

2 h interval gas- and particle-phase measurements of low-molecular-weight organic acids with an on-line MARGA extension

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Introduction

Low-molecular-weight organic acids are emitted primary (biogenic and anthropogenic sources) or are formed secondary by atmospheric oxidation processes. However, several sources are still unknown. Their hygroscopicity can affect the acidity of atmospheric aqueous droplets and atmospheric transport processes lead to an input in remote areas with potential effects on the sensitive ecosystem [1].

A highly time-resolved and near-real-time quantification of these organic acids is challenging because of the low concentrations compared to inorganic species. Filter measurements offer a variety of analytical investigations but are time consuming, have a weak time resolution and are not free of sampling artifacts.

The Monitor for Aerosols and Gases in ambient Air (MARGA, Metrohm-Applikon) quantifies hourly the water-soluble trace gases (HCl, HONO, HNO₃, SO₂, NH₃) and inorganic ions in PM₁₀ (Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺,

K⁺, Mg²⁺, Ca²⁺) at the TROPOS research station Melpitz since 2010. The phase separation is performed by a combination of Wet Rotating Denuder (WRD) and Steam-Jet Aerosol Collector (SJAC) [2].

In the current study, a method was developed to detect formic, acetic, propionic, butyric, pyruvic, glycolic, oxalic, malonic, succinic, malic, glutaric, and methanesulfonic acid in the gas and particle phases. Therefore, an additional IC system (Compact IC) was tested in the laboratory to achieve a separation of all target compounds with low risks of interferences, good precisions and low limits of detection (LOD). The best separation was observed with gradient system, pre-concentration and a special separation column setup.

After successful laboratory tests the Compact IC was combined with the MARGA for on-line ambient measurements. First results are presented [3].

Compact IC Setup



Fig. 1: Setup of the Compact IC system with (a) the first working and (b) the second working station of the autosampler with 120 slots for 12.5 mL vials arranged in two circles. (c) the 800 Dosino for the sample transportation between autosampler and (d) the Compact IC via a 10 mL sample loop (e). A further 800 Dosino (f) for the gradient system. The sample flow between MARGA and Compact IC was controlled by an external six-way valve (g).

Compact IC separation

- Use of pre-concentration column Metrosep A PCC 2 VHC by Metrohm (enrichment factor around 400)
- Gradient system with eluent A (0.5 mM Na₂CO₃/0.75 mM NaOH) and eluent B (20 mM Na₂CO₃/0.75 mM NaOH)
- Combination of two separation columns Metrosep A Supp 16 250 mm and Metrosep A Supp 16 150 mm (Metrohm)

