Laboratory and field based evaluation of chromatography related performance of the Monitor for AeRosols and GAses in ambient Air (MARGA)

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Introduction

Time-resolved simultaneous measurements of the gas and aerosol components of the ammonium-sulfate-nitrate system are required to investigate the processes governing inorganic aerosol formation and aerosol characteristics (e.g., phase partitioning, acidity) and the dry component of nitrogen deposition. The Monitor for Aerosols and Gases in ambient Air (MARGA, Metrohm Applikon) provides near real-time simultaneous measurement of water soluble particulate species as well as their gaseous precursors.

The objective of this study is to evaluate MARGA performance with a focus on accuracy and precision characteristics related to chromatogram processing. MARGA software calculates concentrations from chromatogram peak areas online and a MARGA tool can be used for batch post-processing. To examine MARGA chromatography software characteristics and improve efficiency and flexibility in the reprocessing of raw chromatograms, an alternative to the MARGA chromatography tool was employed. Using field measurements and laboratory standards, analytical accuracy, precision, and method detection limits derived from the two chromatogram processing methods were compared.

Instrument and field sampling

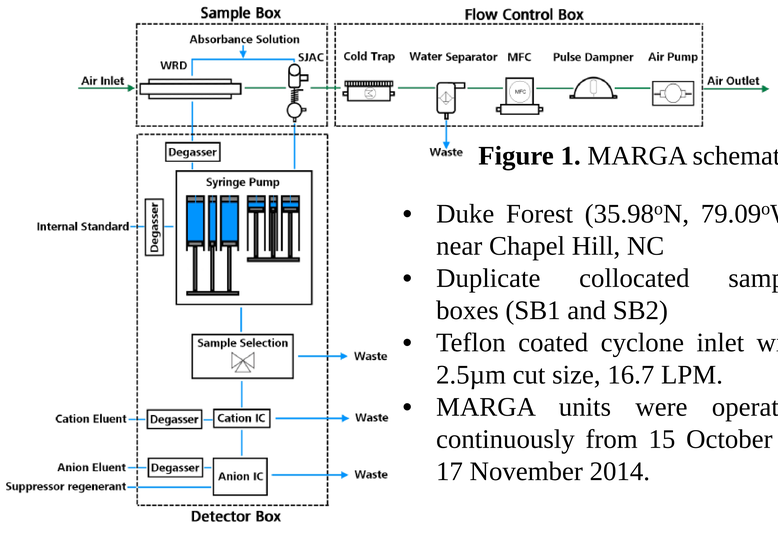

Figure 1. MARGA schematic

- Duke Forest (35.98ºN, 79.09ºW) near Chapel Hill, NC
- Duplicate collocated sample boxes (SB1 and SB2)
- Teflon coated cyclone inlet with 2.5µm cut size, 16.7 LPM.
- MARGA units were operated continuously from 15 October to 17 November 2014.

Issues with MARGA chromatography tool

- Incorrectly defined baseline due to peak fronting and tailing
- Shifting between "drop perpendicular" and "valley to valley" integration options
- MARGA integration parameters are applied to all chromatograms
  - Inability to manually adjust integration for individual peaks
- An alternative chromatography software (Chromeleon V7.2, Thermo Scientific Dionex) was evaluated for batch reprocessing of chromatograms.

Results and discussion

Laboratory study of chromatography characteristics

- MARGA chromatograms were systematically examined by running a multipoint series of liquid external standards.

Table 1. Method detection limits (MDL) for chromatograms processed by MARGA tool and Chromeleon.

	Chromeleon		MARGA tool	
	MDL(µg/m^3)	# of samples	MDL(µg/m^3)	# of samples
NH_4^+	0.02	78	0.04	78
NH_3	0.02	78	0.04	78
SO_4^{2-}	0.08	80	0.13	76
SO_2	0.05	80	0.08	76
NO_3^-	0.08	80	0.14	76
HNO_3	0.08	80	0.14	76

- Method detection limits calculated using the MARGA software are larger than corresponding detection limits calculated with Chromeleon.

Field Study

- The site was impacted by an arctic air mass late in the study period.

	Cold Event			Non-Cold Event		
	Average	Median	Max	Average	Median	Max
NH_3	0.12	0.09	0.29	0.35	0.24	1.62
HNO_3	0.35	0.30	0.82	0.17	0.13	0.97
SO_2	3.22	1.32	32.56	0.73	0.42	8.09
NH_4^+	0.99	0.88	2.20	0.48	0.45	1.21
NO_3^-	1.07	0.72	3.18	0.13	0.09	0.98
SO_4^{2-}	1.93	1.66	4.39	1.33	1.29	3.58
Temperature	4.54	5.00	13.9	12.88	12.20	29.40
RH	50	51	77	70	71	100

Table 2. Summary of concentrations (µg/m^3) of aerosol and precursor gases during and outside of cold air mass periods.

