002). The quantification of this background fraction and the locally emitted or formed fraction of PM₁ is the main goal of this study.

To clarify the approach, the corresponding paragraph was rephrased as follows: “A new method allows for the separation and quantification of the local fraction of PM₁ emitted or rapidly formed in the city, and the fraction of PM₁ originating from the urban background. The method is based on simultaneous on-road mobile and stationary background measurements and the correction of small-scale meteorological effects using the ratio of on-road sulfate to stationary sulfate”.

In section 3.5.1, the following paragraph was inserted: “In contrast to most other studies investigating urban emissions and their downwind plume (e. g. DeCarlo et al., 2010), our goal was not to assess emissions of the city and their fate downwind, but to assess the differences between local emissions and urban background. The city’s emissions of course also contribute to the background but downwind of the city plume. The fraction of secondary components formed during one hour will be counted as local, whereas the fraction formed on a longer timescale will be quantified as urban background”.

However, for this to be meaningful the authors need to compare the relative timescales of sulfate formation to formation/losses of other components of interest.

The fundamental basis of our approach based on sulfate ratios is the assumption that the formation of particulate SO₄ is negligible during 1 hour. Local fractions of the components must either be emitted directly or be formed within 1 hour for the concept to be meaningful. For the latter, apart from ammonium sulfate and ammonium nitrate, only secondary organics (OOA) are of interest. As for OOA, main precursors in the city in winter (when biogenic emissions are much less important) are volatile organic compounds from traffic and biomass burning emissions. Chirico et al. (2010) and Heringa et al. (2011) have shown in their smog chamber experiments that the formation of OOA from diesel or wood burning emissions starts to happen on very short time scales (primary concentrations were more than doubled within 1 hour for a diesel vehicle without aftertreatment, and the organic matter enhancement ratio for wood burning can be up to a factor of 2 after 1 hour). Nitrate is formed more rapidly than sulfate (~10 times faster) and can thus also show a local contribution.

This information was added to section 3.5.1.

Many questions come to mind regarding this normalization such as 1) If OOA is formed on the same timescale as sulfate then what is the point of calculating the near-road or “local” OOA using this method?

See response to the point before. Especially SV-OOA is formed more quickly than ammonium sulfate. “Local OOA” refers to the OOA formed within 1 hour.

2) Why would one expect the WBOA to be different for “local” if PM1 is homogeneously distributed throughout air basin and not emitted from traffic?

Earlier studies have shown that also in the city of Zurich, domestic wood burning can be a significant source of organic aerosol (Lanz et al., 2008; Richard et al., 2011), hence we do expect local emissions and local contributions to PM₁ of wood burning in Zurich. Zurich is a densely populated city, and many people use wood for heating purposes (as e. g. in the residential area Erismannhof mentioned in the manuscript) or have fireplaces for decoration and ambiance reasons.

The following sentence was added to section 3.5.2: "Overall, compared to the high fractions of WBOA measured in Zurich, its local contributions are rather small".

3) What is the significance the conclusion stated in the bottom of p12343: "It can thus be concluded that traffic is the most important local contributor to PM1 measured on road in Zurich." when this normalization would seem to force the WBOA and OOA results to bounce around somewhat negative or positive values as they are arbitrarily scaled to sulfate which may have faster/slower formation rates and also non co-located sources with sulfate?

Concerning local emissions of wood burning and fast OOA formation, see also previous points. As was shown by Lanz et al. (2010), many sites on the Swiss plateau show higher fractions of organic aerosol from wood burning than from traffic in winter, including Zurich (compare also Fig. 6 in our manuscript, the chemical composition at the background site shows 12% WBOA and 6% HOA). Thus, the fact that most of this WBOA abundantly measured in Zurich is to a great extent not locally emitted was a rather unexpected result. At least it was not clear until now.

As for sulfate, SO₂ concentrations in Switzerland are very low (with a mean value of 8 µg m⁻³ in January 2009 (BAFU and EMPA, 2009)). SO₂ is being emitted from the combustion of sulfur-containing fuels. Legal regulations have helped in substantially reducing the sulfur content in fuels in Switzerland, and since the 1980s the SO₂ concentrations have been decreasing continuously (BAFU and EMPA, 2009). Most important emitters are domestic heating appliances in winter, local small industries, or also emissions from traffic. In general, there are no big point sources in Switzerland (no refineries, no SO₂ emitting power plants), leading to a rather uniform sulfate distribution (Christoph Knote, EMPA, personal communication).

This information was added to section 3.5.1.

