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Atmospheric Chemistry and Physics Discussions



# *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 #2**

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General comments:

The paper presents new results of time-resolved measurements (November 2009 to May 2010) for water-soluble ions in particles as well in parallel for trace gases in an urban atmosphere (city of Helsinki). For the measurements the new developed MARGA system, here in the modification with two detector boxes for PM10 and PM2.5 (MARGA 2S ADI 2080, Applikon Analytical BV, The Netherlands), was used. The results were compared with filter sampling, mass concentrations obtained from particle number size distributions and sulfur dioxide concentrations from a UV-fluorescence monitor. The

advantage of the complex sampling principle of the MARGA, using a denuder to select gases from particles in liquid water and a steam jet to bring water soluble ions from remaining particles in a liquid water solution. The function of other instruments that use either systems or one of them in length was discussed in comparison. Diurnal patterns for nitrogen are shown; aerosol acidity was estimated calculating equivalent ratios and the sources of acidic aerosols were studied with trajectory statistics. The manuscript is written systematically and well structured. The results are presented clearly in tables and graphs. The conclusions are a good summary. The cited literature is new and relevant. The paper merits publication in ACP after the consideration of the following remarks: Because I am not a native speaker I can't judge the quality of English writing in general. But some formulations seems to be obscure, therefore I recommend exigent the systematic control by a native speaker.

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). 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 Bobrutzki et al., AMT 3, 91-112, 2010).

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).

At page 4766 line 14 to 17: You speculate about the detected HNO3-concentration and



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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? 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? 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

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."

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



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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.”

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.

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.

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 . . . .”

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

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

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.

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

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.”



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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.”

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.”

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