Comments on RC1:

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 discusses modifications to a MARGA for measurement of gas and particle organic acids, along with the traditional inorganic species. This type of data could be highly useful and so there is significant value in such an instrument. However, overall the paper is of marginal value. It is largely about setting up the ion chromatographic system to separate and measure all the various ions in a reasonable time. This information could have been presented in a technical report. Or alternatively, as there is apparently a paper focused on data analysis and interpretation from this study in progress, an option would have been to include the topics discussed in the coming paper supplemental section.

We thank the reviewer for generally agreeing on the value of our developed method. We have considered the suggestion to combine method development and data analysis in one large paper. However, we consider the modification of the commercial MARGA system and especially the development and validation of the chromatographic separation to be important enough to justify their stand-alone publication, together with an example application. The ion chromatographic separation of the reported acids with sufficient resolution from potentially interfering organic and inorganic ions has actually been quite an analytical challenge and we think it is beneficial to readers to report these developments in detail together with the final method that promises the reliable quantification of the dominant mono- and dicarboxylic acids as well as methanesulfonic acid in the gas and particle-phase. We also think that the described work is fully in line with the scope of AMT, i.e. "the development, intercomparison, and validation of measurement instruments", and would therefore like to publish it as a full paper.

In any case, the authors background on methods is sparse and some new references are missing. For example, there are other IC approaches (capillary ICs) that can effectively measure these ions, see Nah et al, cited below.

We apologize for this oversight and have now included the mentioned paper in the discussion as will be shown in the specific comments below.

Possible artifacts with this method are not discussed, eg, is the denuder 100% efficient at only removing gases?

We agree this is an important point in the evaluation of this system especially regarding the gas and particle-phase contributions in the later interpretation. We inserted a complete new chapter dealing about this topic. Please find more information in the specific comments below.

A major shortcoming is that the ambient data, shown in support of the utility of the instrument, looks poor due to lack of data? Why is this? Did the instrument not work during those periods, or was the species to be measured below the LOD? This needs much more discussion.

In Figure 8, we have now indicated the few periods when the Compact-IC was not working due to cleaning, blank measurements and calibration. Missing concentrations were cut because of high LOD determined after a rather conservative and theoretical German VDI norm. For a better comparison with other instruments, we changed the approach for the LOD estimation. Please

find more information in the specific comments. Additionally, we now discuss possible reasons for the low concentrations in the completely revised chapter 3.7 about the example application in the field.

Example, if most of the species were below LOD for much of the time, why all the work to attempt to measure them with an online system?

The large fraction of below LOD data has also in part resulted from a rather conservative estimation of the LOD according to the German VDI norm. As we now explain in the revised version of section 3.7, the data coverage during the example application period significantly increases if we estimate LODs based on the internationally more established 3σ criterion.

Can one expect to be able to measure them with this instrument at other locations?

More complete data coverage can of course be expected for locations with higher concentrations of the target acids. Also for the Melpitz location, it can be expected that during periods with high precursor concentrations and stronger photochemical conditions or during periods with stronger anthropogenic influence the concentrations will be higher and the MARGA upgrade will be able to measure them.

That is, does this data really demonstrate the value of this instrument, eg, pg 24 line 11 in Conclusion it states: The results of the example application proved the suitability of the MARGA extension for field measurements. In my view the lack of measurement of most species proves it did not perform well – an instrument that runs but provides little data is likely not of much value.

We understand these doubts but would like to argue that even somewhat incomplete data is better than no data at all. Our aim was to investigate the seasonal cycle of the organic acids in the gas and particle-phase and we developed an instrument that is able to analyze these compounds with a good chromatographic separation. We think this aim has been met even if not all of the organic acids could always be detected above LOD at the given site. A longer-term study of gaseous and particle-bound organic acid concentrations in rural Central Europe with high time resolution has not existed so far and even the sometimes low concentrations of the organic acids can help to classify the Melpitz site in the comparison with other locations around the world.

These issues must be addressed prior to publication. Maybe there is another explanation for the lack of ambient data?

We agree these issues were not addressed to a sufficient extent in the original submission and therefore discuss them in more detail in the revised version, as can also be seen in the specific comments below.

Specific Comments.

Introduction: No discussion of recent organic acid aerosol paper, which is directly pertinent. (Nah, T., H. Guo, A. P. Sullivan, Y. Chen, D. J. Tanner, A. Nenes, A. Russell, N. L. Ng, L. G. Huey, and R. J. Weber (2018), Characterization of Aerosol Composition, Aerosol Acidity and Water-soluble Organic Acids at an Agriculture-intensive Rural Southeastern U.S. Site, Atm. Chem. Phys., 18, 11471-11491.)

Thank you for giving references to this interesting paper. We compared our field measurements with this paper and added the following paragraph on Page 3, Line 14:

"Recently, Nah et al. (2018a) presented measurements of low-molecular weight organic acids within the gas and particle-phase with use of a CIMS and a Particle-Into-Liquid-Sampler (PILS) coupled with a capillary high-pressure ion chromatography (HPIC), respectively. They reported hourly concentrations of these compounds in a rural southeastern United States site for two months and were able to investigate the gas-particle partitioning."