The other major shortfall is the lack of discussion of the implications and reference frame for on/road off road (i.e. local vs. regional). What does it mean? As it reads, it appears that the major conclusions of the local vs regional discussion (which is a focal point of the paper) is: 1) enhancement in PM1 on roadways are from traffic and are largely HOA and BC; 2) secondary components on the roadways such as OOA, nitrate were typically a very small contribution (essentially zero given the uncertainties in the technique); and 3) wood burning PM1 was also very small. Aren't these results expected?

See also replies to points before. The low local contribution of WBOA was not necessarily to be expected. Important to note here is also that we were not only driving on busy roads, but as was stated in section 2.1, roads in residential areas were covered as well, where traffic would not necessarily be expected the most important contributor. Again, important is the quantification of the fractions. The word "quantification" was added, in the abstract and in the beginning of section 3.5.1.

What is the relative importance of the measured increase of the “local” concentrations over the “background”? Do the measurements address overall contributions of local traffic to the regional pollution (it doesn’t seem to).

As was stated earlier, the quantification of the urban background fraction and the locally emitted or formed fraction of PM₁ is the main goal of this study, not the investigation of the plume.

The following paragraph was added to section 3.5.1: “In contrast to most other studies investigating urban emissions and their downwind plume (e. g. DeCarlo et al., 2010), our goal was not to assess emissions of the city and their fate downwind, but to assess the differences between local emissions and urban background. The city’s emissions of course also contribute to the regional background but downwind of the city plume. The fraction of secondary components formed during one hour will be counted as local, whereas the fraction formed on a longer timescale will be quantified as urban background”.

If not, then the importance of the observed enhancement on the roadways themselves should be addressed. I.e. Fig 8 shows a 40% increase, on average, of BC, HOA, and CPC. Does this matter?

We are investigating the quality of the air people are breathing. 40% of BC, HOA or CPC are significant amounts of particle mass or number concentrations (compare Fig. 3 for total concentrations). The local contribution is the fraction where local authorities can take measures. Still, the fact that the urban background is dominating even when measuring on major traffic arteries is an interesting result with consequences for the design of mitigation strategies.

The abstract includes the results that >97% of WBOA and OOA and 94% of inorganics are from the regional background? However, surely road traffic in Zurich contributes more than a few percent to OOA and inorganics formed in the urban background through the VOC, SO₂, and NO_x emissions. Isn’t that important? A reader might easily walk away with the notion that mobile emission sources are not important to secondary aerosol formation in Zurich. A more developed discussion of these issues needs to be included, otherwise statements such as those in the abstract and main body stating how this work shows the importance of differentiating regional vs. local pollution should be removed.

Compare previous points. The following paragraph was added to section 3.5.1: “In contrast to most other studies investigating urban emissions and their downwind plume (e. g. DeCarlo et al., 2010), our goal was not to assess emissions of the city and their fate downwind, but to assess the differences between local emissions and urban background. The city’s emissions of course also contribute to the background but downwind of the city plume. The fraction of secondary components formed during one hour will be counted as local, whereas the fraction formed on a longer timescale will be quantified as urban background”.

Another general comment is that throughout the text, results, patterns, and concentrations are described as “similar”. In many of these instances, simple statistical comparisons should be employed to justify these qualitative statements (search for “similar”).

We searched the manuscript for non-quantified “similar” and made the following changes to the manuscript:

P. 12335, line 19-20: second part of the sentence was removed as it did not add quantitative information.

P. 12338, line 9: “2 days with similar total concentrations (14 and 17 $\mu\text{g m}^{-3}$) but different distribution of compounds” – numbers were inserted.

P. 12338, line 24-25: “Interestingly, the WBOA fraction was very similar for both the urban background site (34%) and on-road (32%)” – numbers were inserted.

P. 12339, line 16-17: Sentence was changed to “[...] due to relatively small variations in daily temperature and diurnal patterns.”

P. 12343, line 13-14: Sentence was changed to “Qualitatively, both methods yield similar results, with BC and HOA dominating the local contributions (see Fig. SI-22)”.

P. 12344, line 21: “A similar value (39%) was obtained for particulate PAHs but is not shown here because of large error bars” – number was inserted.

Similarly standard deviations or uncertainties should be added in many cases. For example in the abstract the authors state that >97% of OOA and BBOA are in the background. This is misleading. As shown in Fig. 8, not surprisingly these number have large errors/variation (probably due to limitation in the sulfate normalization) – thus reporting >97% introduces a bias and implies a greater certainty than the observations support. Is it really 97.6+/-15%?