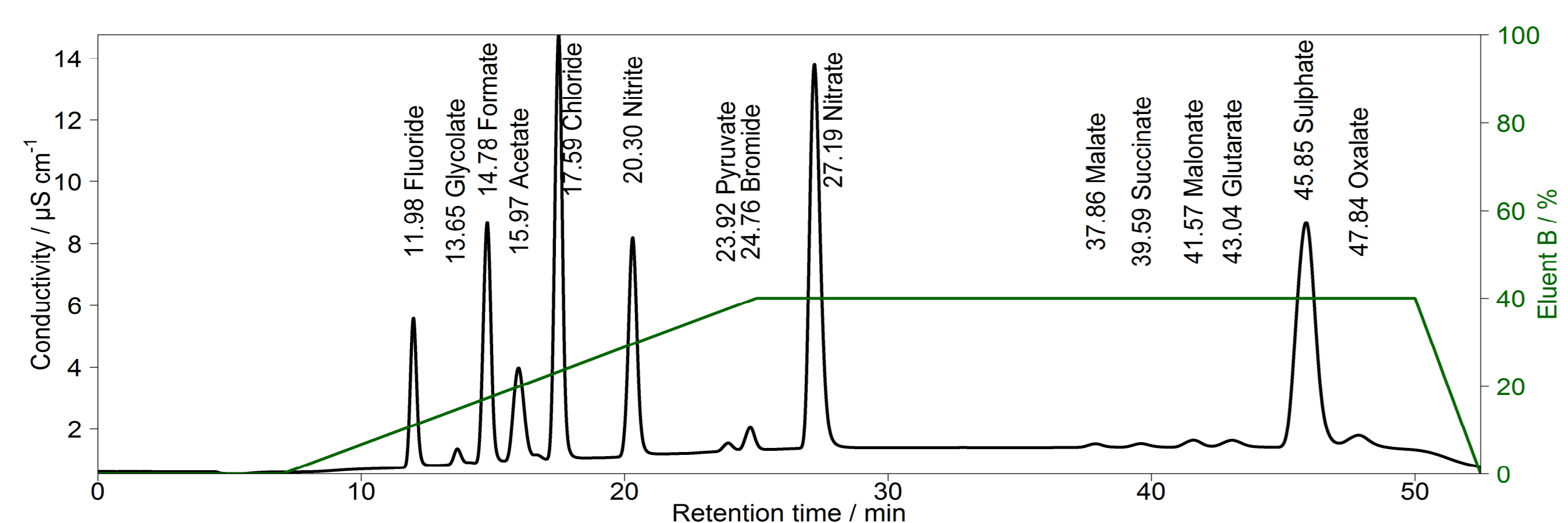


Fig. 2: Final chromatogram after laboratory tests with a standard solution of 50 µg L⁻¹ for Cl⁻, NO₂⁻; 100 µg L⁻¹ for NO₃⁻, SO₄²⁻ and 10 µg L⁻¹ for all other ions. T = 65° C and eluent flow of 0.8 mL min⁻¹.

Ion	Calibration 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

Table 1: Type of mathematical derived calibration curve (see Fig. 3). LODs were estimated from mean blank values plus 3 times the standard deviations (3σ). For species that were not detected in the blank, the LOD represents the smallest observable peaks. The precision was calculated as the relative standard deviation (RSD) of the peak area of 11 injections of a standard over 1 month.

→ Sufficiently low LODs
 → Good repeatability

- Methanesulfonate, propionate and butyrate in ambient samples detected
- Included in analysis without interferences of other species