To further complete the literature study, we also add Ullah et al. (2006) below.

"Ullah et al. (2006) developed an on-line instrument to measure ionic species within the gas and particle-phase. For the separation, they used a membrane denuder to collect the water-soluble gases and a hydrophilic filter sampled the particles. In their ion chromatography analysis, it was possible to quantify formic and acetic acid every 40 minutes.
However, to the author's knowledge,…"

We inserted Hu et al. (2018) as representative for GC-MS analysis on page 2, line 12.
We inserted Mungall et al. (2018) as representative for CIMS measurements on page 2, line 26.
We inserted Deshmukh et al. (2018) as representative fro GC-FID on page 2, line 13:

"…or flame ionization detector (GC-FID) (Deshmukh et al., 2018),…"

Additionally, we included all new references in the reference list.

Pg 2 line 28 and on. CIMS is criticized due to cost, too much data (is that really a problem?) and need for skilled operator. One could argue the same for the MARGA system proposed here. Give numbers for comparison. The MARGA system also likely has the disadvantage that it needs constant attention, unlike a CIMS. This should be clarified.

The reviewer is completely right here. Boring et al. (2002) listed these requirements of MS based measurements, but we agree that the MARGA does not have significant advantages over these in terms of costs or operator skills. We therefore deleted this paragraph on page 2, lines 29-31.

The MARGA system does have some advantages in terms of integrated and parallel gas- and particle phase sampling, however. In addition, it is well suited for longer-term measurements, as it is typically applied as a stationary instrument. Also, chromatographic separation and quantification results in highly confident data, as we can practically rule out significant interferences from other species. This can be an issue with online MS instruments, where species with the same or similar masses can bias the quantification of the target species.

Certainly, MS-based and more traditional liquid-based online instruments both have their justification in certain application areas. As we would like to avoid a deep comparative discussion of their strengths and limitations in this manuscript we now solely focus on the benefits of the MARGA system in the revised paper.

Accordingly, we rewrote on page 3, line 16:

"The present study describes the instrumental development of an online-coupled pre-concentration and ion chromatographic (IC) separation system to determine organic acids in the gas and particle-phase as an extension of the MARGA. The MARGA has been reported a reliable field instrument for long-time measurements in Melpitz and other sites (Stieger et al., 2018 and references therein) and its upgrade with an additional IC separation allows for the analysis of all target compounds with low risk of interferences from other species."

Methods: For cases, such as the measurement of organic acids with the described instrument, where a single detection method is used that cannot distinguish between gas or particle phases of a species and the species exists mainly in one phase, less than perfect gas/particle separation can lead to large measurement errors. For example, in this arrangement with the measurements done in series, gas then particle, say most of species X was in the particle phase (i.e., particle » gas), even a very small percent absorption of particles in the denuder will result in large bias in the gas phase measurement. In the other case, particle « gas, less than 100% gas collection will lead to a large bias in particle measurements, if the particle collection system will also collect the gas, which is likely in this system. For the study of organic acids, this is a large issue, which should be discussed in detail, that is report the denuder gas collection efficiency with uncertainty, and the penetration of particles through the denuder.

This is a good point and we agree it should be discussed in the manuscript to evaluate this system. We used theoretical approaches to calculate the annular denuder efficiencies of each organic acid. High collection efficiencies of over 99% were mostly determined. When applying the resulting denuder efficiencies and the highest gas phase concentrations of each organic acids, the worst-case artifact particulate concentrations are close to the LOD and do therefore not strongly bias the comparisons between gas and particle-phase. For more detailed information we inserted a new chapter "3.5 WRD efficiency and particle penetration":

"3.5 WRD efficiency and WRD particle collection

When measuring the gas and particle-phase with a combination of WRD and SJAC, the collection efficiency of gases and the particle penetration within the denuder should be investigated. In the literature, experimentally derived collection efficiencies are available for annular denuders that correspond with the WRD within the MARGA. Wyers et al. (1993) published an NH_3 efficiency of 98% with an air flow of $30 \, l \, min^{-1}$. Khlystov et al. (2009) investigated the HNO_3 breakthrough in the presence of particles. They found under urban background conditions a breakthrough of 0.6%. The MARGA manufacturer Metrohm-Applikon already tested the denuder efficiency of the WRD for SO_2 and found a recovery of 99.7% (personal communication).