As explained in section 3.5.2, the local contributions vary between different days due to meteorological conditions. Averaging the local contributions from the different days will remove the information on their variation, thus the \pm standard deviations were added. Since stating only average numbers in the abstract might not give sufficient information on this variation, the abstract was changed as following: “Especially during thermal inversions over the Swiss plateau, background concentrations contribute substantially to particulate number concentrations (between 40 and 80% depending on meteorological conditions and emissions, 60% on average) as well as to the mass concentrations of PM_{10} components in downtown Zurich (between 30 and 90%, on average 60% for black carbon and HOA, and between 90 and 100% for WBOA and OOA, and the measured inorganic components)”.

In addition, on p. 12344, line 19, the following information was added: “[...](the error bars denote \pm standard deviation and show the day-to-day variability of the local contribution fraction, see next paragraph)”.

Specific Comments:

1. Page 12324, line 19: What does “It could be shown” mean?

“It could be shown” was removed.

2. Page 12324, line 10- 16: The statement that “The spatial variation of chemical composition of PM_{10} shows uniform distribution throughout the city” needs to be clarified here and within main body. Clearly the composition on-road, and in the square in the middle of the city used as the “urban background” show different composition. The abstract should explain that the background and on-road compositions were characterized and they are respectively similar throughout the city.

In section 3.4, the following paragraph was added: “However, a clear distinction can be made between the urban background site “Zurich Kaserne” and the sites covered during

mobile measurements. At the urban background station, 50% of PM_{10} are comprised of secondary inorganic compounds such as ammonium nitrate and ammonium sulfate, while BC makes up 15%, and the organic fraction is dominated by OOA (49% of organics), followed by WBOA (34%) and HOA (17%). [...].

3. Page 12324, line 19-24: *It needs to be clear that these fractions are for measurements on the road.*

We added “measured on road” to the sentence.

4. Page 12324, line 23: *I can't find where these numbers (94%, 97%) are derived within the paper.*

This information can be derived from Fig. 8, as it shows the local percentage of the measured concentration. The background fraction would be 100% - local fraction. This information was added to the caption of Fig. 8 for clarification.

5. Page 12325, line 8-10: *Many trace gas-phase species have very heterogeneous distributions and/or short atmospheric lifetimes (are the authors comparing to longer-lived gases such CO, CO₂, CH₄, etc. – if so this should be indicated). A more relevant comparison of aerosol to gas-phase species is the complex, multi-phase chemistry and physical processes involved.*

Correct, we are comparing to longer-lived gases. This information was added.

6. Page 12327, line 3: *aerodynamic diameter*

“aerodynamic” was added.

7. Page 12327, line 3-4: *Differentiation of “chemical composition” and “organic components” is unclear.*

“as well as of organic components” was removed since this information was redundant.

8. Page 12328, line 12: *monitored with what? how?*

With an anemometer AM-4203 (Lutron, Taiwan). This information was added to the manuscript.

9. Page 12328, line 16: *Why is turbulent deposition left out here? Shouldn't this be ~2% for these conditions, nearly 10 times greater than the loss calculated here for the combined effects of diffusion and gravitational losses - for the 250cm pickoff, where the AMS and FMPS samples?*

We agree with Referee #2 that the description of turbulent diffusion effects is missing in the manuscript. For particles with a diameter around 10 nm, turbulent diffusion leads to particles losses of ~2%, while for particles with a diameter around 50 nm these losses are reduced to 0.3%. This information was added to the manuscript.

10. Page 12328, line 22-24: *If anisokinetic sampling is discussed, the pick-off configuration should be noted.*

The small stainless steel tubes reached inside the main inlet tube in the flow direction. This information was added to the manuscript.

11. Page 12328, line 23-24: *“but no artifacts could be observed” needs explanation. What evidence was there that large particles were not enriched?*

We ran tests with the main inlet flow switched on and off, and did not observe enhanced mass concentrations with the AMS for the former case. This information was added to the manuscript.

12. Page 12328, line 28: *“led to different instruments” is vague. Clarify. X distance to a common sampling manifold. . . .?*

The paragraph was changed to: “From a common manifold for the front and for the back rack, respectively, copper (or Teflon, for the gas phase instruments) tubing with 0.4 cm inner diameter led to the different instruments (lengths: ~100 cm for particle phase, 200-300 cm for gas phase instruments)”.

13. Page 12329, line 4 (section 2.3): *what m/z range was scanned? Spectrum shown are for m/z 12-100. Was this the range?*

The m/z range scanned was 1-300. This information was added to the text.

