# An assessment of the performance of the Monitor for AeRosols and GAses in ambient air (MARGA): a semi-continuous method for soluble compounds

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# Introduction

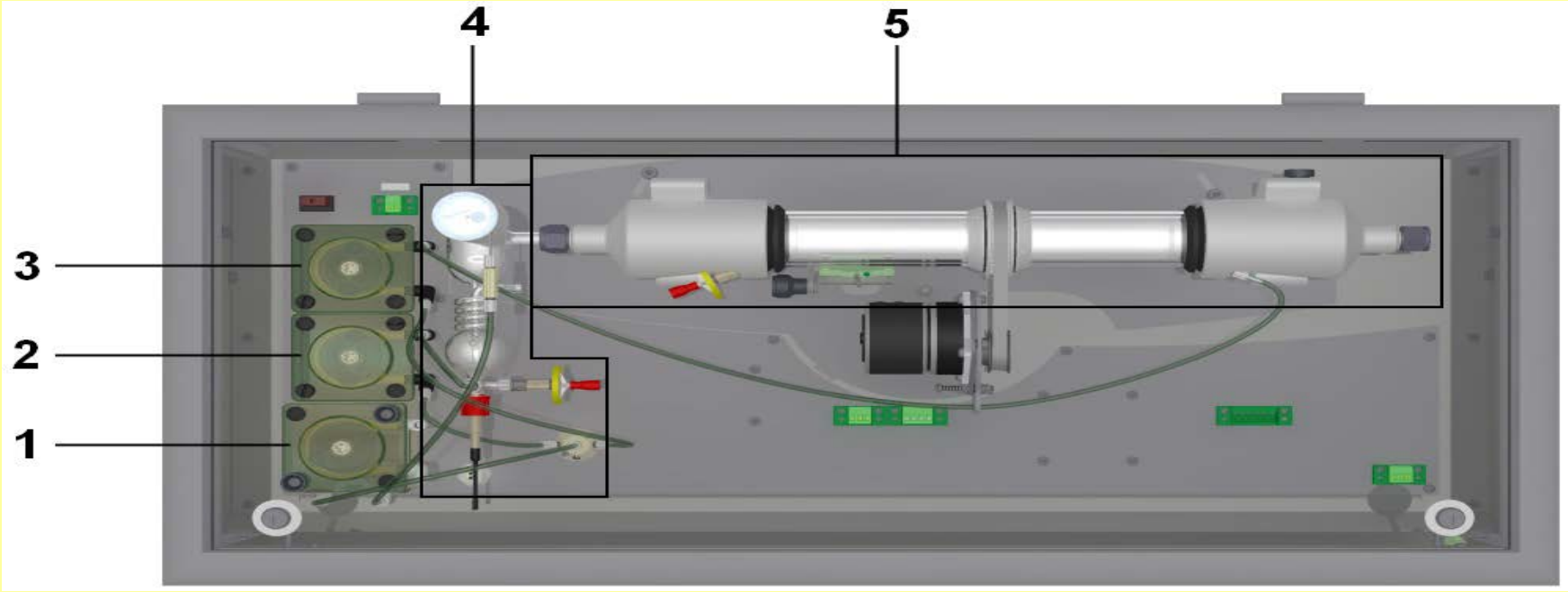
• U.S. EPA Clean Air Status and Trends Network (CASTNet) currently uses filter packs to measure weekly integrated air concentrations of nitrogen and sulfur compounds

• Supplementing CASTNet with semi-continuous monitoring systems at select sites to examine ecosystem exposure to nitrogen and sulfur compounds at higher time resolution and with greater accuracy than the filter pack

• U.S. EPA Environmental Technology Verification (ETV) program verifies the performance of innovative technologies that have the potential to improve the protection of human health and the environment

