



Assessment and comparison of hourly speciated atmospheric nitrogen measurements with integrated methods at a CASTNET site in Beltsville, MD

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The US EPA Clean Air Status and Trends Network (CASTNET) has more than 25-years of atmospheric nitrogen measurements at rural locations across the United States. Routine weekly filterpack measurements include the nitrogen species (HNO_3), nitrate (NO_3^-), and ammonium (NH_4^+). In 2007, CASTNET began participating in the National Atmospheric Deposition Program (NADP) Ammonia Monitoring Network (AMoN) which established a nationwide network of passive NH_3 monitors. Recently, the US EPA has been supplementing these measurements with hourly speciated measurements of atmospheric nitrogen to provide a detailed look at short-term concentration variations and to enable a more complete assessment of contributors to the nitrogen budget. Hourly atmospheric ambient concentrations of nitrogen gases (HNO_3 , NH_3) and aerosols (NO_3^- , NH_4^+) have been measured using the Monitor for AeRosols and Gases (MARGA) systems at the Beltsville, MD (BEL116) CASTNET site during extended sampling periods over the past two years. An experimental hourly trace level total reactive nitrogen sampling system, Nitrotrain, has been developed to analyze the components of the reactive nitrogen sample. The Nitrotrain consists of a solenoid sampling system to divert flows, a single commercially available chemiluminescence analyzer, and four converter boxes: a total nitrogen (TNx) stainless steel converter, two traditional molybdenum (Mo) converters (one at the 10-m sample inlet for NOy and a second at the analyzer for NOx), and an LED-based photolytic NOx converter. Calculated and measured parameters include NO, NOx, NHx, NO2 from the Molybdenum converter, and NO2 (true) from the photolytic converter. Nitrogen measurements taken at the Beltsville site since December of 2014 will be compared and analyzed to assess instrument performance of the Nitrotrain and the MARGA against the established CASTNET integrated sampling methods.