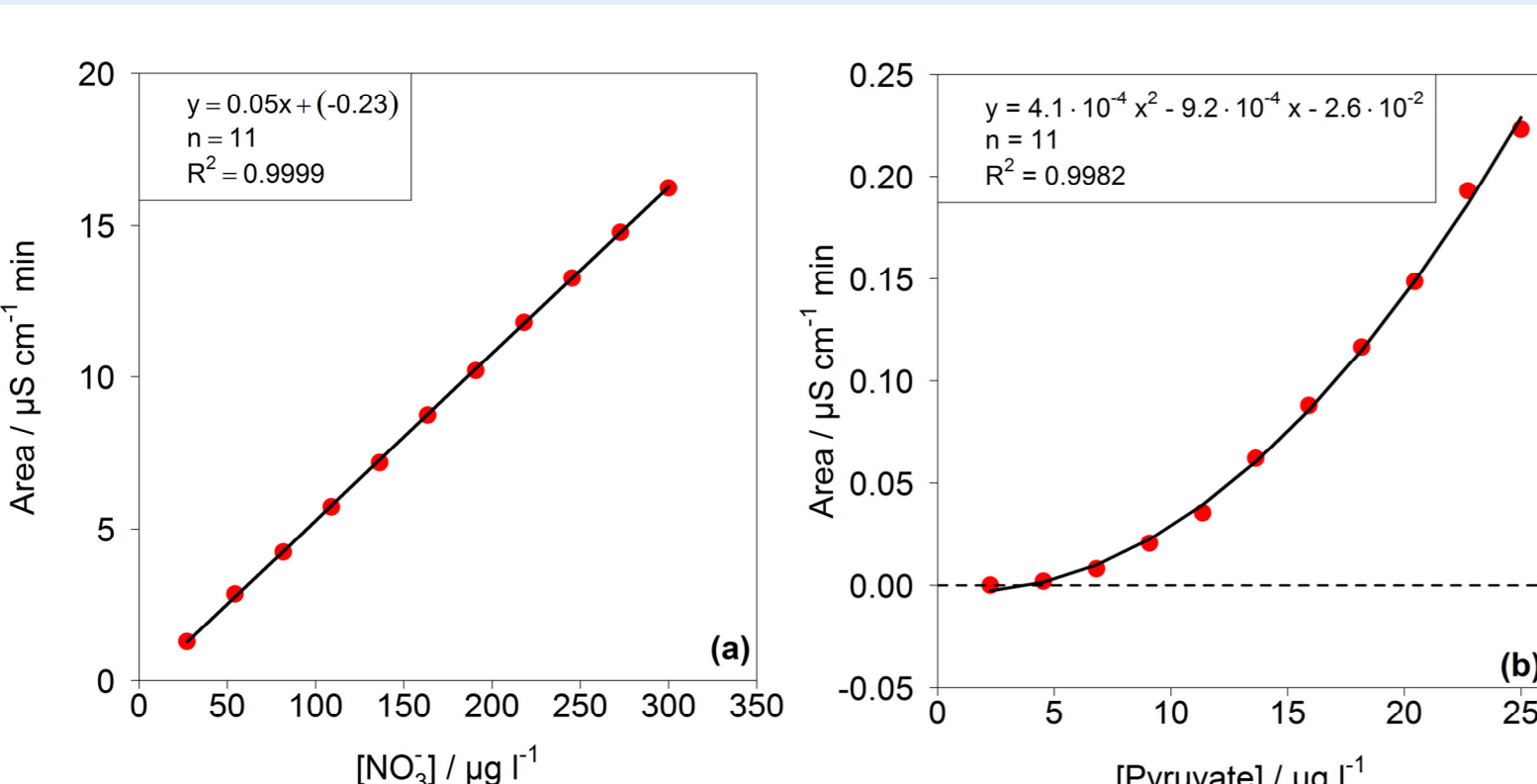


Fig. 3: Linearity test for (a) linear NO₃⁻ and (b) quadratic pyruvate. Test were performed by double injection of 11 standards with evenly distributed concentrations with maximum concentrations of 300 and 25 µg L⁻¹, respectively. Equations were derived by DIN 32645 (2008) for linear calibration curves and DIN ISO 8466-2 (2004) for nonlinear second-order functions.