# Monitor for AeRosols and GAses in ambient air (MARGA)

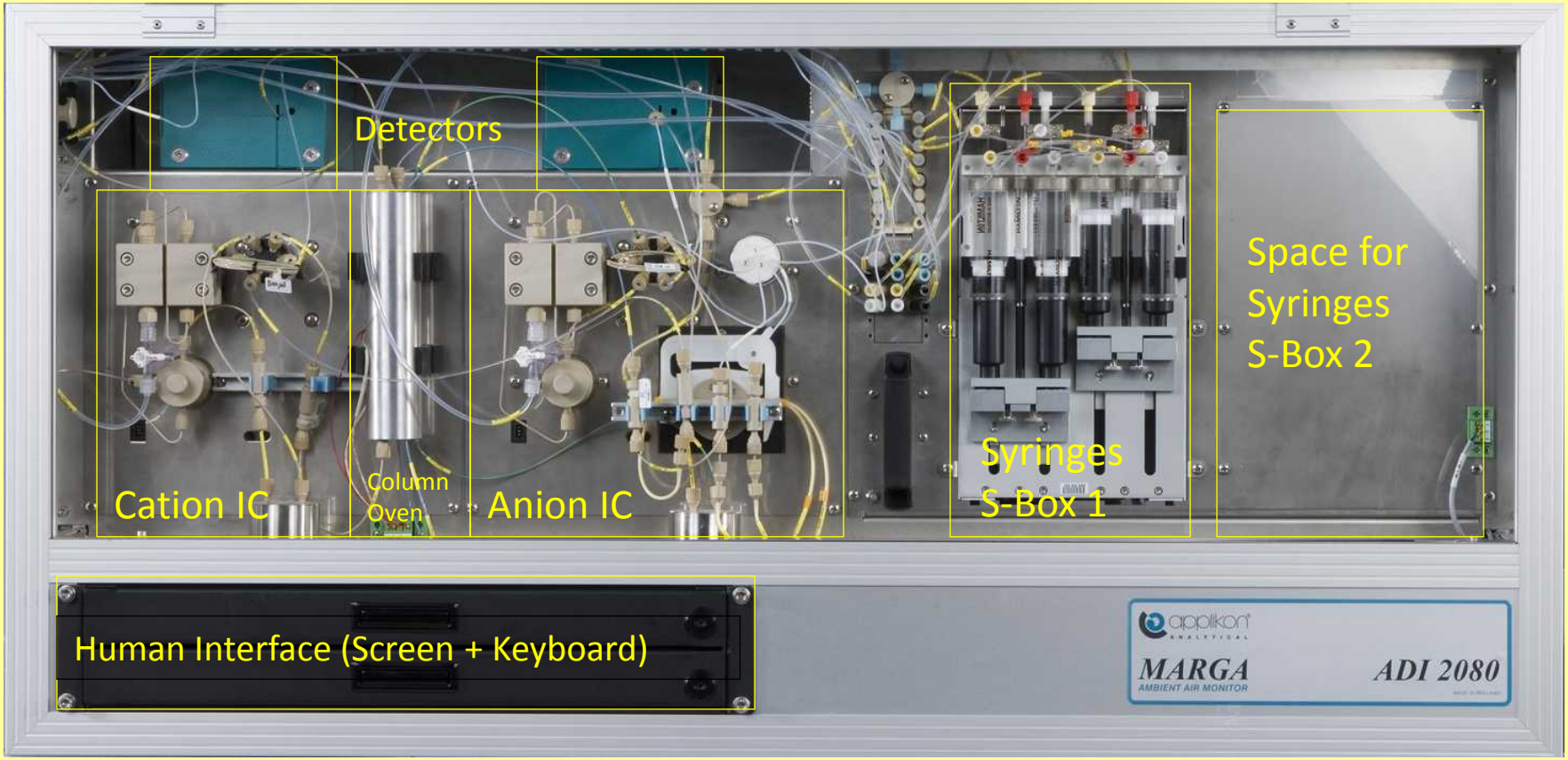
- Sample Box




1 – SJAC Supply Pump & Waste Pump
2 – SJAC Fill Pump
3 – WRD Fill Pump
4 – Steam Jet Aerosol Collector (SJAC)
5 – Wet Rotating Denuder (WRD)

