

Ulla Makkonen, Aki Virkkula, Jenni Mäntykenttä, Hannele Hakola, Petri Keronen, Ville Vakkari, and Pasi P. Aalto: Semi-continuous gas and inorganic aerosol measurements at a Finnish urban site: comparisons with filters, nitrogen in aerosol and gas phases, and aerosol acidity, *Atmos. Chem. Phys. Discuss.*, 12, 4755–4796, 2012.

REPLIES TO REVIEWERS

General

We thank the reviewers for reading the paper and finding relevant points to be corrected and modified. We have been able to answer all the points, see below.

Detailed answers to reviewers comments

The reviewer comments are presented below in **bold font**, the replies in regular style font.

Referee #1

Page C1337 “...The poor agreement for Na⁺ was not discussed in the manuscript, although it should...”

This is true. Now we have added the text:

The MARGA software does not always recognize small ammonium and sodium peaks which eluate next to each other. This leads to underestimation of both compounds. It was later found that this artifact could be solved by using a concentration column. This was observed when the same MARGA unit was used at another site first with and then without a concentration column. These results will be presented in a forthcoming paper (manuscript in preparation), however, and will not be discussed further in this paper.

However, since the authors' MARGA data for Mg²⁺ and Ca²⁺ (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.

For the present data set the reviewer is absolutely right, the Mg²⁺, Ca²⁺, and Na⁺ are questionable. But to the question of the reviewer: already for the ions that did work well, the MARGA has one advantage over AMS: it measures also supermicron particles that the AMS cannot do. For nitrate, for example, this is a real advantage since it is often on the surface of large particles.

However, there is hope. We found in the following campaign – the same that is referred to in the previous reply – that this problem was solved when the the loop was replaced with a concentration column. It was thus shown that the reason for high Mg²⁺ and Ca²⁺ was either a dirty loop or sensitivity or the MARGA software could not calculate the small peak areas to concentrations correctly. As mentioned above, these results will be presented in a forthcoming paper (manuscript in preparation), however, and will not be discussed further in this paper.

Specific comments:

1. Page 4756, lines 9-10: There is an error in the slopes for NH₄⁺ and Na⁺ listed here. “0.68, 0.89, 0.84, 0.52, 0.88, 0.17, 2.88, and 3.04 for Cl⁻, NO₃⁻, SO₄²⁻, NH₄⁺, Na⁺, K⁺, Mg²⁺, and Ca²⁺” should be replaced by “0.68, 0.89, 0.84, 0.88, 0.52, 0.17, 2.88, and 3.04 for Cl⁻, NO₃⁻, SO₄²⁻, NH₄⁺, Na⁺, K⁺, Mg²⁺, and Ca²⁺”.

Corrected and changed a bit. Reviewer #2 suggested that the list is presented in another way to make reading easier, so it now reads

“Linear regression yielded the following MARGA vs. filter slopes: 0.72 for Cl⁻, 0.90 for NO₃⁻, 0.85 for SO₄²⁻, 0.91 for NH₄⁺, 0.49 for Na⁺, 3.0 for Mg²⁺, and 3.0 for Ca²⁺ and 0.90 for the MARGA vs. SO₂ monitor. “

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.

Sure, the reviewer is right. The sentence was changed to

“The disadvantage of it is that it does not detect some other important elements such as sodium, one of the main constituents of sea salt, and calcium and magnesium, significant constituents of both soil dust and 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”.

The words were replaced by *“northeast of the 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.

The sentence was changed to

“This is reasonable as it is well known that the latter two exist both in soil dust and sea salt and that the size distributions of both of these aerosol types are dominated by coarse particles. “

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.

This is a sensible question and after some rethinking we changed the approach. The calculations were repeated so that also here the values below detection limit were used and then replaced by 0.5×detection limit. But we have now reduced the amount of data points taken into the regressions by accepting only those sampling periods during which at least 50% of hourly data were > detection limits. We have added the following explanation to the text:

“ Values below detection limit (*dl*) were taken into account by giving them the value of 0.5×*dl*. For the regressions, only those filter sampling periods were used during which at least 50% of the MARGA data of the ion to be analyzed were > *dl*, in order to reduce the weight of the more uncertain data. The reason is that for some ions there were several sampling periods during which no hourly data were > *dl*. The extreme example is K⁺ that did not have any single filter sampling period during which all hourly data were > *dl*, and there were only 5 sampling periods out of 88 during which at least 50% of the hourly data

were $> dl$ (Table 3). If K^+ data from all the 88 filter sampling periods had been used for the regressions, most of the data points used for the fitting would have been given the same value, $0.5 \times dl$ and the regression would have been meaningless. On the other hand, if only those sampling periods had been taken into account during which concentrations during all 24 hours had been $> dl$, the amount of data points would have been reduced unnecessarily much. For instance, ammonium concentration may have been $< dl$ during 2 hours of some sampling period and it makes sense in replacing these two values by $0.5 \times dl$ and calculate the sampling-period average. The approach used now is a compromise between these two: using either all data even if most of them were $< dl$ or not using any of the data where any hourly value was $< dl$. “

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.

