

Comments on RC2:

First, we thank the referee for the careful reading and the helpful comments on our manuscript. We pasted the referee comments below (**bold**), followed by our author responses in-line and refer to our manuscript in the uploaded version of 10th October 2018.

This paper presents a method for making hourly integrated gas and particle-phase organic acid measurements. This is accomplished by extending a Monitor for AeRosols and Gases in ambient Air (MARGA) system to include an additional Compact ion chromatograph. The details of the organic acid column testing and how the extension to the MARGA works are provided. Example application data from measurements made in Melpitz, Germany are presented.

Overall this is a good paper. I really just have a number of comments to help with the flow of the paper. All of these are outlined below and need to be addressed before the paper can be considered for publication.

We thank the reviewer for his positive overall judgement.

General Comments

General Comments - I think it would be helpful throughout the paper to refer to the Compact-IC as the additional Compact-IC or additional IC-system. This would really help to separate it from the ICs that are part of the original MARGA set-up.

This is a good point. We will refer to Compact-IC throughout the manuscript. We changed:

Page 1, Line 13

Page 1, Line 20

Page 4, Line 4

Page 18, Line 3

Page 19, Line 3 (Figure caption)

Page 19, Line 6 (Figure caption)

Specific Comments First line of Title – Is two-hourly really correct? My initial thought was that it should be two hour integrated measurements. But actually isn't it that the hourly integrated sample from the MARGA is then additionally measured 1 hour later for organic acid. So then I think it is actually hourly integrated quantification of low-molecular weight organic acids.

This is right. We measured the organic acids from hourly integrated MARGA samples but we need two hours for the analysis of the gas and particle-phase. That is why we collect one hourly integrated sample every two hours. Every other hour, the MARGA sample outflow is discarded. Thus, we achieve 12 samples per day for WRD and SJAC each. We added this information also later in the Sample handling chapter. We changed the title and hope it is less confusing:

“Development of an online-coupled MARGA upgrade for the two hours interval quantification of low-molecular weight organic acids in the gas and particle-phase”

Abstract Page 1, Line 12 – Same as above. I think two-hourly time resolution should be one hour integrated measurement

We add a sentence on page 1, line 13:

“Therefore, every second hourly integrated MARGA gas and particle-sample were collected and analyzed by the Compact-IC resulting in 12 values per day for each phase.”

Page 1, Line 15 – Suggest removing the for before gradient

We deleted the “for”.

Page 1, Line 25 – Suggest removing the a after indicate

We deleted the “a”.

Page 1, Line 26 – Believe that something is missing at the end of the sentence. Should it be as a source or was present?

You are right, something was missing. We added at the end of the sentence “...formation as a source.”

Introduction Page 1, Line 28 – Suggest changing were measured to have been measured

We replaced “were measured” with “have been measured”.

Page 2, Line 2 – Suggest changing formed secondary to formed as secondary products

We rewrote this to “...formed as secondary products...”.

Page 2, Line 7 – Suggest changing have a sensitive influence on the ecosystem to have an influence on a sensitive ecosystem

We rewrote the sentence to: “...can have an influence on the sensitive ecosystem...”

Page 2, Line 21 – (Stieger et al., 2018) should be Stieger et al. (2018)

(Stieger et al., 2018) is correct but we can imagine that this is irritating. We rewrote the sentence:

“Recently, Stieger et al. (2018) showed that off-line filter analysis involves the risk of possible evaporation artifacts of volatile particulate compounds from the filter or the adsorption of gaseous compounds. Additionally, Boring et al. (2002) mentioned the difficulty of sampling very small particles by impaction techniques.”

Page 2, Line 34 – Suggest changing filter to filters

We changed it to “filters”.

Page 3, Line 2 – Suggest changing resolution of to resolution from

We replaced “of” by “from”.

Page 3, Line 3 – Suggest changing filter to filters

We changed “filter” to “filters”.

Page 3, Line 6 – Suggest changing A detection to The detection

We changed “A detection” to “The detection”.

Page 3, Line 11 – Suggest changing Therefore to In this case

We changed “Therefore” to “In this case”.

Page 3, Line 12 – Suggest changing is limited to was limited

We changed “is limited” to “was limited”.

Page 3, Line 18 – Suggest changing applied to employed

We changed “applied” to “employed”.

Page 3, Line 19 – Suggest changing of successful field application, first to of a successful field application, the first

We rewrote the phrase to “As a demonstration of a successful field application, the first...”

Page 3, Line 20 – Suggest adding an a before focus

We added an “a”.

2.Instrumentation and materials Page 3, Line 29 – Should Rotation be Rotating?

You are right. We changed it to “Rotating”.