# MARGA

- Analytical Box



# ETV Methodology

- Conducted in Research Triangle Park, NC from September 8th-October 8th, 2010

- Precision - comparing duplicate MARGA units

- Accuracy - comparing duplicate MARGA units to duplicate reference denuder/filterpacks

- Reference denuder/filterpack
  - Sodium Carbonate ($Na_2CO_3$) and phosphorous acid ($H_3PO_3$) denuders
    $SO_2$, $HNO_3$, $NH_3$
  - Teflon filter, Nylon filter, and a citric acid cellulose filter
    $SO_4^{2-}$, $NO_3^-$, $NH_4^+$
  - 12-hour integrated samples

Denuder/filter pack system

- TECO 43S pulsed fluorescence analyzer
  - $SO_2$
  - *5 minute readings*

# CASTNeT Performance goals

- **Accuracy**
  - Assessed by averaging 1-hour MARGA data into 12 hours

  1) Linear regression with a goal of slope between 0.8-1.2

  2) Median Absolute Relative Percent Difference (MARPD) between MARGA and reference concentrations with a goal of ≤ 40%

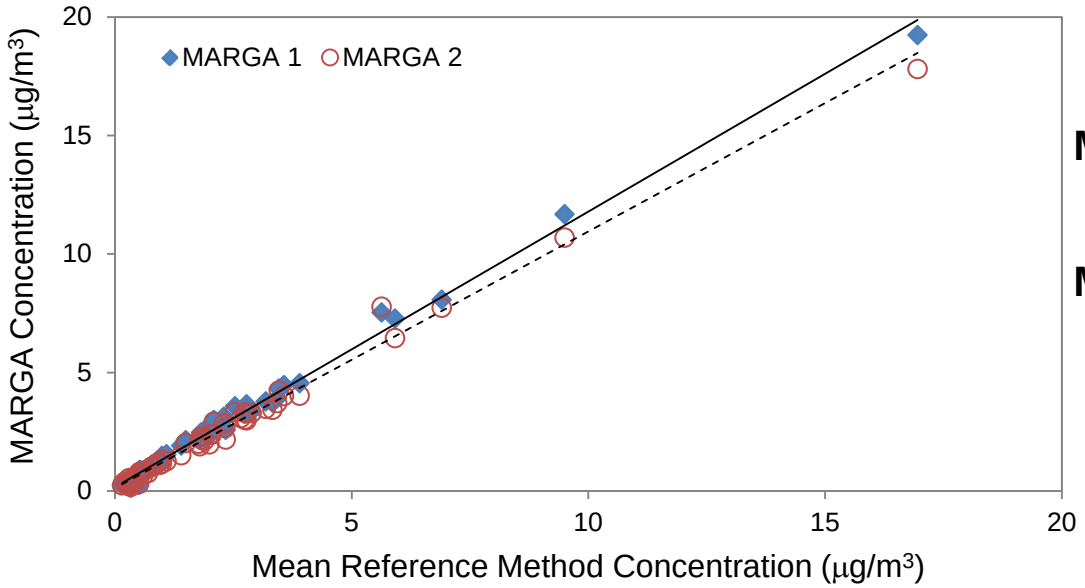
- **Precision**
  - Assessed by using 1-hour data and averaging 1-hour MARGA data into 12 hours

  1) MARPD of corresponding 1-hour concentrations of each MARGA unit with a goal of ≤ 40%

  2) MARPD between MARGA units < than $95^{th}$ percentile of the relative percent difference ($RPD_{REF0.95}$) of the reference units