14. Page 12329, line 26: *“extend the concentration range”? Was the range extended or was the upper limit extended?*

The upper limit was extended. The sentence was changed accordingly.

15. Page 12330, line 7: *Explain “specially formulated” or provide reference.*

“Specially formulated” was deleted.

16. Page 12331, line 6: *Not require any priori knowledge regarding what?*

Regarding sources. This information was added to the sentence.

17. Page 12331, line 14-19: *Comparison to an HR-AMS is circular – it has same bounce issues. Was the comparison really to the SMPS and TEOM? If so how did those two comparisons compare. Were they statistically the same or was an average taken? Time dependence?*

Compare also point 9 by Referee #1: We agree that the HR-ToF-AMS data has the same CE issues as the Q-AMS, however, once CEs have been determined independently, comparing mass loadings of two AMS is still a valid quality check. The corresponding paragraph in the manuscript was changed as following: “The CE of the Q-AMS was determined to be 0.85, based on a comparison of the mass concentrations of the sum of Q-AMS and MAAP data (non-refractory PM₁ plus BC) with a tapered element oscillating microbalance (TEOM) monitor (Thermo). This comparison was performed in the time period of 27 November 2007 to 10 January 2008. An Aerodyne high-resolution time-of-flight (HR-ToF-AMS) was measuring at the background site during December

2008. The CE of the HR-ToF-AMS was determined to be 1 (Richard et al., 2011). Q-AMS (CE = 0.85) and HR-ToF-AMS (CE = 1) agreed very well (maximum difference 10% for all comparison periods). A high ammonium nitrate fraction (42% of total PM₁ mass on average) and possible high aerosol water content due to a lack of a specific drying unit in the sample air (see section 2.3) support the relatively high Q-AMS CE. Comparisons of various AMS datasets from all over Europe within the EUCAARI/EMEP project show that ammonium nitrate fractions of > 0.25 can already lead to a CE above 0.5 (Nemitz et al., 2011, in preparation). Interestingly, Hildebrandt et al. (2010) found, based on the method by Kostenidou et al. (2007), exactly the same CE for this instrument, when it was operated in Crete”.

18. Page 12331, line 19-20: CE for the AMS has been shown to increase above 0.45 for NH₄NO₃ mass fraction greater than 0.4/0.45 (see work by Eiko Nemitz/Anne Middlebrook) so current evidence points against this speculation.

Comparisons of various AMS datasets from all over Europe within the EUCAARI/EMEP project show that ammonium nitrate fraction of > 0.25 can already lead to CE above 0.5 (Nemitz et al., in preparation).

19. Page 12331, line 23: It's not clear how this is a relevant comparison. CE from AMS ranging from 0.4 to 1 have been reported for numerous studies at different locations for various reasons.

As the AMS deployed on Crete and described by Hildebrandt et al. (2010) was the physically exact same instrument as the one used for the measurements presented here, we feel that this is a relevant comparison.

20. Page 12331, line 20-23: This statement is incorrect. Choosing to not downweight the m/z44 –dependent fragments does not force any factor solutions to have the mass spectral characteristics of the frag table dependencies of m/z 44. This is already true whether downweighted or not. Choosing to not downweight m/z44-dependent factors is simply increasing the weight of m/z44 by a factor of 4 relative to normally calculated errors. Essentially, a more “poor man’s pmf”-like approach. It is good that the authors explain the steps taken, but the reasoning should be correct.

Referee #2 is right. According to this suggestion, the sentence was changed to: “Increasing the weight of m/z 44 by a factor of 2.24 (the square root of the number of m/z 44-related ions, Ulbrich et al., 2009) relative to normally calculated errors was just sufficient a priori information to yield an atmospherically relevant PMF solution”. The m/z’s proportional to m/z 44 were also mentioned (16, 17, 18, and 28).

21. Page 12332, line 25-28: Needs more explanation. One might expect that the differences in season over the range of Dec to Feb for Part 1 would warrant separation more than Part 2 (December only) from December in Part 1. Is the reasoning due to instrumentation differences such as tuning, etc.?

The same question was raised by Referee #1. Compare section 3.2, the major difference was bad resolution in the quadrupole for the second part. This additional information was added. During part 1, the AMS was not taken out of the van and was running more or less continuously, thus stable conditions could be provided during that period.

22. Page 12333, line 23-24: For such a “weekend effect” it would be expected that NO_x would decrease and CO remain similar. Was this observed?

Unfortunately, as described in the manuscript, NO_x and CO were not measured during part 1.