In the present study, the collection efficiencies of the annular WRD were theoretically calculated for the different inorganic and organic acids following different approaches suggested in the literature (Possanzini et al., 1983;Winiwarter, 1989;De Santis, 1994;Berg et al., 2010). For each approach, all equations for the denuder efficiency calculation are given in the supplement. Calculated denuder efficiencies are summarized in Table 4. The calculated efficiencies according to Possanzini et al. (1983), De Santis (1994) and Berg et al. (2010) are higher than 99% indicating a nearly complete absorption of the investigated gases within the WRD. Denuder efficiencies derived from the approach of Winiwarter (1989) ranges between 95% for glutaric acid and nearly 100% for the inorganic gases as well as formic acid. However, compared to the other three studies, Winiwarter (1989) did not consider the geometry of an annular denuder in his approach and is therefore considered to be less accurate. Regarding the efficiencies calculated after Possanzini et al. (1983) and the highest formic acid gas-phase concentrations of $7.58 \, \mu g \, m^{-3}$ measured by the Compact-IC, the potential particulate artifact concentration would result in $2.3 \, ng \, m^{-3}$, which is below the LOD of the method. The calculated WRD efficiencies of Possanzini et al. (1983) were used to calculate the potential particulate artifact concentrations from the gaseous concentrations for the complete measurement campaign. These concentrations were compared with real particulate concentrations. It was found that the artifact concentration is far below the real measurements. Only an average of 0.15% of the real particulate formate concentrations could be explained by possible formic acid

breakthrough. For acetate, propionate, butyrate, pyruvate and glycolate, percental values of 3.7%, 0.6%, 0.3%, 0.4% and 0.2% were calculated, respectively, and were similar low. Thus, interferences of gaseous compounds in the SJAC are negligible.

Another method to evaluate the WRD collection efficiency of gases is the comparison of measured compounds that are predominantly found in the gas phase. The inorganic nitrite (NO_2^-) of HONO is quantified by the Compact-IC. The NO_2^- concentration within the particle-phase is near zero. For the three highest HONO concentrations during the measurement campaign (on average 5.1 µg m^{-3}) only 66.2 ng m^{-3} particle-phase NO_2^- were observed resulting in a maximum HONO breakthrough of 1.3%. The same calculation were performed for formic and acetic acid that are most abundant in the gas-phase (Nah et al., 2018a), resulting in a potential maximal breakthrough of 0.7% and 0.1%, respectively. Thus, the calculated denuder efficiencies are in same range with the experimental derived ones reported in the literature.

For the WRD particle collection, Wyers et al. (1993) investigated possible particulate ammonium collection within the denuder. A sampling of ammonium sulphate particles of 0.1 and 1 µm median volume diameter resulted in a particle collection of 0.6% within the denuder for both sizes. In the same range are the experimentally derived particle collections of Possanzini et al. (1983) with 0.2% for 0.3-0.5 µm particles and 1.4% for particles larger than 3 µm.

The three highest concentrations of the DCAs were compared with the gas-phase concentrations measured in the field. The oxalate concentrations in the particle-phase ranged between 327 ng m^{-3} and 543 ng m^{-3}. At the same time, no gas-phase concentrations were detected. For the other particulate dicarboxylic acids and methanesulfonate, detectable gas-phase concentrations were not observed during periods with high particulate concentrations indicating a negligible effect of particle collection within the WRD.

In conclusion, the calculated denuder efficiencies that are in agreement with the literature as well as low rates of denuder breakthrough and low particulate losses within the WRD approve the use of a coupled WRD/SJAC system as valid method to separate the gas and particle-phases for the sampling of the low-molecular weight organic acids."

Table 4. Diffusion coefficients (D) calculated according to Fuller et al. (1966) and calculated annular denuder efficiencies (E) according to the equations of Winiwarter (1989), Possanzini et al. (1983), De Santis (1994) and Berg et al. (2010) for gases.

Gas	D / cm^2 s^{-1}	$E_{Winiwarter}$ / %	$E_{Possanzini}$ / %	$E_{De\ Santis}$ / %	E_{Berg} / %
HCl	0.163	99.75	99.99	>99.99	>99.99
HONO	0.171	99.81	99.99	>99.99	>99.99
HNO$_3$	0.157	99.69	99.99	>99.99	>99.99
SO$_2$	0.149	99.58	99.98	>99.99	>99.99
NH$_3$	0.199	99.93	>99.99	>99.99	>99.99
Formic acid	0.143	99.48	99.97	>99.99	>99.99
Acetic acid	0.119	98.76	99.89	99.99	99.98
Propionic acid	0.104	97.87	99.74	99.96	99.95
Butyric acid	0.094	96.95	99.55	99.91	99.90
Pyruvic acid	0.103	97.80	99.72	99.96	99.94
Glycolic acid	0.114	98.52	99.85	99.98	99.97
Oxalic acid	0.113	98.46	99.84	99.98	99.97

Malonic acid	0.100	97.54	99.68	99.94	99.93
Succinic acid	0.0912	96.62	99.47	99.89	99.87
Malic acid	0.0892	96.37	99.41	99.88	99.85
Glutaric acid	0.0827	95.41	99.15	99.80	99.77
Methanesulfonic acid	0.114	98.52	99.85	99.98	99.97

We added additional information in the Supplement:

WRD efficiency

d_i - inner diameter (4.2 cm)
d_o - outer diameter (4.5 cm)
d - hydrodynamic equivalent diameter ($d_o - d_i = 0.3$ cm)
L - length of the denuder (30 cm)
D - diffusion coefficient (calculated according to Fuller et al. (1966))
u - flow velocity (16.7 l min^{-1})
E - denuder efficiency

Table S2. Equations for the calculations of the efficiencies (E) for annular denuders.