# Accuracy Results

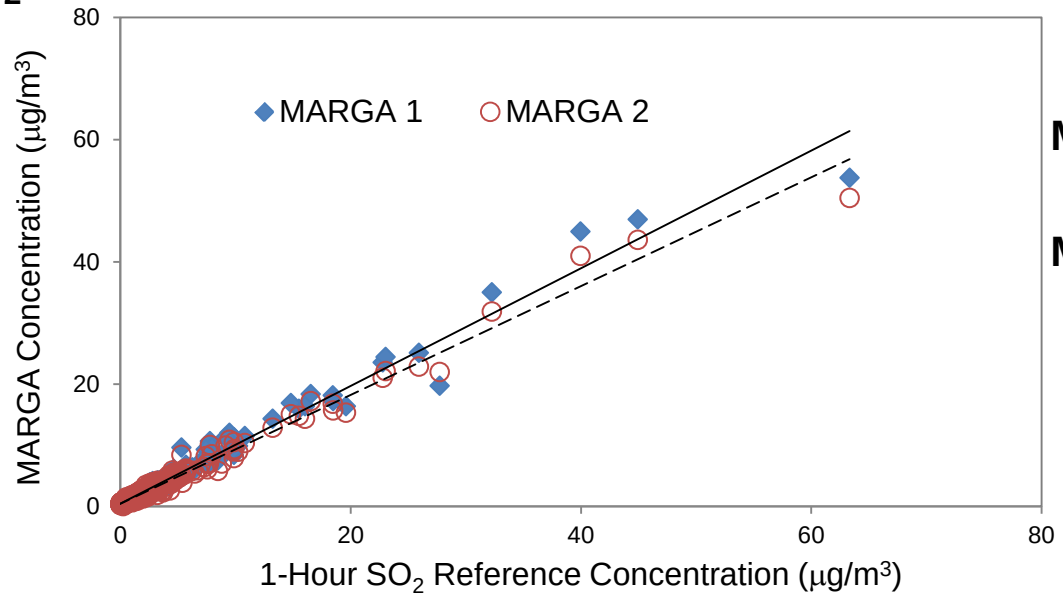
## $SO_2$




**MARGA 1 = 1.163x + 0.163**
**$R^2$ = 0.994**

**MARGA 2 = 1.083x + 0.125**
**$R^2$ = 0.990**

## $SO_2$ -TECO

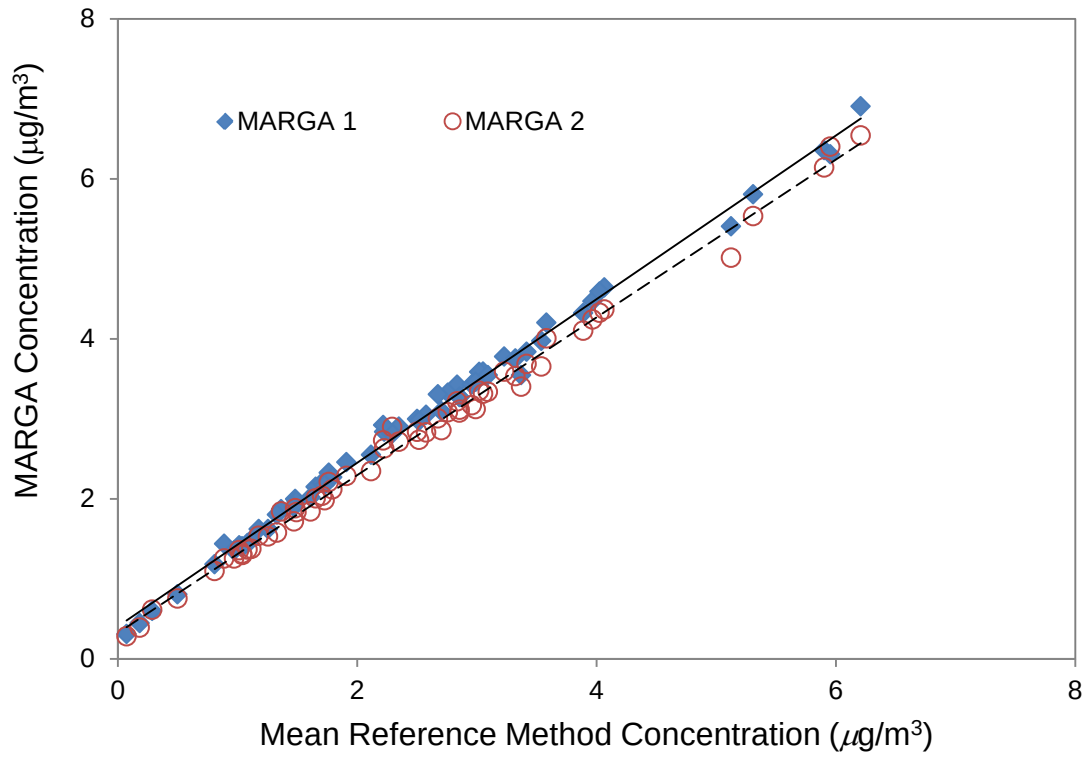



**MARGA 1 = 0.962x + 0.498**
**$R^2$ = 0.979**

**MARGA 2 = 0.890x + 0.437**
**$R^2$ = 0.982**

# Accuracy Results

$SO_4^{2-}$

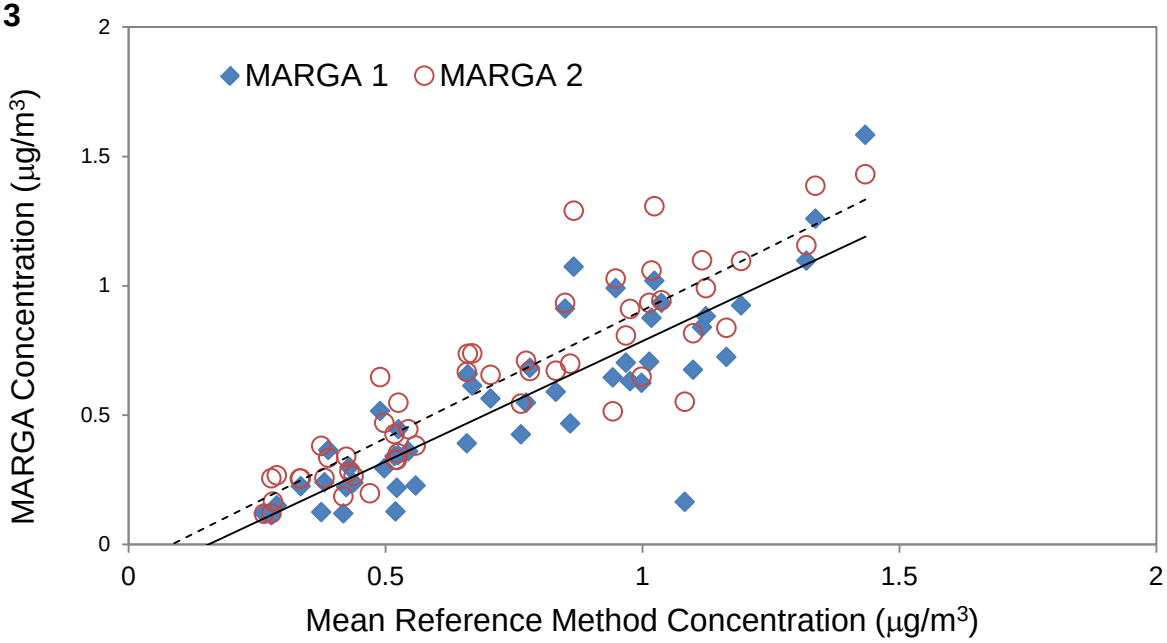



**MARGA 1 = 1.023x + 0.300**
**$R^2$ = 0.995**

**MARGA 2 = 0.986x + 0.223**
**$R^2$ = 0.994**

# Accuracy Results

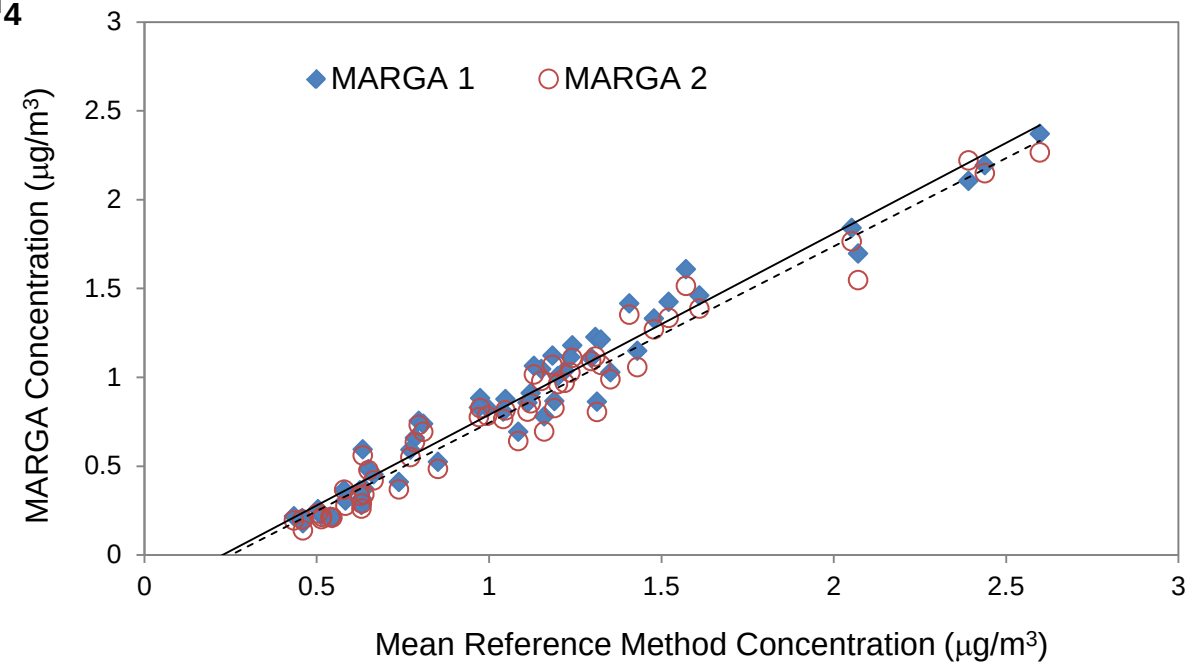
## $NH_3$




**MARGA 1 = 0.930x - 0.144**
**$R^2$ = 0.732**

**MARGA 2 = 0.987x - 0.083**
**$R^2$ = 0.803**

## $NH_4^+$

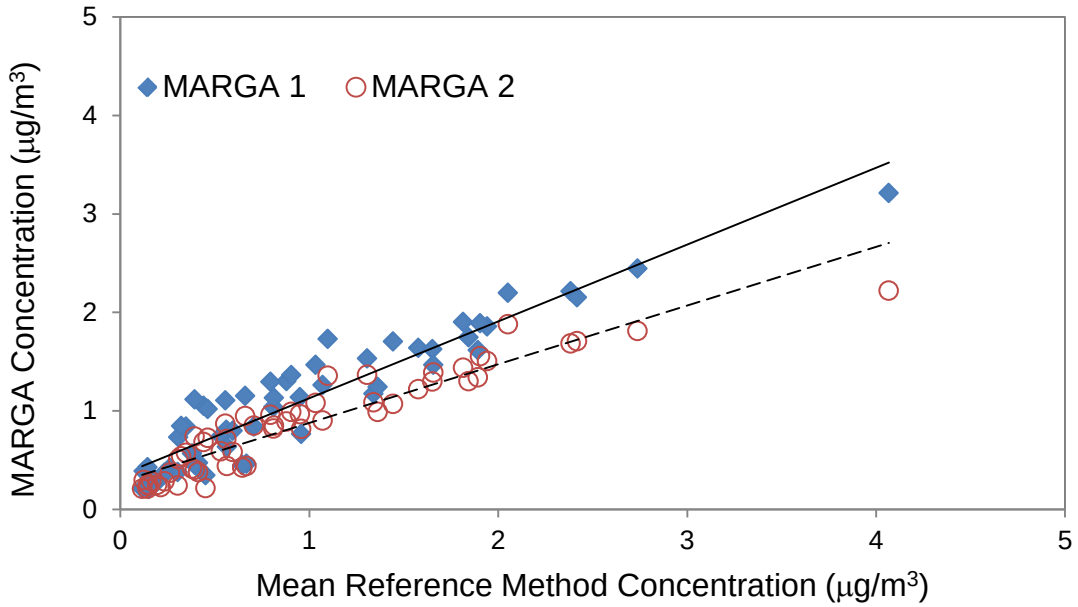