23. Page 12334, line 4: Seems inconsistent with previous statement. On p12327, lines 23-23 it states: “Mobile measurements were usually performed during morning and evening times, when traffic and domestic heating emissions are at their maximum”. (also remove “times” or replace with “periods”)

“times” was replaced by “periods”. For p. 12334, line 4, statement was replaced by “[...] and evening emissions from wood burning for domestic heating purposes are usually higher than morning emissions” to make it less strong.

24. Page 12334, line 10-12: Tell reader where these averages correspond to.

The information “in Switzerland” was added to the text.

25. Page 12334, line 13. Why compare to annual mean? Are average winter measurements not available?

The annual mean was replaced by the average value for December 2008 – February 2009 (30 ppb) measured by NABEL.

26. Page 12334, line 19: Evidence for “breakup of the inversion in late afternoon”?

Temperature differences between urban background site Kaserne and Üetliberg (altitude 800 m a.s.l., compare Fig. 6) show a clear inversion breakup on 16 December 2008 around 4 pm due to a weather change. As stated in the manuscript, on 16 December 2008 we observed a change in meteorological conditions (the start of a frontal passage including rain). We added the information on the frontal passage in the text.

27. Page 12335-6, line 25-5. Why go through this mathematical reintegration? The explanation requires quite a bit of extra text. Wouldn't it be easier just to highly downweight m/z 29 and perform the PMF analysis as usual, yielding the same result?

Downweighting m/z 29 was our first idea as well (we tried factors of several orders of magnitude until 1000). This improved the solution in the way that we did not get a single “29” factor anymore for $p > 2$, but interestingly, the separation of OOA and WBOA did not work anymore (compare also response to point 21 of Referee #1), especially m/z 60 would be split and show up in both factors. As we expected to find the same sources for part 2 as for part 1 and as we knew that the resolution and thus the performance of the instrument was poor compared to for part 1, we decided to try to completely remove m/z 29, which yielded the results presented here.

28. Page 12336, line 11: Indeed, m/z 57 for Part 2 as shown in Fig. 3 is “very low” compared to the Part1 solution spectrum, but m/z s 41, 43, and 55 range from 1/3 to 3/4 of values for the Part 1 solution so “very low” is a bit of an overstatement.

We agree with Referee #2 and changed “very low” to “lower than”.

29. Page 12337, line 13: Does SI-19/20 shows data for both Parts? Indicate in caption. Maybe color the two parts differently? Also add R² values to SI-20.

As introduced on p. 12337, line 5-13, the problem of noisy data was distinct for part 2 data only, hence Figs SI-19/20 show data from part 2 only. R² values are already added in the manuscript.

30. Page 12337, line 15-19: I don't see the value in showing the correlations of OOA, HOA, and BBOA with m/z 44, 57, and 60. You can see from the spectra in Fig. 3 that these m/z are primarily contained in those respective factors. Moreover, the OOA factor was solved using an “upweighted” m/z 44 and the BBOA was chosen for a nonzero fpeak value due to higher m/z60 for one solution.

We agree with Referee #2 that these m/z's are marker masses in the respective factors and thus not fully independent. However, these correlations still give an impression of the quality of the fit, and maybe more importantly, of the quality of the input matrices and are therefore shown.

31. Page 12337, line 20-22: This statement needs more explanation. It is repeated later in 3.5.1, but with no further explanation.

Szidat et al. (2006) quantified contributions from fossil fuel usage (75% and biomass burning (25%) to elemental carbon (EC) for winter 2002/2003 in Zurich. This information was added to the manuscript.

32. Page 12337, line 28-29: The anticorrelation of OOA and temperature is not clear in Fig. SI-18. Perhaps include the OOA vs T correlation in SI-19/20 in place of m/z 44,57,60 correlations.

For part 2, there is no anti-correlation between OOA and temperature. For part 1, excluding 15 February 2008 and 19 February 2008, a slight anti-correlation (slope -0.4, R² of 0.3) can be determined. The paragraph was changed to: “Ambient temperature shows a slight anti-correlation with OOA for part 1, 27 November 2007 – 08 January 2008 (slope = -0.4, R² = 0.3) (Fig. SI-16 and SI-18), indicating the importance of thermal inversions (with low boundary layer temperatures) for the build-up of secondary particle mass”.

33. Page 12338, line 5-6: This isn't very clear from Fig. 4. In fact, in many case it appears to be the opposite.

It is the case for 27 – 29 November 2007, 08 January 2008, 15 February 2008, 19 February 2008, and 15 – 16 December 2008. Since there are big gaps between the different driving episodes, a comparison of one episode to the other is difficult for this case since they all represent different meteorological conditions. Sunday, 16 December 2007, was different due to the legal ban of heavy duty vehicles as stated in the text.

