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Interactive comment on “Semi-continuous gas and inorganic aerosol measurements at a Finnish urban site: comparisons with filters, nitrogen in aerosol and gas phases, and aerosol acidity” by U. Makkonen et al.

Anonymous Referee #1

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This manuscript presents and discusses measurements of 5 gases (HCl, HNO₃, HONO, NH₃, SO₂) and of 8 inorganic aerosol constituents (Cl⁻, NO₃⁻, SO₄²⁻, NH₄⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺) in PM_{2.5} and PM₁₀ aerosols that were performed with an on-line MARGA 2S monitor from November 2009 to May 2010 in Helsinki, Finland. The data for SO₂ were compared were those from a conventional SO₂ monitor and good agreement was obtained. For the PM₁₀ aerosol data a comparison was made with the data derived from a PM₁₀ sampler with Teflon filter. Here, good agreement was obtained for NO₃⁻, SO₄²⁻, and NH₄⁺, while the agreement was poor for the cationic

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species Na^+ , K^+ , Mg^{2+} , and Ca^{2+} . The poor agreement for Na^+ was not discussed in the manuscript, although it should; that for K^+ was attributed to many below detection limit values and as explanation for the high MARGA versus filter slopes for Mg^{2+} and Ca^{2+} , it was suggested that the cut-off point of the PM_{10} inlet of the filter sampler might have been lower than $10 \mu\text{m}$. However, as indicated below, this possible explanation makes little sense. The quality of the authors' MARGA data for Mg^{2+} and Ca^{2+} is definitely questionable.

As indicated by the authors, an advantage of the MARGA is that it provides a much better time resolution for the aerosol species than filter sampling does. AMS has the same advantage, but cannot detect refractory species, such as sodium, magnesium, and calcium, which can be measured with the MARGA. However, since the authors' MARGA data for Mg^{2+} and Ca^{2+} (and possible also those for Na^+) are questionable, are there any advantages of the MARGA over AMS left for aerosol analysis, considering that AMS provides also data for the organic aerosol, which the MARGA does not. The authors should comment on this.

The gas and aerosol data and their seasonal and diurnal variation are nicely discussed in the manuscript. Of particular interest are the authors' discussion of the fractionation of nitrogen into gas (excluding NO_x) and aerosol phases and the source analysis of aerosol acidity.

Overall, this is an interesting manuscript, which deserves to be published in ACP, but revision is needed. Clarification is needed on several occasions.

Specific comments:

1. Page 4756, lines 9-10: There is an error in the slopes for NH_4^+ and Na^+ listed here. "0.68, 0.89, 0.84, 0.52, 0.88, 0.17, 2.88, and 3.04 for Cl^- , NO_3^- , SO_4^{2-} , NH_4^+ , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} " should be replaced by "0.68, 0.89, 0.84, 0.88, 0.52, 0.17, 2.88, and 3.04 for Cl^- , NO_3^- , SO_4^{2-} , NH_4^+ , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} ".

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2. Page 4757, line 13: That Ca is the main constituent of soil dust is incorrect. O, Si, Al, and Fe are present in higher concentrations than Ca is. The sentence should be corrected by replacing “are the main constituents” by “are main constituents”. Incidentally, Ca is not only an important constituent of soil dust, but also of sea salt.
3. Page 4759, line 18: “northeast of the city center” is not clear enough; I suggest replacing it by “northeast of the city center of Helsinki”.
4. Page 4762, lines 19-21: As indicated above, Ca is not only a main constituent of soil dust, but also of sea salt. This is even more the case for Mg. Anyway, as is the case for soil dust, also sea salt is mostly present in coarse particles. The text should be modified here.
5. Page 4763, lines 16-19: For Table 2, data below the detection limit were replaced by one half the detection limit. Why was the same not done here when calculating the regressions? It is stated in on page 4764, lines 2-4, that the slopes would even be lower then.
6. Page 4763, lines 19-21: It should be indicated which version of Excel was used for the MS Excel “linest” function and for the various other calculations. Also, all linear regression calculations were done with an offset included. Were the offsets statistically significant? In those cases where the offset was not significant, it would have been better to redo the regression calculations with the offset forced to zero.
7. Page 4764, lines 26-27: The possible explanation given here is not convincing at all. Why should the cut-off diameter of the filter sampler have been lower than 10 μm ? If this would indeed have been the case, why was the MARGA versus filter slope for Na^+ , which is also predominantly associated with coarse particles, then substantially smaller than 1?
8. Page 4765, lines 10-11: It is unclear what was done with upper limit data when doing the calculations here. For example, when there was an upper limit for the $\text{PM}_{2.5}$

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size fraction, but not for PM10, was the upper limit then set equal to half the upper limit or to zero? Or were such data then excluded from the calculation?

9. Page 4767, lines 22-26: It is not very clear whether these statements pertain to the authors' data or to the data of Fisseha et al. (2006). I presume that they pertain to the authors' data, but this should be made more clear.

10. Page 4769, lines 5-7: This sentence is somewhat confusing. Should there perhaps be a comma after "agriculture"?

11. Page 4769, lines 24-26: One or more references are needed to substantiate the statement in this sentence.

12. Page 4769, lines 26-28: A possible explanation for the higher SO₂ levels during the day than in the night would be welcome.

13. Grammatical / technical corrections:

p. 4757, l. 24: replace "concentrations several" by "concentrations of several".

p. 4760, l. 8: replace "on the 19" by "on 19".

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 4755, 2012.

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