**MARGA 1= 1.020x - 0.231**
**$R^2$ = 0.959**

**MARGA 2 = 0.993x - 0.250**
**$R^2$ = 0.958**

# Accuracy Results

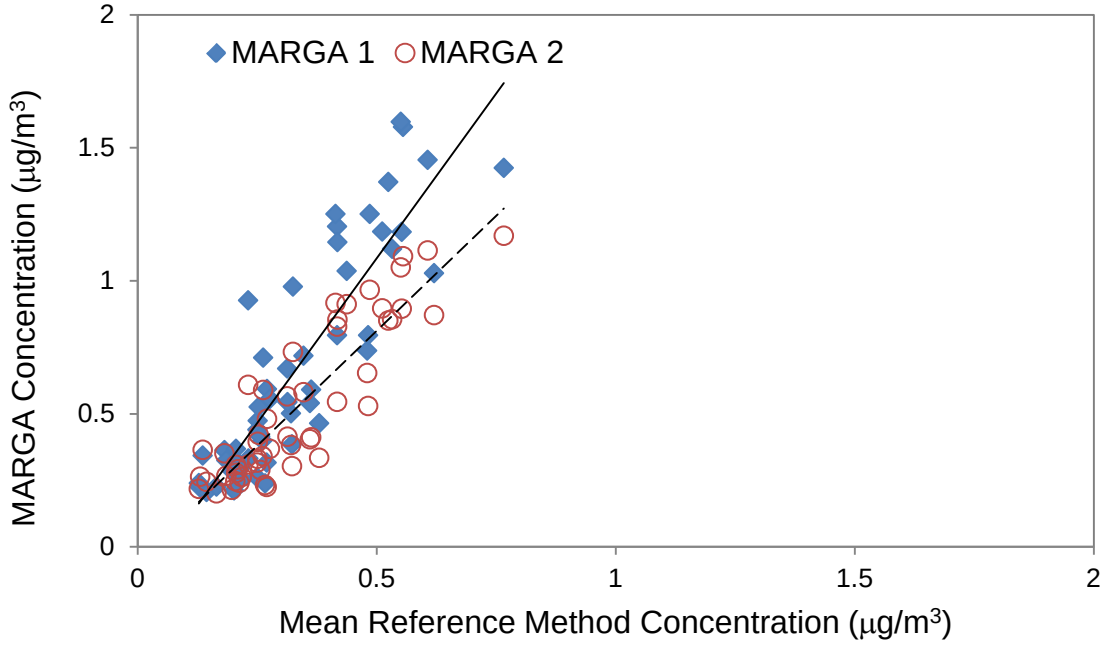
## $HNO_3$




**MARGA 1 = 0.780x + 0.347**
**$R^2$ = 0.884**

**MARGA 2 = 0.596x + 0.282**
**$R^2$ = 0.883**

## $NO_3^-$




**MARGA 1 = 2.476x - 0.154**
**$R^2$ = 0.774**

**MARGA 2 = 1.729x - 0.053**
**$R^2$ = 0.786**

# Accuracy- MARPD

- Goal: MARPD ≤ 40 %

| | MARGA 1 | | MARGA 2 | |
|---|---|---|---|---|
| Target Analyte | MARPD | CASTNET Goal | MARPD | CASTNET Goal |
| $SO_2$ | 31.2% | ✓ | 18.9% | ✓ |
| $HNO_3$ | 34.1% | ✓ | 25.8% | ✓ |
| $NH_3$ | 33.1% | ✓ | 18.2% | ✓ |
| $SO_4^{2-}$ | 17.3% | ✓ | 9.1% | ✓ |
| $NO_3^-$ | 86.9% | | 58.7% | |
| $NH_4^+$ | 19.2% | ✓ | 25.3% | ✓ |
| $SO_2^a$ | 19.8% | ✓ | 14.1% | ✓ |

# Precision- 1 hour data

- Goal: MARPD ≤ 25 %