34. Page 12338, line 21-23: *Confusing. Reword to be more clear which “this study” refers to. Does it refer to the results in this paper or one of the referenced papers? If this study, then average organic composition is shown in Fig. 4, not Fig*

We agree that this part is confusing. We decided to move the paragraph from p. 12338, line 20, to p. 12339, line 10, to the next section, after the sentence introduced at point 2. It was rearranged as following: “At the background station, 50% of PM₁ at the background site are secondary inorganic compounds such as ammonium nitrate and ammonium sulfate, BC makes up 15%, and the organic fraction is dominated by OOA (49% of organics), followed by WBOA (34%) and HOA (17%). Lanz et al. (2008) found in their analysis of Zurich Kaserne data 3 - 13% HOA, 52 - 57% OOA, and 35 - 40% WBOA for winter 2006. The differences to the average organic composition measured throughout the city as described in the previous section can be explained by the different setup of measurements – the contribution of HOA is expected to be larger on-road than for stationary measurements at the urban background site. Interestingly, the WBOA fraction was very similar for both the urban background site (34%) and on-road (32%), implying that the WBOA source is either regional, or well mixed on the local scale due to its emission typically from chimneys and subsequent downmixing. Richard et al. (2011) found a much lower ratio WBOA/HOA (17%/22%) for Zurich Kaserne, 01 - 18 December 2008, and a higher OOA percentage (60%). During December 2008, homeless people were regularly lighting fires in the late afternoon close to the measurement station. We hypothesize that this led to a local WBOA factor in the solution of Richard et al. (2011), explaining less of the variation of PM₁ and ignoring the regional WBOA contribution due to its similar temporal pattern with regional OOA, at least to some extent. To better compare the data from Richard et al. (2011) to our results, the PMF2 algorithm was run on the last part of their dataset only (15 -18 December 2008, the period of part 2 of the mobile measurements), when the open fires were banned from the site. The variation of the 3 factor contributions became much more congruent with the results found for this study: HOA 15%, OOA 50%, WBOA 32% (plus 3% in the residual). For the other sites,[...]”

6. 35. Page 12339, line 17: *“similarity of diurnal patters” to what? Consistent diurnal patterns?*

Compare response to general comment on page 4. Sentence was changed to “[...] due to relatively small variations in daily temperature and diurnal patterns.”

36. Page 12342, line 18: *How is this comparison to NO₂ oxidation rate relevant for support of use of sulfate as a normalization factor? Wouldn't it be more relevant to compare the formation/loss rates of sulfate to the formation/loss rates compounds of interest for this study such as OOA, WBOA, HOA, BC (and maybe additionally inorganics)? Much more discussion of the rational for using sulfate as this central component in the analysis of this paper is needed.*

See discussion on the second main point.

37. Page 12342, line 26: *Was the requirement of being in the boundary layer applied as a criterion for inclusion/exclusion in the analysis?*

As stated on p. 12343, lines 6-7: “Confirming assumption 3, dilution effects (i.e., intrusion of air masses from above the boundary layer with a different relative composition) in

open spaces (as opposed to street canyons) or elevated areas such as Meierhof Square and Üetliberg can lead to concentrations of S at position p that are lower than at the background site. Thus, the calculated local contribution becomes negative, showing also the limitations of the method presented here”.

Assumption 3 explains negative local contribution values, but was not used as a criterion to exclude/include data.

38. Page 12343, line 11-13: What evidence do you have for this overestimation? Is this just assumed? If so, then it would have been known a priori in which case why do the analysis?

Figure SI-22 visualizes the statement and was referenced in the manuscript.

39. Page 12343, line 26: What other than traffic could be the most important local contributor to on-road PM1 (except re-suspended dust, which is not included in this analysis)?

See replies to points above. The low local contribution of WBOA was not necessarily to be expected. Important to note here is also that we were not only driving on busy roads, but as was stated in section 2.1, roads in residential areas were covered as well, where traffic would not necessarily be expected to be the most important contributor.

40. Page 12344, line 17: “emitted” is poor word choice. Some components in Fig. 8 are secondary.

“or formed” was added.

41. Page 12344, line 25-26: Why is this “interesting”? Isn’t this completely expected? A result otherwise would be noteworthy.