	Winiwarter (1989)	Possanzini et al. (1983)	De Santis (1994)	Berg et al. (2010)
X	$\dfrac{2LD}{d^2u}$	$\dfrac{\pi LD(d_i + d_o)}{4ud}$	$\dfrac{\pi LD(d_i + d_o)}{ud}$	Efficiencies were calculated with their described spreadsheet calculator
E	$1 - 9.11 \cdot e^{-3.884^2 X}$	$1 - 0.82 \cdot e^{-22.53X}$	$1 - 0.91 \cdot e^{-7.54X}$	

We included new citations in the reference list.

Due to the new Table 4, we changed the old Table 4 to Table 5 on:
Page 20, Line 27,
Page 21, Line 12

Due to the new chapter, we changed chapter 3.5 to 3.6 and 3.6 to 3.7

Results: What is the cause for all the missing data in Fig 8, data below LOD? Is so this should be discussed. Ie, give report fraction of data above LOD for all species in the ambient study.

The missing concentrations were predominantly below the LOD. However, we realised that the originally applied German VDI norm represents a rather conservative approach for the calculation of the LOD and resulted in rather high LODs. When including all below LOD values that were originally removed from the data set, we observed much less missing data and much better data coverages. We have therefore decided to replace the originally applied VDI LOD calculation approach with an estimation approach that is internationally more established. We now calculate the LOD from mean blank values plus three times the standard deviation (3σ) or, for acids with no blank signals, from the smallest observable peaks. These LODs are lower than the originally reported ones and range between 0.5 ng m^{-3} for malonate and 17.4 ng m^{-3} for glutarate.

Although the data coverage was improved by applying the 3σ method, some values for several organic acids were still below the LOD or were not detected. As additional information, we included in Figure 8 periods in grey, in which no data were available because of instrumental issues like cleaning procedures, blank measurements or calibration of the Compact-IC.
Possible reasons for not detectable concentrations are changeable weather conditions, lower temperatures, and cloudy weather during the first days, leading to lower emissions of the acids or to less effective formation from their atmospheric precursor species.

We completely revised the chapter 3.7 Example application in the field. In Figure 8, we marked periods with grey where no data are available because of instrumental issues. We added Table 6 with the percental data coverages of each organic acid during the example measurement period. In the newly revised chapter, we explain the low concentrations as follows:

"3.7 Example application in the field

To prove the suitability of the complete setup, two weeks of the one year measurement campaign are presented. Figure 8 displays the measured organic acids in the gas and particle-phase from 3rd May 2017 until 14th May 2017. Included grey shaded periods display downtimes of both the MARGA and the Compact-IC because of MARGA cleaning procedure (12th May), blank measurements of the complete new MARGA setup (12th May) or measurements of calibration standards (5th, 9th, 12th May). Table 6 gives the percental data coverage, i.e. concentrations above LOD, for each organic acid in the gas and particle-phase during the uptime periods.
Very good data coverages were found for formate and acetate in both phases as well for glycolate and methanesulfonate in the particle-phase with percental values over 90%. Table 6 indicates the dominance of non-glycolate MCAs in the gas phase while DCAs were predominantly detected in the particle-phase. This finding is in agreement with the higher vapour pressures of MCAs (Howard and Meylan, 1997).
For the calculations of mean concentrations, all values below LOD were included and not detected data were set to zero. Mean (maximum) concentrations of 306 ng m^{-3} (2207 ng m^{-3}) were observed for gaseous acetic acid followed by formic 199 ng m^{-3} (919 ng m^{-3}), propionic 83 ng m^{-3} (524 ng m^{-3}), pyruvic 76 ng m^{-3} (253 ng m^{-3}), butyric 34 ng m^{-3} (343 ng m^{-3}) and glycolic acid 32 ng m^{-3} (259 ng m^{-3}). This is in agreement with other studies. Fisseha et al. (2006) monitored in the city of Zurich, Switzerland, mean concentrations of acetic acid between 1.09 µg m^{-3} in September and 1.97 µg m^{-3} in March. Formic and propionic acid ranged between 0.24 µg m^{-3} and 1.07 µg m^{-3} as well as between 0.16 µg m^{-3} and 0.03 µg m^{-3}, respectively.