| Target Analyte | MARPD | CASTNET Goal | Number of Hourly Data with Both Monitors above 2 x DL | Number of Hourly Data below 2 x DL | |
|---|---|---|---|---|---|
| | | | | MARGA 1 | MARGA 2 |
| $SO_2$ | 10.4% | ✓ | 691 | 4 | 28 |
| $HNO_3$ | 24.8% | ✓ | 582 | 62 | 129 |
| $NH_3$ | 22.4% | ✓ | 561 | 138 | 103 |
| $SO_4^{2-}$ | 6.5% | ✓ | 666 | 4 | 53 |
| $NO_3^-$ | 27.3% | | 520 | 129 | 157 |
| $NH_4^+$ | 6.3% | ✓ | 636 | 59 | 81 |

- Low $NO_3^-$ concentrations

- Both MARGA units met the data completeness and reliability goals

# Precision- 12 hour data

- Goal: MARPD ≤ Reference $RPD_{95}$

| Target Analyte | Reference MARPD | Reference $RPD_{95}$ | MARGA MARPD (%) | CASTNET Goal |
|---|---|---|---|---|
| $SO_2$ | 4.8% | 20.5% | 8.7% | ✓ |
| $HNO_3$ | 7.2% | 29.9% | 26.5% | ✓ |