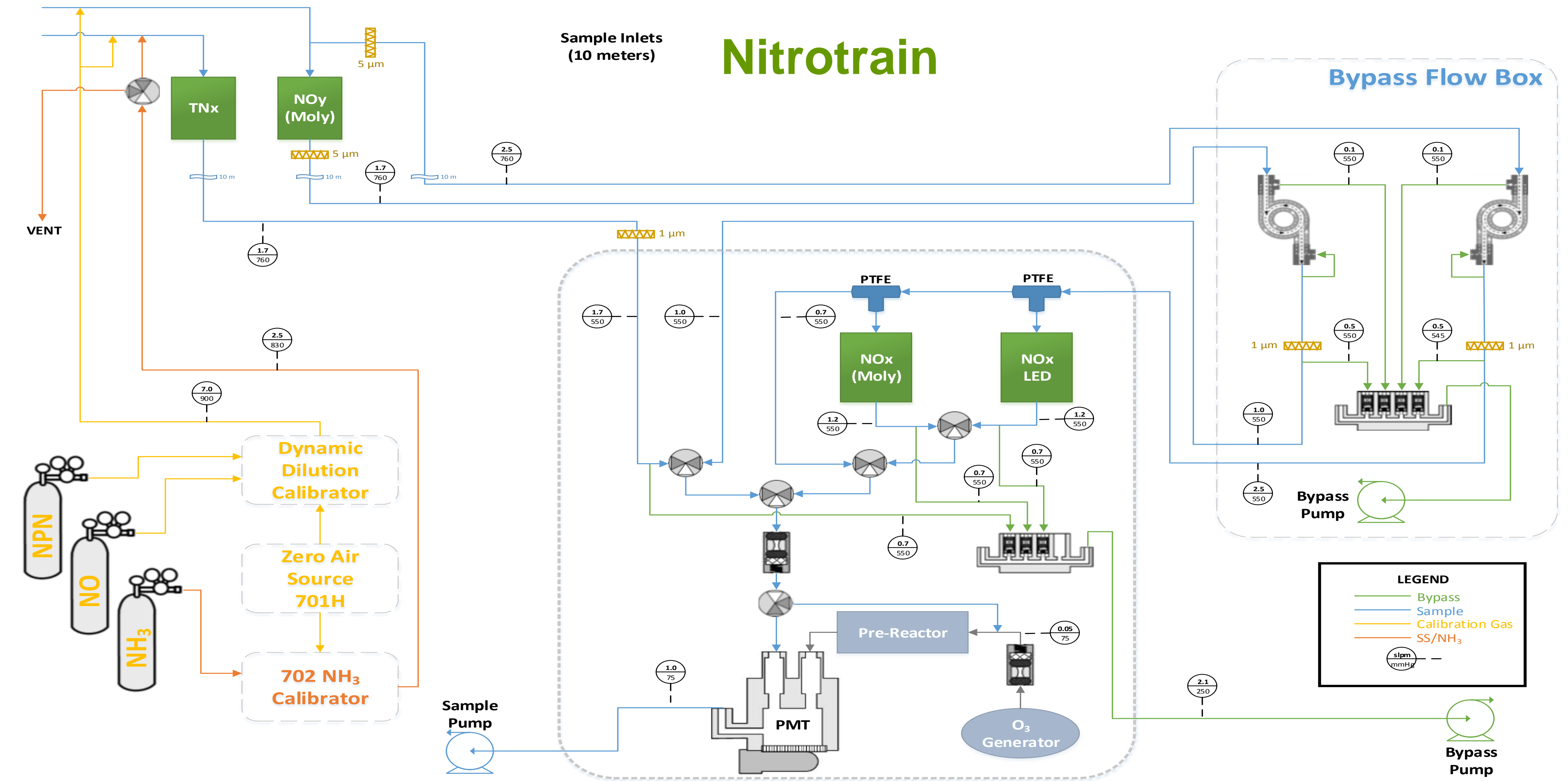


MARGA

Photo of MARGA instrument (Metrohm Applikon, the Netherlands). The sampling compartment (top) contains the Wet Rotating Denuder (WRD) that removes and samples soluble gases (HNO_3 , HONO , SO_2) from a sampled airflow prior to entry into the Steam Jet Aerosol Collector (SJAC) where soluble particles are grown by deliquescence, removed, and sampled via impaction. Samples are then fed semi-continuously on the hour into an on-line ion chromatography analyzer.

Beltsville setup and inlet locations

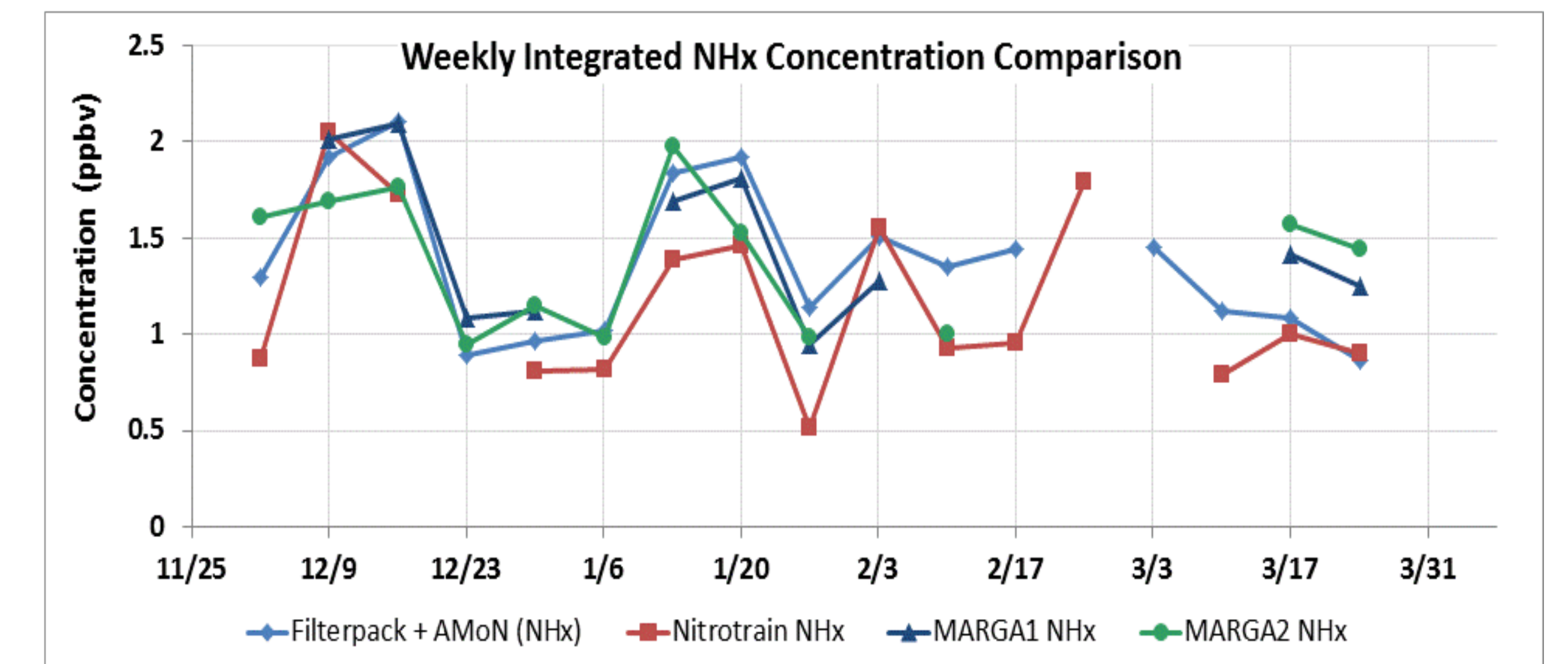
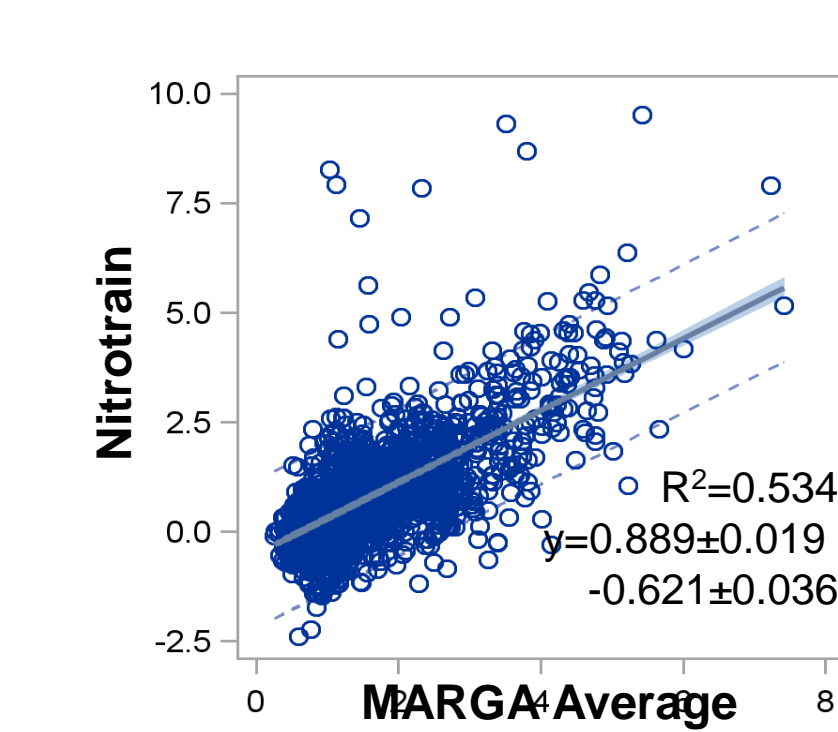
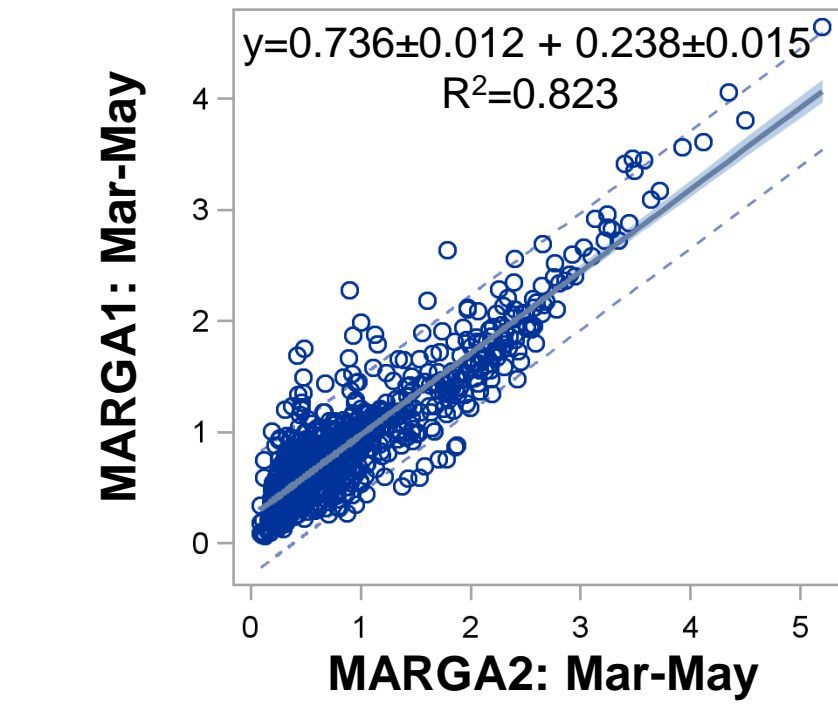