Concerning local emissions of wood burning and fast OOA formation, see also previous points. As was shown by Lanz et al. (2010), many sites on the Swiss plateau show higher fractions of organic aerosol from wood burning than from traffic in winter, including Zurich (compare also Fig. 6 in our manuscript, where the chemical composition at the urban background site shows 12% WBOA and 6% HOA). Thus, the fact that most of this WBOA abundantly measured in Zurich is to a great extent not locally emitted is an interesting result.

42. Page 12345, line 6-9: Results like this should not just be reported with no discussion. A reader is likely to assume this suggests a problem with the methods used here. Is the NO_x enhancement lower b/c the composition of traffic such as diesel vs. gasoline? Is the relative CO increase less simply b/c CO has a larger relative background?

For CO, which is more inert than NO_x, higher background levels and hence lower local contributions are expected. Referee #2 is right that the local contributions from NO_x seem low, especially when compared to the local contributions from HOA and BC, also emitted from traffic. Important to note here is the fact that CO and NO_x measurements were only added in December 2008 (part 2), days with generally lower local contributions than during the first period of measurements. Mean local contributions of HOA and BC for this same period only are ~20% and ~30%, respectively, lower than

their mean values for the whole data set. This important information was added to the caption of Fig. 8.

43. Page 12346, line 24: “domestic wood burning was in general more important than traffic”. Averages are 32% vs 24%. Is this really significant, or are they really similar (give standard deviations or some measure of variability)?

Compare also point 3 of Referee #1’s comments. As can be seen in Fig. 6, generally WBOA concentrations are higher than HOA concentrations. We believe this small difference to be significant, and our PMF results are also consistent with previous studies. As spatial and temporal variability is discussed in detail throughout the manuscript, adding standard deviations would not change the significance of the – anyway qualitative – statement.

44. Page 12346, line 25-26: This explanation might explain why nitrate is larger in winter than summer, but not why nitrate dominates over sulfate in winter. Probably related to sources too?

Referee #2 is right, sources play an important role, too. Compare discussion on main points.

45. Page 12347, line 6: Fig SI-21 shows PM10, not PM1. Also, it does not show chemical components as this sentence suggests.

The reference to the figure was deleted.

46. Page 12347, line 8-10: Strategies for mitigating what? Without clarification, statements like this are meaningless. What factors does this study address that are relevant to air pollution controls? This study does not estimate how much road traffic contributes to overall air pollution in Zurich. The primary emission contributions are estimated only for narrow bands of on-road traffic veins. Presumably road traffic contributes significantly SOA production via VOC emissions and secondary inorganics via other gaseous emissions but these effects are not addressed here. All of these end up in the same soup that is the Zurich air basin, while roadways have 65% more HOA, BC, and particle number concentration than the urban background. Is this important?

As stated in previous points, the main goal of the study was the quantification of the local fraction of primary emissions and the fraction of secondary components formed “locally”, i. e. within 1 hour. Local authorities can only influence mitigation strategies for the local fraction of the pollution, thus we believe this quantification to be important. The local contribution was not only estimated for narrow traffic veins, but also for residential areas and peripheric regions of the city. Secondary formation of the precursors emitted by the sources discussed here were mentioned, but are not the focus of the study.

47. Supplementary Information is poorly organized. The line numbers restart several times, but don’t necessarily correspond to separate sections.

The line numbers were changed accordingly.

48. SI “PMF Diagnostics”, line 4-20: Did you try running PMF for increasingly larger numbers of factors to see if the “amine contamination” factor could be separately

resolved (and then presumably recombine any main factors that split) – in order to remove this contamination from the 3 main factors? If so, this is important to note.

Yes, PMF was run for up to 8 factors. The amine factor would stay, but the other factors would split into “single mass” factors, where a recombination to a meaningful factor would be different. This information was added to the SI.

Technical suggestions:

49. Page 12324, line 22: make “mass concentrations”

Sentence was changed accordingly.

50. Page 12326, line 15: quantify “especially high”.

During the study period of Lanz et al. (2008), PM10 concentrations of up to 120 $\mu\text{g m}^{-3}$ were measured. The number was added to the text.

51. Page 12326, line 18-19: put restrictions on

The sentence was changed accordingly.

52. Page 12326, line 24-28: wording awkward. Make parallel structure to previous statements.

Paragraph was rephrased and reads now as follows: “Previous studies either featured the same type of instruments at various sites simultaneously (e. g. Mejia et al., 2008; Xie et al., 2008), or a set of various instruments mounted on a mobile platform. Many mobile measurements have been performed using aircraft (e. g. Schneider et al., 2006; Bahreini et al., 2003; DeCarlo et al., 2008), or, if ground-based, focused on vehicle exhaust (e. g. Canagaratna et al., 2004; Zavala et al., 2009; Thornhill et al., 2010). Only few studies dealt with ground-based spatially resolved particle characterization or source apportionment (Bukowiecki et al., 2002; Bukowiecki et al., 2003; Weimer et al., 2009).