The Excel was version 2010, and it has now been indicated. However, the explanation for the discrepancy between the two regressions was found. It was simply due to sloppy data handling: the data ranges used for the regressions within the scatter plots and with the *linest* command were not the same. Now this has been doublechecked and the regressions yield the same results, as seen in Figures 3 and 6 and Table 3. The slopes and offsets have changed slightly after the first manuscript because we have recalculated the filter-sampling period averages with another approach. See the reply 5 above.

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?

The reviewer is right. The “inlet explanation” was wrong. The Mg^{2+} , Ca^{2+} , and Na^+ are questionable, and it has been discussed in this reply already. It was found in the following campaign that the reason for high Mg^{2+} and Ca^{2+} was either a dirty loop or the MARGA software could not calculate the small peak areas to concentrations correctly. In addition, the software does not always recognize small ammonium and sodium peaks which eluate next to each other. This leads to underestimation of both of these compounds. It was later found that all these artifacts could be significantly reduced by using a concentration column.

As mentioned above, these results will be presented in a forthcoming paper (manuscript in preparation), however, and will not be discussed further in this paper. But due to this observation, we have now removed the speculation of the different cutoff diameters of the inlets from the paper, it is definitely not the right explanation for the cation problem.

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 $\text{PM}_{2.5}$ size fraction, but not for PM_{10} , was the upper limit then set equal to half the upper limit or to zero? Or were such data then excluded from the calculation?

For the size fractionation plot, i.e., Figure 4, and the associated discussion, only those data were used, that were collected after 19 January 2010 when the PM10 inlet and the PM2.5 cyclone were installed. This is explained now in the text also.

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.

They pertain to our data, it has been made clearer now.

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

Yes, corrected

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

We have added some references.

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

This was somewhat an enigma but it could be explained by using data from air quality measurement stations at different distances from the harbours of Helsinki. The closer to the harbors the station was, the higher the SO2 concentration and the clearer the diurnal cycle was. The conclusion was that it is due to emissions from ships that are well-known emitters of sulfur. However, we don't present data from the other stations because that is out of the scope of the present paper.

13. Grammatical / technical corrections:

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

Done

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

Done

Referee #2

Some formulations seems to be obscure, therefore I recommend exigent the systematic control by a native speaker.

We have not done this, due to “logistic problems”, it would delay the resubmission considerably.

Specific comments:

Some goals for using a MARGA-system are formulated in the introduction (replacement of the traditional EMEP-filter pack method and characterization of the chemical composition of particles < PM10 or < PM2.5). However the authors should give here also a hint of the benefit using the time resolved data for gases and water soluble ions in particles for model evaluations (e.g. Schaap et al., ACP 11, 11041-11053, 2011, Aan de Brugh et al., ACPD 11, 28273–28317, 2011).

Done

Also the possibility of a replacement of wet chemical methods with a high maintenance effort or expensive physical methods for the measurement of NH₃ should be mentioned (e.g. von Bobruzki et al., AMT 3, 91-112, 2010).

Done

At page 4757 starting at line 22 you discuss shortly the function of the “ambient ion monitor” (AIM, URG Corporation, USA) that use also a SJAC. Here you should more specific and give the information that there are four different types of the URG 9000 (A-D) exists with different performances (Nie et al., 2010 use type B).

Done

At page 4766 line 14 to 17: You speculate about the detected HNO₃-concentration and compare with findings in Scotland (Cape, 2009) and decide that your mean concentration for the MARGA is higher as in Scotland but in the range of filter pack measurements at stations faraway and nearby the MARGA (SMEAR II and III). You know that HNO₃ is a very sticky species. Can you exclude losses of HNO₃ in your sampling system?

No, we cannot. Now we just mention:

“However, we cannot exclude losses in our inlet system and underestimation due to that. To evaluate inlet losses our present data are not sufficient”

You should test the influence of the cyclone comparing the results for HNO₃ measurements. for comparable meteorological conditions in the period without a specific inlet (1 November 2009 to 19 January 2010) and with the Teflon coated cyclone in use (19.January to 24 May 2019) Was there made a comparison with a cyclone in the PM10 line and without one in the PM2.5 line?

No, there was not. This is a good remark and we will make a systematic test of the inlet losses in the near future. However, when the nitric acid time series are plotted, there is no clear decrease at the time of the change of the inlets. On the contrary, the concentrations were increasing. But this is due to increasing solar radiation as discussed in section 3.4.1. So, to evaluate inlet losses our data are not sufficient.