Another urban site is described by Lee et al. (2009). In Seoul, they reported formic, acetic and propionic acid concentrations of around $3.83 \, \mu g \, m^{-3}$, $4.99 \, \mu g \, m^{-3}$ and $1.54 \, \mu g \, m^{-3}$, respectively. Higher concentrations of formic and acetic acid at urban sites could be favored due to anthropogenic emissions. Khare et al. (1999) and references therein summarized formic and acetic acid concentrations and reported concentrations of $1.72 \, \mu g \, m^{-3}$ and $2.25 \, \mu g \, m^{-3}$ at a semiurban site in Central Germany, respectively. The amount of formic and acetic acid measured at the semiurban site Bondville, United States, are around $0.6 \, \mu g \, m^{-3}$ and $1 \, \mu g \, m^{-3}$, respectively (Ullah et al., 2006). Nah et al. (2018a) detected at the rural Yorkville, Georgia, site averaged concentrations of formic and acetic acid of $2.2 \, \mu g \, m^{-3}$ and $1.9 \, \mu g \, m^{-3}$, respectively

DCAs and methanesulfonate were rarely detected in the gas-phase due to the low vapour pressures of these compounds. Thus, an existence of these species is more likely in the particle phase. However, malonate, succinate, malate and glutarate were rarely or not at all detected in the particulate phase (Table 6). Oxalate is the predominant DCA in the particle phase with a percental data coverage of 77.3 %. Interestingly, also formic and acetic acid were detected in the particulate phase. Mean (maximum) concentrations of $31 \, ng \, m^{-3}$ ($209 \, ng \, m^{-3}$), $30 \, ng \, m^{-3}$ ($465 \, ng \, m^{-3}$), $34 \, ng \, m^{-3}$ ($282 \, ng \, m^{-3}$), $26 \, ng \, m^{-3}$ ($162 \, ng \, m^{-3}$) and $18 \, ng \, m^{-3}$ ($54 \, ng \, m^{-3}$) were monitored for oxalate, methanesulfonate, formate, glycolate and acetate, respectively.

As comparison, Parworth et al. (2017) detected average glycolate concentrations of $26.7 \, ng \, m^{-3}$ with a nighttime maximum of around $60 \, ng \, m^{-3}$ in Fresno during winter. Mean concentrations of particulate oxalate, acetate and formate of $0.07 \, \mu g \, m^{-3}$, $0.06 \, \mu g \, m^{-3}$ and $0.05 \, \mu g \, m^{-3}$ were measured by Nah et al. (2018a), respectively. van Pinxteren et al. (2014) presented oxalate concentrations measured by impactors in Melpitz during autumn. A mean concentration of $52 \, ng \, m^{-3}$ was published. Additionally, mean values measured in Falkenberg (approximately 25 km northeast of Melpitz) during summer peaks in $80 \, ng \, m^{-3}$. A predominant peak of methanesulfonate was observed on 8th May 2017. This happened simultaneously with a sudden increase of wind speed (Figure S19). Northwesterly winds transporting marine air masses to Melpitz appear to be the most likely explanation as marine DMS oxidizes within the aqueous phase to methanesulfonate (Hoffmann et al., 2016;Lana et al., 2011).

The comparison with the literature shows rather low concentrations of the organic acids in the particle-phase during the example application in the field. A possible reason are the changeable weather conditions. The temperature varied during the first seven days between 0°C and 15°C. Afterwards, sunnier and warmer conditions were present resulting in an increase of formic, acetic and propionic acid concentrations probably because of a relationship between temperature, global radiation and higher organic acid concentration.

Highest values for temperature and global radiation were observed during daytime (Figure S19) why it is expected to measure elevated concentrations in this time. Diurnal cycles of formic acid and particulate oxalate are illustrated in Fig. 9a,b, respectively. Both compounds had the lowest concentrations in the early morning and increased in the afternoon until the maxima were reached in the evening following the observed average temperature. This trend is in agreement with previous studies (Lee et al., 2009;Millet et al., 2015;Khare et al., 1997;Nah et al., 2018b;Martin et al., 1991). During night, concentrations decreases due to deposition processes. Simultaneously, a decreasing surface temperature cools down the lower air layers leading to an inversion layer that suppresses the vertical mixing. The increasing concentrations after sunrise are likely a result of downward mixing of enriched layers above the boundary layer (Khare et al., 1999). Biogenic emissions and photochemical processes lead to increasing concentrations during daytime (Khare et al., 1999;Liu et al., 2012b).

Nah et al. (2018a) reached the same conclusion from their study. They found higher concentrations during warm and sunny days caused by elevated availability of biogenic precursors. During their two month measurement campaign in late summer and autumn, the maximum temperature ranged in average between 25°C and 30°C with high solar irradiances. Interestingly, for several days the temperature decreased below 20°C with a simultaneous

decrease of several DCA concentrations. Thus, the low concentration found during the example application are probably a result of lower temperatures, low global radiation and, probably, lower amounts of biogenic precursors in spring.