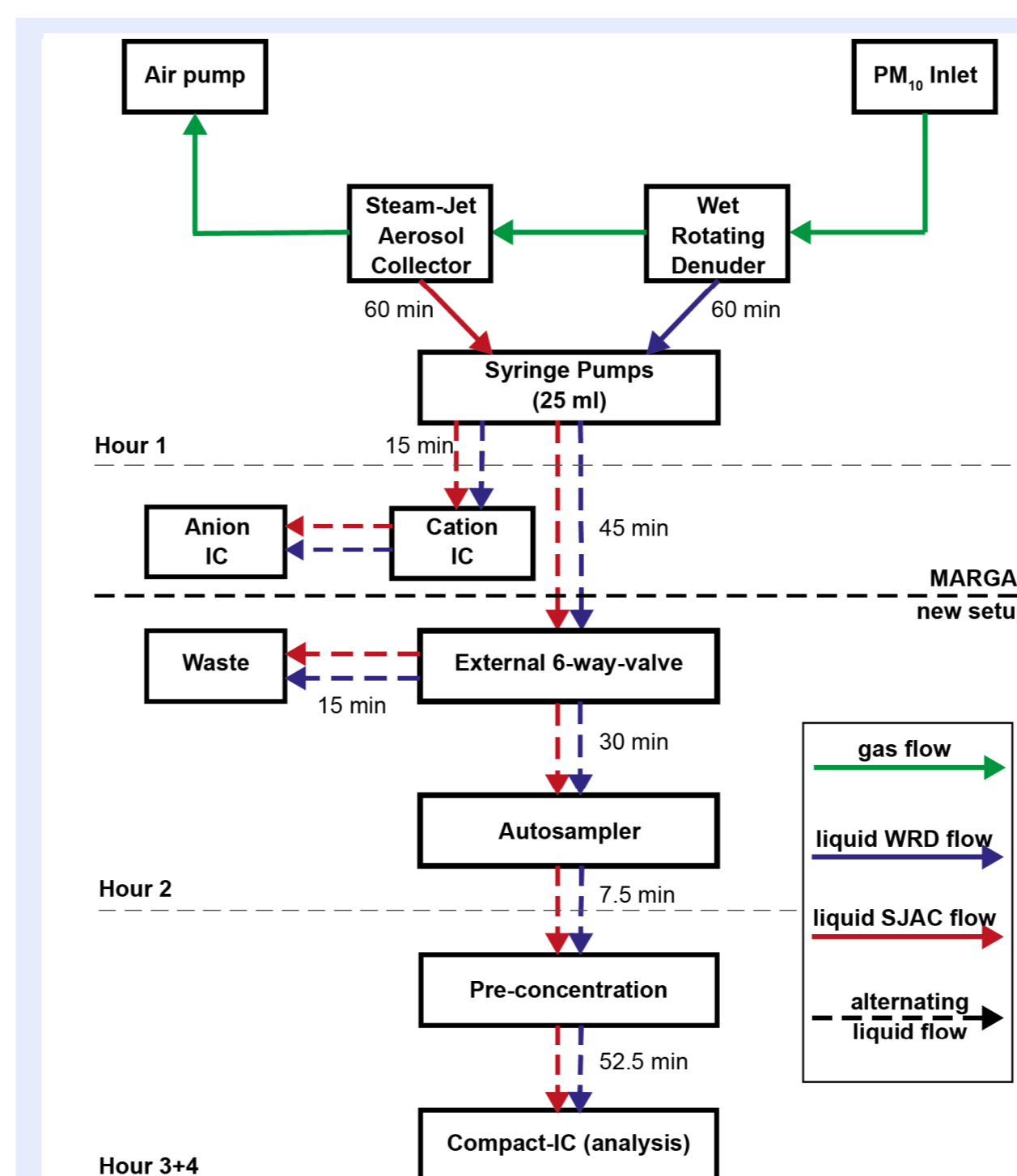
Summary

A method is presented to detect low-molecular-weight organic acids in a two-hourly time resolution in both gas and particle phases. Therefore, a MARGA was combined with a specialized Compact IC. Good repeatabilities and low LODs were achieved.

Measurements show a dominance of MCAs in the gas phase whereas DCAs and Methanesulfonate are found predominantly in the particle phase. In parallel with temperature, high concentrations during daytime indicate a photochemical formation by atmospheric precursors.

The measurements of organic acids were extended for one year to investigate the seasonal behaviour of their concentrations on a high resolved basis, their sources and their role on the tropospheric multiphase chemistry.

Sample handling



- Gas and particle sampling within the MARGA during the first hour
- In the second hour, the samples are transported either to the MARGA ICs or to the autosampler
- In the third hour, the gas-phase sample is transported from the autosampler to the Compact IC and is analyzed
- Particle-phase sample is transported and analysed in the fourth hour

- Hourly integrated MARGA samples were collected every 2 h by the autosampler
- Two-hourly time resolution for gas and particle compounds

WRD efficiency and particle collection

- Possible artifact formation of trapped particles within the denuder or inefficient gas sampling
- Use theoretical calculations for annular denuders
- Worst gas-phase collection efficiency was 99.15% for glutaric acid
- Neglectable losses

- Comparison of oxalate and methanesulfonate in gas and particle phases show neglectable particle losses within the denuder

Measurement results

- Results during example application from 3 to 14 May 2017
- Monocarboxylic acids (MCA) dominate the gas phase while dicarboxylic acids (DCA) and methanesulfonate are predominantly in the particle phase

Data availability

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

Table 2: Data availability for the organic species measured in the gas and particle phase. All data above the LOD.