53. Page 12326, line 28: substitute “dealt with” with something less colloquial that is more descriptive.

We replaced “dealt with” by “covered”.

54. Page 12327, line 20: “were inserted” is odd wording

Sentence was rephrased to “After each loop, stationary data were acquired at the urban background site “Kaserne” for a few minutes”.

55. Page 12328, line 5: missing semicolon.

Dot was replaced by semicolon.

56. Page 12328, line 11: second hyphen not needed.

Second hyphen was removed.

57. Page 12329, line 5: "collected" rather than "taken"?

"Taken" was replaced by "collected".

58. Page 12330, line 3: "all drives" rather than "each drive"

"each drive" was replaced by "all drives".

59. Page 12330, line 7-8: Unclear wording.

Sentence was rephrased to read "A chromium trioxide converter oxidized NO to NO₂ by CrO₃ with an average effectiveness of 82%, allowing for the detection of NO_x".

60. Page 12333, line 16: Is it necessary to add "in the SI"?

"in the SI" was removed.

61. Page 12323, line 13/23: Make tenses consistent throughout. In line 13, the past tense "formed" is used. In line 23, the present "shows" is used. If anything, the former may describe an ongoing phenomenon and could warrant the present tense.

"shows" was changed to "showed".

62. Page 12339, line 2-6: Run-on sentence. Not clear what point is being made. Reword.

Sentences were rephrased to "During December 2008, homeless people were regularly lighting fires in the late afternoon close to the measurement station. We hypothesize that this led to a local WBOA factor in the solution of Richard et al. (2011), explaining less of the variation of PM₁ ignoring the regional WBOA contribution due to its similar temporal pattern with OOA, at least to some extent."

63. Page 12339, line 6-9: Unclear sentence. Again not clear what "this study" refers to. What is being compared?

Paragraph was rephrased to "To better compare the data from Richard et al. (2011) to our results, the PMF2 algorithm was run on the last part of their dataset only (15 -18 December 2008, the period of part 2 of the mobile measurements), when the open fires were banned from the site. The variation of the 3 factor contributions became much more similar to the results found for this study:".

64. Page 12339, line 12: reword "most likely generally" to be more descriptive.

We rephrased this sentence to "ammonium nitrate formation is unlikely to be limited by ammonia".

65. Page 12339, line 18: replace "to" with "vs."

"To" was replaced by "vs.".

66. Page 12342, line 20: "concentration" not "fraction", right?

Referee #2 is right, it should be “concentration”. “Fraction” was replaced.

67. Page 12343, line 23: *“relative terms” not clear.*

“terms” was replaced by “values”.

68. Page 12347, line 23: *measure “in” downtown*

“in” was inserted.

69. Page 12347, line 23: *remove “of”*

“of” was removed.

70. Figure 1 caption: *remove “black” from last line; all lines are black.*

“vertical” was removed.

71. Figure 1: *Why is Sunday the only day shown at that top?*

Because 16 December 2007 is the only Sunday measured in the dataset. Sunday is important as there are different emission patterns expected than for the other weekdays due to the legal ban of heavy duty vehicles on Swiss roads. This information was added to the figure caption.

72. SI-3,4 caption: *Replace “factorial” with “factor”*

“factorial” was replaced accordingly.

73. SI “PMF Diagnostics”, line 19: *“non-normally” has extra space*

Extra space was removed.

74. SI - paragraph above Fig. SI-6, line 6: *remove extra “and”*

Extra “and” was removed.

75. Figure SI-9,11: *Might be nice to add to the legend the final assignment of each factor. In parenthesis such as (“ $f_{peak} -0.1$ assigned to OOA”) would be fine (since presumably the other f_{peak} are not necessarily the same assigned component factor).*

SI, p.6 reads: “The rotational freedom of the chosen solution may be explored through a non-zero valued user-specified rotational parameter f_{peak} . f_{peak} imposes rotations on the emerging solutions. f_{peak} values are not chosen per factor, but per solution, hence there is one f_{peak} value for all 3 factors. In Figs. SI-9,11, the chosen f_{peak} is framed by boxes. This information was added in the corresponding figure caption.

76. Figure SI-14: *Add “for Part 1” to last sentence.*

“for part 1” was added.

77. *Figure SI-22 caption: Panel B not described.*

Description of panel B was added.

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