The application in the field demonstrates the suitability of the developed setup. The measured concentrations of low-molecular weight organic acids in Melpitz are partly lower than concentrations, which can be found in the literature. The increase of the concentrations after 11th May 2017 indicate an influence of the increasing temperature and the available sunlight, which is needed for biogenic emissions or photochemical reactions of atmospheric precursors. Further in-depth analyses and detailed results of the one year measurements with the extended MARGA system will be presented elsewhere (Stieger et al., manuscript in preparation)."
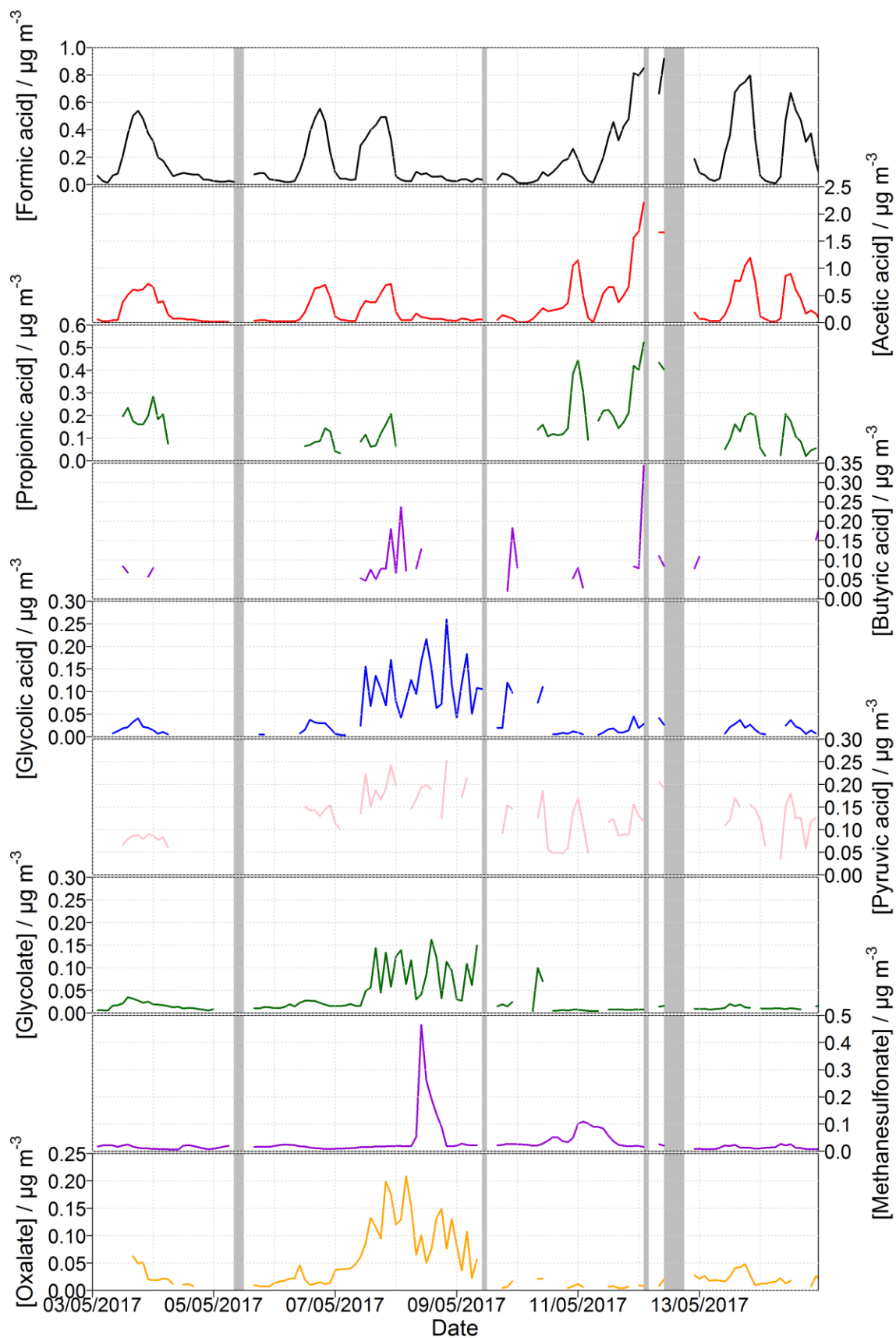
Figure 8. Measured concentrations for gaseous formic, acetic, propionic, butyric, glycolic and pyruvic acid as well as for particulate glycolate, methanesulfonate and oxalate from 1st May until 14th May 2017 for an example application. The grey shaded areas represent periods without data because of instrumental issues.

Table 6. Data coverage for the organic species measured in the gas and particle phase from 3rd May 2017 until 14th May 2017 during instrument uptime periods shown for data above the LOD.