IC comparison

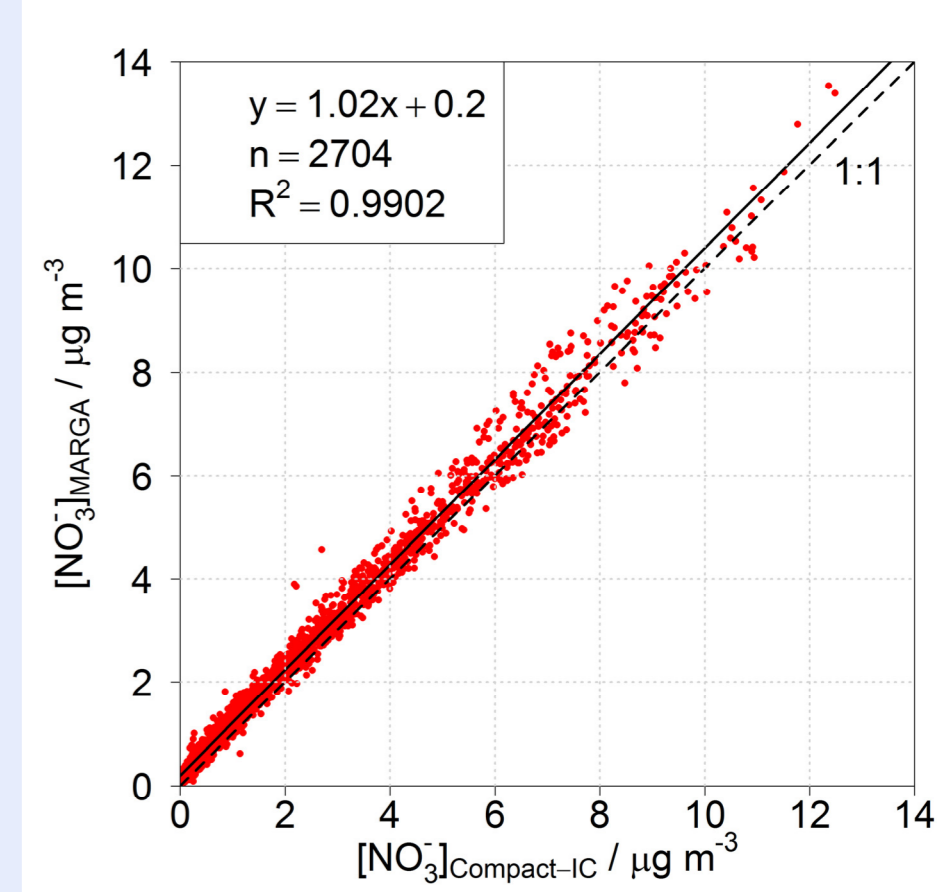
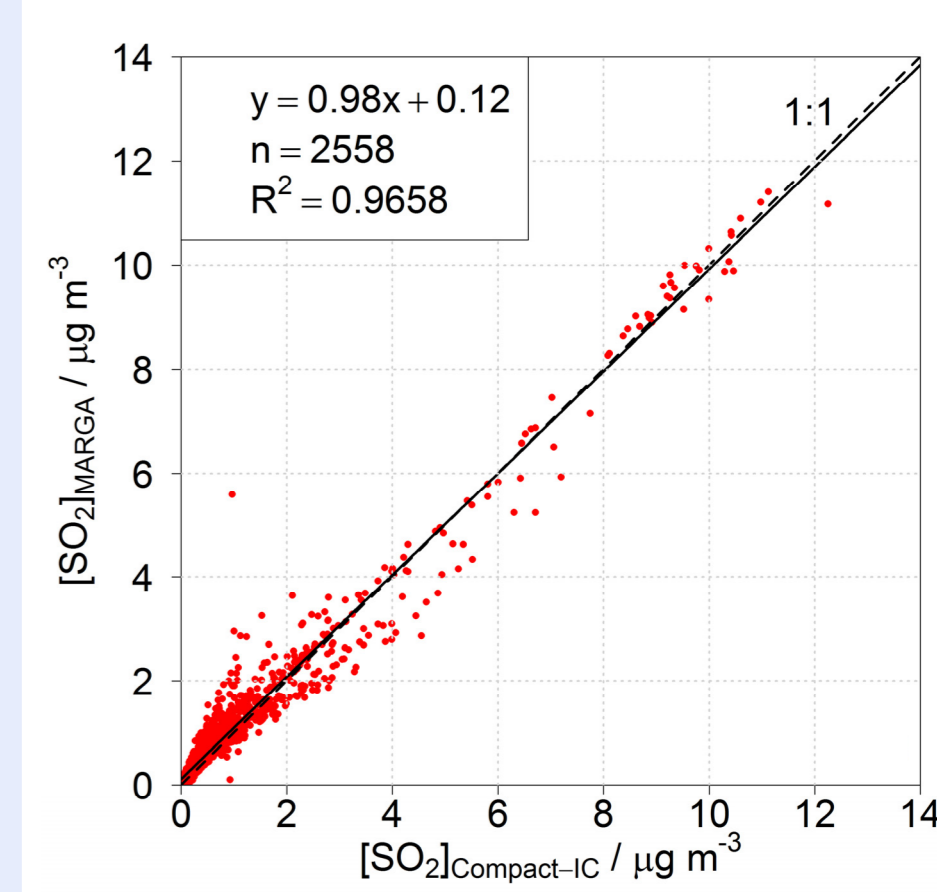