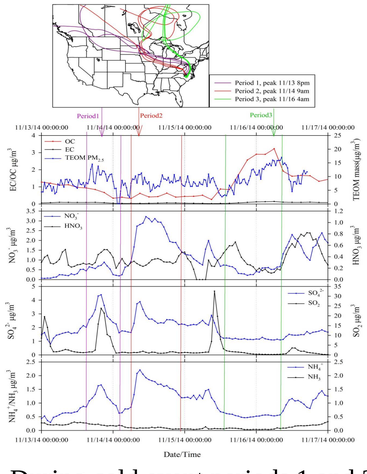

Figure 2. High concentration periods (cold event) observed during mid-November 2014. Period 1: highest SO_4^{2-}; Period 2: highest NH_4^+ and NO_3^-; Period 3: highest OC. Corresponding back trajectories (arrival at 500AGL, backwards for 168 hrs) of individual period peaks (±2 hrs) are also presented.

- During cold event periods 1 and 2, the majority (estimated inorganic portions summing SO_4^{2-}, NO_3^- and NH_4^+ were 61±31% and 83±24%, respectively for period 1 and 2) of the $PM_{2.5}$ mass was inorganic compounds, while in contrast, inorganic compounds only accounted for 22 ± 11% of $PM_{2.5}$ mass during period 3.

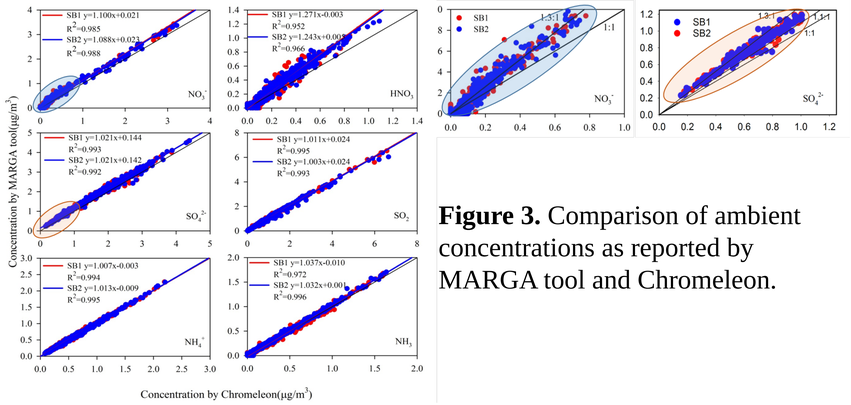

Figure 3. Comparison of ambient concentrations as reported by MARGA tool and Chromeleon.

- NO_3^- and SO_4^{2-} from MARGA software were ≈ 30% and 10% larger than Chromeleon, respectively, for concentrations below ≈ 1 µg m^{-3}.
- Differences increase at lower concentrations.

Impact of chromatography related biases were assessed using aerosol neutralization state as an example. Two metrics based on molar ratios include:

$$R1 = \frac{NH_4^+}{SO_4^{2-}} \qquad R2 = \frac{NH_4^+}{NO_3^- + 2 \times SO_4^{2-}}$$

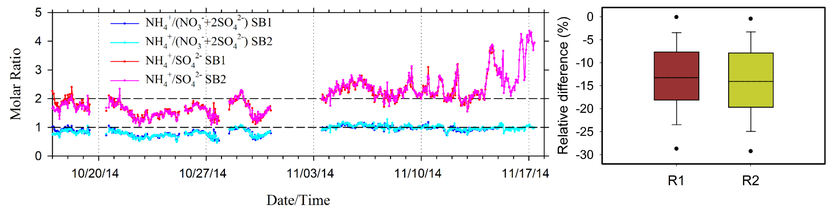

Figure 4. a) Time series of molar ratios (R1and R2) of particulate NO_3^-, SO_4^{2-} and NH_4^+ and b) box plots of relative differences in R1 and R2 between Chromeleon and MARGA tool. Negative values indicate Chromeleon > MARGA tool.

- Average differences in aerosol neutralization state were ≈ - 13% and - 14% for R1 and R2, respectively.

Conclusions

- Close examination of chromatograms revealed a number of issues with the MARGA chromatography software tool. Hence, an alternative software, Chromeleon (Thermo Scientific Dionex), was used to reprocess the raw chromatograms.
- Differences in anion concentrations between the two chromatography methods produced non-trivial errors in concentrations < 1 µg m^{-3} and metrics of aerosol neutralization.
- The cause of this bias is unclear but can be controlled by correcting anion concentrations with multi-point calibration curves rather than relying solely on the MARGA LiBr internal standard.

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