Compound	Gas-phase / %	Particle-phase / %
Formate	100	99.2
Acetate	99.2	96.2
Propionate	51.9	0.8
Butyrate	30.8	6.1
Pyruvate	58.6	5.3
Glycolate	70.7	90.9
Oxalate	25.6	77.3
Malonate	2.3	23.5
Succinate	3.8	9.1
Malate	1.5	27.3
Glutarate	0	0
Methanesulfonate	24.1	99.2

As we use a new LOD approach, we changed the section 3.2 to:

"3.2 Limits of detection, linearity and precision

All values of the Limits of Detection (LOD), linearity and precision for each species are given in Table 3. The linearity of the calibration curve was determined after Funk et al. (2005). For the linear calibration function ($y = a + bx$), the slope b and the intercept a can be calculated as follows (DIN 32645, 2008):

$$Q_{xx} = \sum_{i=1}^{n} x_i^2 - \frac{(\sum_{i=1}^{n} x_i)^2}{n} \tag{1}$$

$$Q_{yy} = \sum_{i=1}^{n} y_i^2 - \frac{(\sum_{i=1}^{n} y_i)^2}{n} \tag{2}$$

$$Q_{xy} = \sum_{i=1}^{n} (x_i y_i) - \frac{\sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i}{n} \tag{3}$$

$$b = \frac{Q_{xy}}{Q_{xx}} \tag{4}$$

$$a = \bar{y} - b\bar{x} \tag{5}$$

where Q_{xx}, Q_{yy} and Q_{xy} are the square sums, $\bar{x}$ and $\bar{y}$ the means and n the number of calibration points.

The calibration of a non-linear second-order function ($y = a + bx + cx^2$) was calculated considering DIN ISO 8466-2 (2004). Simultaneous to the Eq. (1) to (3), the following quadratic sums were added:

$$Q_{x^3} = \sum_{i=1}^{n} x_i^3 - \sum_{i=1}^{n} x_i \frac{\sum_{i=1}^{n} x_i^2}{n} \tag{6}$$

$$Q_{x^4} = \sum_{i=1}^{n} x_i^4 - \frac{(\sum_{i=1}^{n} x_i^2)^2}{n} \tag{7}$$

$$Q_{x^2y} = \sum_{i=1}^{n} (x_i^2 y_i) - \sum_{i=1}^{n} y_i \frac{\sum_{i=1}^{n} x_i^2}{n} \tag{8}$$

The intercept a and the coefficients b and c were calculated as follows:

$$c = \frac{Q_{xy} Q_{x^3} - Q_{x^2y} Q_{xx}}{Q_{x^3}^2 - Q_{xx} Q_{x^4}} \tag{9}$$

$$b = \frac{Q_{xy} - c Q_{x^3}}{Q_{xx}} \tag{10}$$

$$a = \bar{y} - b\bar{x} - c \frac{\sum_{i=1}^{n} x_i^2}{n} \tag{11}$$

The residual standard deviation for the linear $s_{y,l}$ and the non-linear case $s_{y,nl}$ are:

$$s_{y,l} = \sqrt{\frac{\sum_{i=1}^{n} [y_i - (bx_i + a)]^2}{n-2}} = \sqrt{\frac{Q_{yy} - \frac{Q_{xy}^2}{Q_{xx}}}{n-2}} \tag{12}$$

$$s_{y,nl} = \sqrt{\frac{\sum_{i=1}^{n} (y_i - \hat{y}_i)^2}{n-3}} \tag{13}$$

To test each ion's linearity, the difference of the variances DS^2 was calculated after Funk et al. (2005):

$$DS^2 = (n-2)s_{y,l}^2 - (n-3)s_{y,nl}^2 \tag{14}$$

with the degree of freedom of $f = 1$. For a F-Test, the test value TV was determined:

$$TV = \frac{DS^2}{s_{y,nl}^2} \tag{15}$$

This test value was compared with a F-Test table ($f_1 = 1$, $f_2 = n - 3$, $P = 99$ %). If $TV \leq F$, the calibration function is linear. For the other cases, the calibration function is a non-linear second-order function. In the case of the present work $F = 11.26$. The resulting TV values for each ion are summarized in Table S1. Depending on the result of the linearity test, linear or quadratic calibration functions were fitted. As examples for a linear and a quadratic fit, the calibration functions of NO_3^- and pyruvate are respectively displayed in Fig. 6. Other calibration functions are given in the supplement (Fig. S16). The linearity test was performed through a double injection of 11 standards with evenly distributed concentrations over one order of magnitude, where the maximum concentration corresponded to standard 3 in Table 1.

The Limits of Detection (LOD) for the Compact-IC were estimated from mean blank values plus three times the standard deviation (3σ). For species that were not found in the blank measurements, the LOD represents the smallest observable peak. The LODs as atmospheric concentrations varied between 0.5 ng m^{-3} for malonate and 17.4 ng m^{-3} for glutarate and were considered sufficiently low for field application of the system. The precision of the method was calculated as the relative standard deviation (RSD) of the peak area of 11 injections of standard 3 (Table 1) over one month. For all ions, the precision is below 3 %, indicating a good repeatability."

Table 3. Type of calibration curve, LODs and the method precision for each ion.

