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Interactive comment on “Spatial variation of chemical composition and sources of submicron aerosol in Zurich: factor analysis of mobile aerosol mass spectrometer data” by C. Mohr et al.

Anonymous Referee #2

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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

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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.

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). 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. 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

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method? 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? 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?

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? 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). 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? 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.

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”). 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%?

Specific Comments:

1. Page 12324, line 19: What does “It could be shown” mean? 2. Page 12324, line 10-16: The statement that “The spatial variation of chemical composition of PM1 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. 3. Page 12324, line 19-24: It needs to be clear that these fractions are for measurements on the road. 4. Page 12324, line 23: I can’t find where these numbers (94%, 97%) are derived within the paper. 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. 6. Page 12327, line 3: aerodynamic diameter 7. Page 12327, line 3-4: Differentiation of “chemical composition” and “organic components” is unclear. 8. Page 12328, line 12: monitored with what? how? 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

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gravitational losses - for the 250cm pickoff, where the AMS and FMPS samples? 10. Page 12328, line 22-24: If anisokinetic sampling is discussed, the pick-off configuration should be noted. 11. Page 12328, line 23-24: “but no artifacts could be observed” needs explanation. What evidence was there that large particles were not enriched? 12. Page 12328, line 28: “led to different instruments” is vague. Clarify. X distance to a common sampling manifold. ...? 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? 14. Page 12327, line 26: “extend the concentration range”? Was the range extended or was the upper limit extended? 15. Page 12330, line 7: Explain “specially formulated” or provide reference. 16. Page 12331, line 6: Not require any priori knowledge regarding what? 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? 18. Page 12331, line 19-20: CE for the AMS has been shown to increase above ~ 0.45 for NH_4NO_3 mass fraction greater than 0.4/0.45 (see work by Eiko Nemitz/Anne Middlebrook) so current evidence points against this speculation. 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. 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. 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.? 22. Page

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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? 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”) 24. Page 12334, line 10-12: Tell reader where these averages correspond to. 25. Page 12334, line 13. Why compare to annual mean? Are average winter measurements not available? 26. Page 12334, line 19: Evidence for “breakup of the inversion in late afternoon”? 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? 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/zs 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. 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. 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 non-zero peak value due to higher m/z60 for one solution. 31. Page 12337, line 20-22: This statement needs more explanation. It is repeated later in 3.5.1, but with no further explanation. 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. 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. 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 6. 35. Page 12339, line 17: “simi-

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larity of diurnal patterns” to what? Consistent 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 rationale for using sulfate as this central component in the analysis of this paper is needed. 37. Page 12342, line 26: Was the requirement of being in the boundary layer applied as a criterion for inclusion/exclusion in the analysis? 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? 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)? 40. Page 12344, line 17: “emitted” is poor word choice. Some components in Fig. 8 are secondary. 41. Page 12344, line 25-26: Why is this “interesting”? Isn't this completely expected? A result otherwise would be noteworthy. 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? 43. Page 12346, line 24: “domestic wood running 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)? 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? 45. Page 12347, line 6: Fig SI-21 shows PM₁₀, not PM₁. Also, it does not show chemical components as this sentence suggests. 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

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

Technical suggestions:

49. Page 12324, line 22: make "mass concentrations" 50. Page 12326, line 15: quantify "especially high". 51. Page 12326, line 18-19: put restrictions on 52. Page 12326, line 24-28: wording awkward. Make parallel structure to previous statements. 53. Page 12326, line 28: substitute "dealt with" with something less colloquial that is more descriptive. 54. Page 12327, line 20: "were inserted" is odd wording 55. Page 12328, line 5: missing semicolon. 56. Page 12328, line 11: second hyphen not needed. 57. Page 12329, line 5: "collected" rather than "taken"? 58. Page 12330, line 3: "all drives" rather than "each drive" 59. Page 12330, line 7-8: Unclear wording. 60. Page 12333, line 16: Is it necessary to add "in the SI"? 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. 62. Page 12339, line 2-6: Run-on sentence. Not clear what point is being made. Reword. 63. Page 12339, line 6-9: Unclear sentence. Again not clear what "this study" refers to. What is being compared? 64. Page 12339, line 12: reword "most likely generally" to be more descriptive. 65. Page 12339, line 18: replace "to" with "vs." 66. Page 12342, line 20: "concentration" not "fraction", right? 67. Page

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12343, line 23: “relative terms” not clear. 68. Page 12347, line 23: measure “in” downtown 69. Page 12347, line 23: remove “of” 70. Figure 1 caption: remove “black” from last line; all lines are black. 71. Figure 1: Why is Sunday the only day shown at that top? 72. SI-3,4 caption: Replace “factorial” with “factor” 73. SI “PMF Diagnostics”, line 19: “non-normally” has extra space 74. SI - paragraph above Fig. SI-6, line 6: remove extra “and” 75. Figure SI-9,11: Might be nice to add to the legend the final assignment of each factor. In parenthesis such as (“fpeak -0.1 assigned to OOA”) would be fine (since presumably the other fpeak are not necessarily the same assigned component factor). 76. Figure SI-14: Add “for Part 1” to last sentence. 77. Figure SI-22 caption: Panel B not described.

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