Page 3, Line 30 – Suggest adding a the before WRD

We added “the”.

2.2.Additional IC system Page 4, Line 6 – Believe the word compounds should be components

We changed “compounds” to “components”.

Page 4, Line 7 – Suggest changing the as after systems to a comma, adding a comma after Scientific, and putting a period after alternatives

Page 4, Lines 8-9 – Suggest having a new sentence begin with But the liquid. Also suggest adding a comma before especially and after autosampler

We rearranged the sentences to “Comparable IC systems, for example from Thermo Scientific, were considered as possible alternatives. However, the liquid handling via the autosampler, especially the liquid flows from the MARGA to the necessary autosampler and the capacity of the autosampler, limited the use of other IC systems.”

Page 4, Line 29 – Suggest adding a the before MARGA

We added a “the”.

Page 5, Line 8 – Suggest adding the phrase in the standard after ion

We added the suggested phrase.

3.Results and discussion 3.1.Development of the IC separation Page 7, Line 7 – Suggest adding a the before WRD

We added a “the”.

Page 7, Line 10 – What is the eluent used for the isocratic separation on the Metrosep A Supp 16 250 mm column? I believe that only the chemicals used have previously been mentioned and not the eluent.

We included the eluent concentration and rearranged the sentences to: “First analyses were performed with an isocratic system and the separation column Metrosep A Supp 16 250 mm with an eluent of 7 mM Na₂CO₃ and 0.75 mM NaOH. The resulting chromatogram is shown in Fig. 2,…”

Page 7, Lines 26-27 – The authors mention that it could be expected that the separation would worsen for high concentrations with this anion-exchange column. But no explanation for this is provided. I think it would be helpful to add some text for readers not as familiar with chromatography.

We added a further sentence.

“Regarding the low standard concentrations, the separation can be expected to worsen for high concentrations with this anion-exchange column. Higher ion concentrations would broaden the single peaks, which leads to co-elution.”

Page 8, Line 11 – Suggest changing tailing to tail

We replaced “tailing” by “tail”.

Page 9, Line 9 – Suggest changing differently to different

We replaced “differently” by “different”.

Page 9, Lines 10-11 – The authors list the Na₂CO₃ part of the eluent, but not the NaOH part. I think it would be more accurate to include it since that both eluents A and B have to be made as a mixture.

You are right. We added the information.

Page 9, Line 13 – Suggest changing analysis time before of the F- peak to time before the F- peak eluted. Also suggest removing the the before eluent

We rewrote the sentence.

“In this example, the fraction of eluent B was increased to 50% shortly before the beginning of the analysis to shorten the analysis time before the F⁻ peak eluted. At retention time $t = 5$ min eluent B was set to 0 %,...”

Page 9, Line 15 – Suggest changing succeeding to successful

We wanted to express that the decrease to 0% is necessary for the next (following) analysis. We hope that the replacement of “succeeding” with “subsequent” is more clear.

Page 10, Table 2, first line of caption – Suggest adding a the before varied, changing column to the, and adding the words column along after 250 mm

We changed everything.

“Overview of the varied flows and eluent compositions in the isocratic system using the Metrosep A Supp 16 250 mm column with their effects on separation and reference to the corresponding figures in the supplement.”

Page 11, Figure 4, third line of caption – Suggest adding a the before green

We added “the”.

Page 11, Line 10 – Suggest changing tailing to tail

We changed “tailing” to “tail”.

Page 11, Line 11 – Suggest changing Change to Changing

We corrected “Change” to “Changing”.

Page 12, Line 1 - Suggest changing prolonged to extended

We changed “prolonged” to “extended”.

Page 12, Line 3 – Suggest changing Resulting from the to Due to the. Also suggest removing the word long before coupled

We rewrote the sentence.

“Due to the increased back-pressure of the coupled columns,...”

Page 12, Line 5 - Suggest changing prolonged to extended

We changed “prolonged” to “extended”.

Page 12, Line 8 – Suggest changing carryovers to carryover and adding a for before starting

We corrected this to: “...led to a carryover of...” and “...was found for starting...”

Page 12, Line 11 – Suggest removing the the before eluent

We deleted the “the”.

Page 12, Line 13 – Suggest changing solutions, but was to solutions and was

We replaced “..., but...” with “...and...”

Page 12, Lines 13-14 - Suggest changing by the used chemicals or the used glassware is likely to from the chemicals or glassware used is likely

We rearranged the sentence to: “Thus, a contamination from the chemicals or glassware used is likely.”

Page 12, Figure 5, first line of caption – Suggest adding the word columns after 150 mm and elution after gradient

We inserted both words.