Ion	Cal. curve	LOD / ng m^{-3}	precision / %
F$^-$	quadratic	4.4	0.3
Cl$^-$	linear	16.2	1.9
NO$_2^-$	linear	2.3	0.4
Br$^-$	quadratic	17.0	0.2
NO$_3^-$	linear	5.4	0.7
SO$_4^{2-}$	quadratic	5.5	0.4
Methanesulfonate	quadratic	1.3	0.5
Formate	linear	6.2	0.5
Acetate	quadratic	3.9	1.0
Glycolate	quadratic	3.8	2.9
Propionate	linear	12.5	0.7
Butyrate	linear	16.0	0.5
Pyruvate	quadratic	13.4	0.1
Oxalate	linear	1.4	0.1
Malonate	linear	0.5	0.1
Malate	quadratic	3.6	0.2
Succinate	quadratic	11.7	1.0
Glutarate	quadratic	17.4	0.1

New references were included in the reference list.

Page 22, Fig 9. Maybe the diurnal profile was not due to photochemical formation, but instead temperature?

You are right. The direct comparison of the average temperature and the diurnal behaviour of formic acid and oxalate show very good agreements. During night, the surface cools down. Consequently, the air temperature above the surface decreases leading to a near-ground inversion. In this case, a vertical mixing is prohibited and the concentrations decreases due to deposition. The daily course is discussed within the revised chapter 3.7. As graphical overview, we inserted the average temperature in Figure 9a.
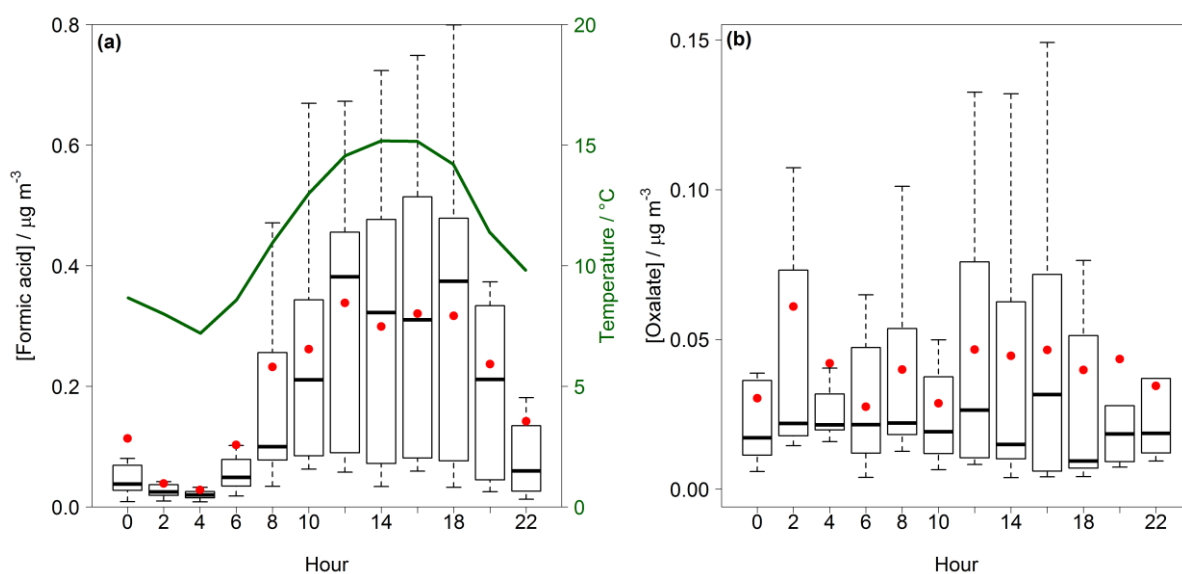

Figure 9. Box-Whisker-Plot for the diurnal variation of gaseous formic acid (a) and particulate oxalate (b) in Melpitz for the example application in the field. The red dots represent the mean, the box the 25th and 75th percentile and the upper whisker the 75th percentile plus the 1.5-fold interquartile range (IQR) and the lower whisker the 25th percentile minus the 1.5-fold IQR. In (a) the average temperature is given in green.

Pg 23, line 19-20. If most of the data is below LOD, how can the authors claim the instrument was a success?

We understand this criticism. We changed our LOD calculation to the internationally better known 3σ approach also to make the described setup more comparable to others. The new approach resulted in an improved data coverage of the organic acids (up to 100%). Not detectable concentrations for some DCAs in the particle-phase and some MCAs in the gas-phase are a result of low concentrations during the studied period due to lower temperatures and cloudy weather.

However, also very low concentrations during the example application are part of the result of a one-year measurement campaign to investigate the seasonal course of different organic acids in Melpitz. Additionally, these low concentrations help us to evaluate Melpitz in comparison with stations around the world.

The described method showed a good intercomparison between MARGA and Compact-IC indicating a trustworthy calibration. The separation of the gas and particle-phase by the WRD/SJAC setup within the MARGA show negligible interferences.

All the findings in the revised manuscript let us claim that the instrument was a success.

Additionally we added on page 24, line 11:

"To the author's knowledge, high resolved data of low-molecular weight organic acids are not available for rural Central Europe. Before our investigation, a quantification of these acids in the particle-phase was only possible with filter measurements resulting in a low time resolution and potential artifacts from adsorption or revolatilisation."