| $NH_3$ | 10.0% | 40.7% | 18.8% | ✓ |
| $SO_4^{2-}$ | 2.8% | 11.4% | 6.8% | ✓ |
| $NO_3^-$ | 9.3% | 59.9% | 23.9% | ✓ |
| $NH_4^+$ | 3.2% | 13.0% | 6.5% | ✓ |

# Ongoing work on ETV data

- Further examination of MARGA accuracy and precision after adjusting data for external standard solutions and flow rate calibrations

- Comparison of ion balance

- Investigation of potential reasons for $HNO_3$ and $NO_3^-$ disagreement between methods.
  - *Loss of $HNO_3$ with tubing walls.*
  - *$NO_3^-$ volatility in the reference filter pack*
  - *MARGA measuring other $NO_3$ compounds*

- Relationships between method agreement and meteorological conditions

# Conclusions

• The MARGA units performed well for $SO_2$, $SO_4^-$, $NH_3$ and $NH_4^+$, with these compounds meeting the accuracy and precision goals

• The MARGA units did not perform as well for $HNO_3$ and $NO_3^-$, with both species linear regression slopes not achieving the accuracy target

• The $NO_3^-$ MARPD between both MARGA units and the reference filter pack was greater than 40%

• The $NO_3^-$ MARPD (1-hour data) between the MARGA units was greater than 25%, however the MARGA units MARPD for $NO_3^-$ (12-hour data) were less than the Reference $RPD_{95}$

• Poor performance of $NO_3^-$ may be due to $NO_3$ volatility in the reference filter pack or that the MARGA is measuring other $NO_3^-$ compounds. Comparison of $NO_3^-$ concentrations is difficult due to low concentrations.

# Acknowledgements

• Solomon Ricks, Keith Kronmiller and Nealson Watkins of EPA-OAQPS for providing hourly $SO_2$ and meteorological data