Page 4764 and Figure 3: You discuss the comparison of results using the *linest* function in MS Excel and “the other regression method”. In Figure 3 you write about “using the fitting routine within the scatter plots”. I think that you mean this with “the other regression method” in the text. In that case you cannot get different results because both methods use the ordinary least squares for a linear model between an independent and a dependent variable (only the dependent variable contains noticeable observation errors). Is there a mistake in the calculation (also depending from Excel version)? For the discussed problem it should be in any case more exact to use the orthogonal regression (total least squares or rigorous least squares) for a linear model in which observational errors on both dependent and independent variables should be incorporate. Functions for this type of regression are not integrated in original MS-Excel versions

The explanation for the discrepancy between the two regressions was found. It was simply due to sloppy data handling: the data used for the regressions within the scatter plots and with the *linest* command were not the same. Now this has been doublechecked and the regressions yield the same results, as seen in Figures 3 and 6 and Table 3. So, we don't speculate about regression methods further.

Page 4770-4771, line 24- line 2: Please avoid discussing a correlation. Alternatively you can write: “Nitrate is formed when nitric acid gets into the aerosol phase. The scatter plot of nitric acid vs. nitrate is shown in Fig. 12. Both species correlates not well, that can be seen also for winter and summer in Figs. 7 and 8. A probable explanation is that the nitrate observed is more from long-range transport whereas the nitric acid is more from local sources.”

Done

Page 4771, line 17: You should give a citation for the sulfate –to-sodium ratio (0.25) in sea water.

Done

Page 4773, line 4: Please constrict your recommendation for a replacement of filter sampling by a MARGA-system only of the results in this study. Instead of “At the present stage this cannot be recommended.” You should write “From the results of this study this cannot be recommended.”

Done

Minor comments and technical issues:

Page 4756, line 8: In the sentence “Linear regression yielded” you should write for better reading the resulting slopes behind the ions, e.g. “Linear regression yielded MARGA vs. filter slopes for Cl⁻ (0.68), NO₃⁻ (0,89) etc. . . . and for the MARGA vs. SO₂ monitor 0.90.

We have replaced the sentence with this:

“Linear regression yielded the following MARGA vs. filter slopes: 0.72 for Cl⁻, 0.90 for NO₃⁻, 0.85 for SO₄²⁻, 0.91 for NH₄⁺, 0.49 for Na⁺, 3.0 for Mg²⁺, and 3.0 for Ca²⁺ and 0.90 for

the MARGA vs. SO₂ monitor. For K⁺ there were not enough data points to calculate a statistically significant linear regression. “

Page 4775, line 9: “EU 2008/50/EC: Directive 2008/50/EC of the European Parliament and of the Council of 21 May 10 2008 on ambient air quality and cleaner air for Europe . . .” The integrated link is broken.

Corrected

Page 4763, line 2: Please write instead of “Here the mass concentration from the DMPS data was calculated assuming the density of 1,5 g cm⁻³.” “Here the mass concentration from the DMPS data was calculated assuming the density of 1,5 g cm⁻³ for spherical particles to generate an independent estimate for aerosol mass concentration.” Cancel now the sentence starting “This figure is shown because ...”

Done

Page 4763, line 6: change the word “with” to “of”.

Done

Page 4763, line 16: The sentence “In the averaging the . . .” is written ponderously and should be rewritten.

It is now rewritten and changed significantly. See the reply to the question 5 of Referee #1 above.

Page 4764, line 12: cancel the sentence “After sampling the filters are stored and handled in a laboratory that is clean.”, because these fact is self-evident.

Done

Page 4766, line 8: replace “at” by “in”.

Done

Page 4768, line 19-20: Replace the misplaced word “also”, resulting in “. . ., suggesting that at our site traffic is also a major source of HONO.”

No, this is what we do not do. The placement of the word “also”, suggested by the reviewer changes the idea of the sentence too much. If it were like the reviewer suggests, the sentence would mean that “at our site traffic is a source of many things, among others HONO”. Which is true. But this is not what we wanted to say. We have just written a couple of sentences earlier that Kurtenbach et al. 2001 found that traffic is a source of HONO.

We want to emphasize that this is the case *also at our site*, not just in the traffic tunnel discussed by Kurtenbach et al. But we change the order of the words a little bit, so that instead of the original order “...suggesting that at also our site traffic is a major source of HONO.” we now write “...suggesting that also at our site traffic is a major source of HONO.”

Page 4769, line 11: Cancel the redundant sentence “This is just we have observed:” and write the following sentence as “We observed that most NH₃ concentrations were below detection limit in January and February.”

We canceled the sentence but changed it to another:

“We observed a seasonal cycle that is consistent with the above. “ because we consider it to be a relevant link to the introductory part of the same section 3.4.2.

Page 4772, line 18-19: Please write instead of “. . . the continental aerosol is neutralized and the marine not.”, “the continental aerosol is neutralized and the marine aerosol not.”

Done.