Fig. 6: Comparison of inorganic SO₂ and NO₃⁻ between MARGA IC and Compact IC.

Diurnal variation

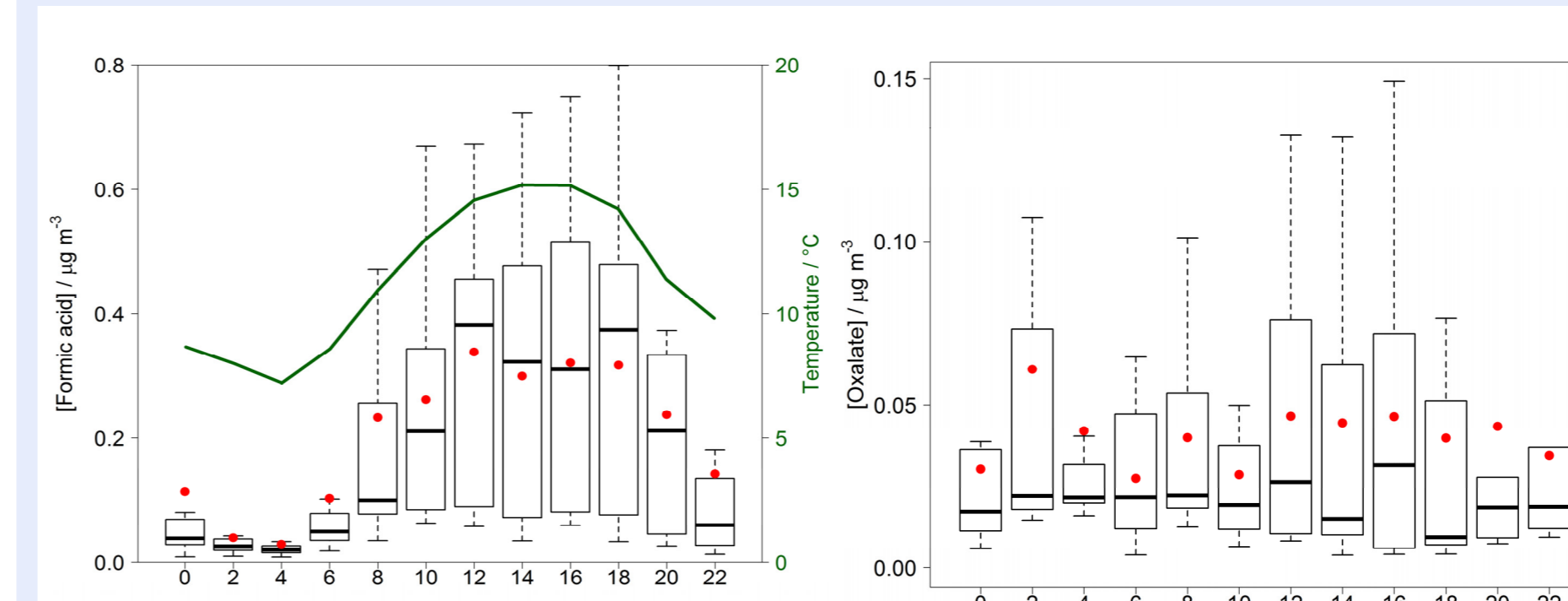


Fig. 5: Diurnal variation of gaseous formic acid and particulate oxalate as box-whisker plot. Red dots are the mean. Average temperature in green.

References

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