Page 12, Figure 5, third line of caption – Suggest removing the phrase with a gradient system

We deleted this phrase.

Page 12, Figure 5, fourth line of caption – Suggest adding a the before green

We added “the”.

3.2.Limits of detection and precision Page 14, Line 11 – (Funk et al., 2005) should be Funk et al. (2005)

Again, this is a little bit irritating in the manuscript. We rewrote this phrase to: “...was calculated after Funk et al. (2015):”

Page 15, Line 2 – Suggest adding a the before case and removing the is before F

We added a “the” and removed the “is”.

Page 15, Line 9 – Suggest adding a the before quotient

We removed this part from the manuscript. As we used the 3σ approach for the determination of the LOD.

Page 15, Line 10 – Suggest removing the phrase results in the standard deviation of the method as it is stated previously in the sentence

We removed this part from the manuscript.

Page 15, Line 12 – A colon is missing after given by

We removed this part from the manuscript.

Page 16, Line 10 – A colon is missing after $x = 0$ is

We removed this part from the manuscript.

Page 16, Line 12 – A colon is missing after xLOD

We removed this part from the manuscript.

Page 17, Line 1 – A colon is missing after T is

We removed this part from the manuscript.

Page 17, Line 9 – Suggest changing of peak areas to of the peak area

We corrected this to "...of the peak area...".

3.3.Sample handling Page 18, Line 5 – Suggest changing display to displays

We added the "s".

Page 18, Line 12 – Suggest changing solutions were directed into the waste to solution was directed to waste

As two solutions (WRD and SJAC) were directed to waste, we keep the plural but changed "into the waste" to "to waste". Additionally we clarified that both solutions are meant and include this information in the sentence as follows: "...transferred the samples from the WRD and SJAC to the...". Please see also the authors comment below when add additional information to the chapter.

Page 19, Figure 7 - Might suggest changing either the black or blue line in plot b to another color as these two look very similar

We changed the color from black to orange.

Page 19, Figure 7, Fourth line of caption – Suggest adding a the before new

We added a "the".

Page 20, Line 1 – Believe a two-hourly time resolution should be a hour integrated measurement

We add additional information to the chapter on page 18, line 7 that should improve the understanding:

“...This sampling required one hour and yields 25 ml of sample solution in each of the two syringes.

In the second hour, the MARGA syringe pumps transported the solutions to the IC system within the MARGA to analyze the inorganic compounds in the gas and particle-phase, as well as to the autosampler of the Compact-IC. Thereby, the WRD solution was injected with a flow of $0.417 \text{ ml min}^{-1}$ into the MARGA-IC to rinse the sampling lines and to fill the injection loop for the first 13 minutes. Afterwards the analysis of this sample followed for 17 minutes. In the second 30-minutes interval, the SJAC sample was injected and analyzed. Only during the injections into the MARGA-IC of both the WRD and SJAC samples, no solutions were transported via an external 6-way-valve (Fig. 1 (g)) either to the autosampler or to the waste. As the vials in the autosampler had a volume of 12.5 ml, the 6-way-valve transferred the samples from the WRD and SJAC to the autosampler only for the first 45 minutes and the rest of the solutions were directed to waste. In the third hour, the WRD sample was pre-concentrated and was analyzed by the Compact IC. Afterwards, the SJAC sample was pre-concentrated and was analyzed in the fourth hour.

To achieve a pre-concentration and analysis of one sample in one hour, the transfer of analytes from the autosampler to the Compact-IC and the pre-concentration of the sample had to be performed within the remaining 7.5 minutes, as the final Compact-IC analysis described previously needed 52.5 minutes. Therefore, the sample flows were increased to 4 ml min^{-1} , which is the maximum for what is allowed for the pre-concentration column. For the quantification of the organic acids with the Compact-IC, the hourly integrated MARGA samples were collected every two hours. ...”

Page 20, Line 3 – Suggest adding the word column after pre-concentration

We do not want to express the column in this sentence but the process of the pre-concentration. Instead, we added “of the sample” after “pre-concentration”.

3.4.MARGA absorption solution Page 20, Line 13 – Suggest adding a the before absorption

We added “the”.

Page 20, Line 14 – Suggest changing Metrohm-Applikon, the Netherlands, allowed integrating the to Metrohm-Applikon (Netherlands) allowed for integration of the

We rewrote the sentence as suggested.

Page 20, Line 19 – The authors mention that the absorption solution in the MARGA was replaced with a 1% H₂O₂ solution. But what is the typical solution used? It is not actually mentioned and this would be helpful to note since the authors are saying that it is important that the concentration be changed to add the additional analysis of organic acids.

We added the original concentration of H₂O₂ in the first line of the current chapter and rewrote the sentence: “The original MARGA absorption solution in the denuder and SJAC contains 10 mg l⁻¹ H₂O₂ to avoid...”. Five lines later, we gave the information that we excluded H₂O₂ because of potential artifact formation with the organic acids and used ultrapure water as the absorption solution.

3.5. Intercomparison of inorganic ions Page 20, Line 23 – Suggest adding a the before MARGA

We added “the”.

Page 21, Line 1 – It should be a R2

We replaced “an” by “a”.

Page 21, Table 4, First line of caption – Suggest adding a the before MARGA

We added “the”.

Page 21, Line 19 – Suggest adding a the before MARGA

We added “the”.

3.6. Example application in the field Page 23, Line 8 – Suggest changing averaged concentration in this to average concentration over this

We completely revised this chapter.

Page 23, Line 9 – Suggest changing averaged to average

We completely revised this chapter.

Page 23, Line 20 – Suggest adding a the before gas

We completely revised this chapter.

Page 23, Line 21 – There should be no hyphen between one and year

We completely revised this chapter but we removed the hyphen also on page 3, line 20 and on page 20, line 26 to make it consistently.

4. Conclusions Page 24, Line 10 – Suggest removing the it before was the case

We removed “it”.

Page 24, Lines 13-14 – the time resolution is listed as two hours, but I believe it is actually hour integrated

Yes, we collect hourly integrated MARGA samples but only every second hour. This is the reason why we got only every second hour the information and we called this a time resolution of two hours. We additional rewrote the sentence:

“Additionally, obtaining every second hour information of the organic acids allowed for the investigation of diurnal cycles, improving the knowledge of their primary and/or secondary sources.”

Page 24, Line 14 – Suggest adding a for before the investigation

We included “for”.

Data availability Page 24, Line 18 – Suggest changing from authors on request to from the authors upon request

We changed the sentence as suggested.

Author contribution Page 24, Line 20 – Suggest changing concepted to provided the concept for

We replaced “concepted” by “provided the concept for”.

Acknowledgements Page 25, Line 2 – Suggest changing support of to support for

We replaced “of” by “for”.

Page 25, Line 3 – Suggest adding a the before deployment and changing system by to system from

We added a “the” and replaced the “by” by “from”.

**References Page 26, Line 6 – Believe Rondonia should have an accent mark
Page 27, Line 20 – Believe Gelencser is missing accent marks**

We updated both citations.

Supporting Information Page 15, Figure S15 - The same gradient program as for all the other tests is being used, correct? If so, then I might suggest just saying that in the caption. But if the authors do want to keep the program in the corner of the plot then it should probably say %B so it more clear.

The conditions (eluent concentration and flow) of these chromatograms in the supporting information differ from the method described in the main manuscript. This is the reason we plot also the time program in the figure. Additionally, we rewrote the figure caption.

“Figure S15. Temperature variation of the column oven for 55 °C (black) and 65 °C (red). Eluent A concentration is 1 mM Na₂CO₃ / 0.75 mM NaOH and eluent B is 14 mM Na₂CO₃ / 0.75 mM NaOH. Chromatogram of a standard solution with aqueous concentrations of 50 µg l⁻¹ for Cl⁻, NO₃⁻, SO₄²⁻, 25 µg l⁻¹ for NO₂⁻ and 3 µg l⁻¹ for F⁻, Br⁻ as well as all organic acids. Eluent flow of 1.0 ml min⁻¹.”

We added “%B” in the figure time program.

Page 15, Figure S15 - Pyruvate/bromide and oxalate are mentioned in the text, but they are not actually labeled in the figure. It might be helpful to include them for the reader.

We added the mentioned compounds in the figure.

Page 18, Figure S17, first line of caption – Suggest adding a the before MARGA

We added the “the”.

Page 18, Figure S17, second line of caption – Suggest changing during one-year measurement to during the one year long measurement

We changed the phrase as suggested.

Page 19, Figure S18, first line of caption – Suggest adding a the before MARGA

We added “the”.

Page 19, Figure S18, second line of caption – Suggest changing one-year measurement to one year long measurement

We changed the phrase as suggested.

Page 10, Figure S19 – RH and P on the right hand y-axis should be capitalized

We capitalized “RH” and “P” in Figure S19.

Additional changes:

Page 4, Line 10

We changed “11 ml” to “12.5 ml”

Page 10, Line 4-5

We shifted these two lines above the Table 2.

Page 25, Line 13

We updated this reference of Boreddy et al. (2017).

Page 28, Line 26

We updated this reference of Röhrl and Lammel (2002).