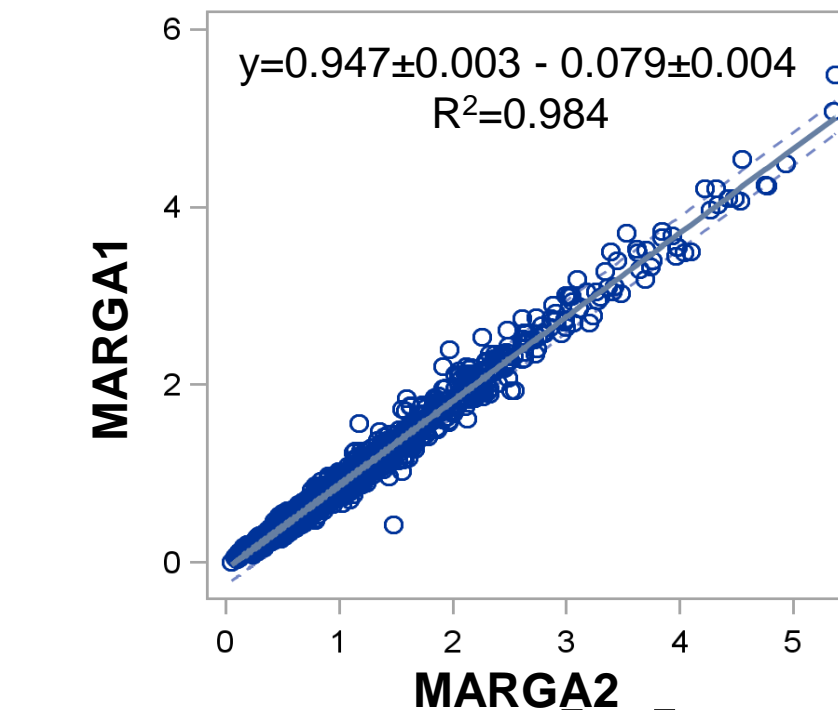
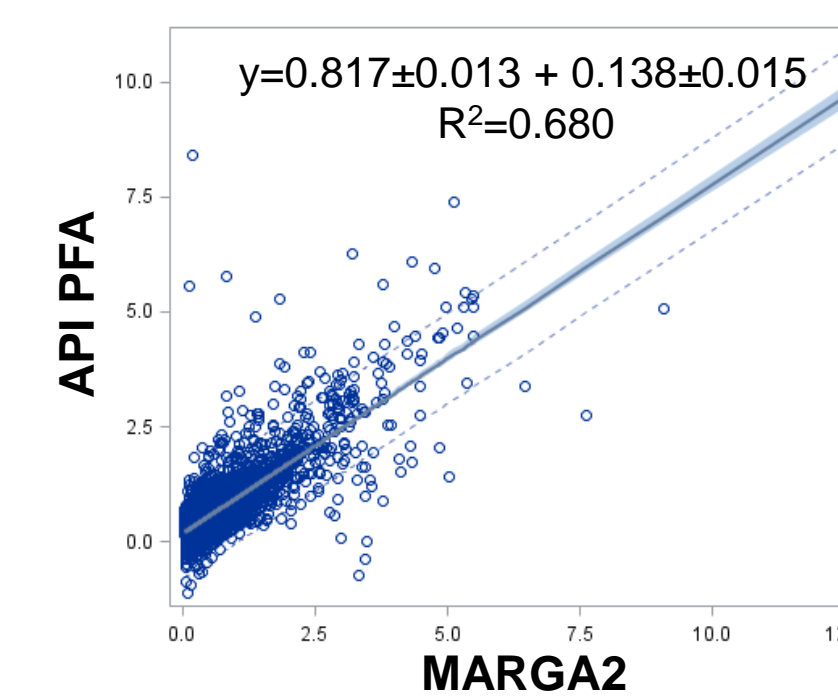
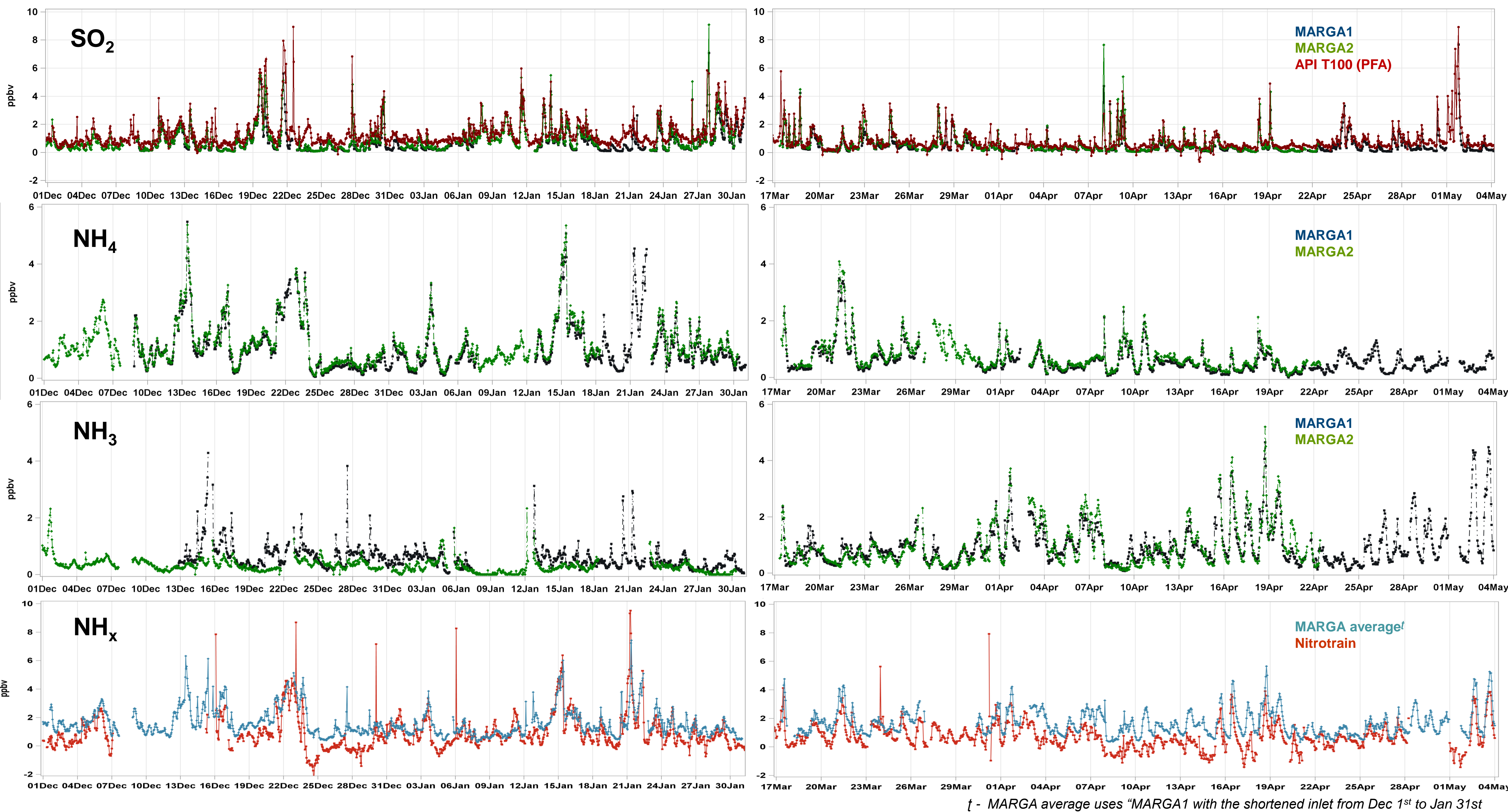
The CASTNET site in Beltsville, MD hosts a large number of instruments. Pictured is the walk-up tower that holds the sampling inlet and stainless steel TNx and the aloft Mo converters of the Nitrotrain and other trace gas instruments (~10-m). To the right is the standard 10-m tilt down tower that contains the CASTNET filterpack and the Ozone inlet. The trailer to the left houses both of the MARGAs that have been configured with a roof-top set-up (~5-m) or a side inlet (~3-m) to minimize adsorption losses of sticky gases (e.g. HNO_3 , NH_3). The AMoN sampler (~2m) is not pictured.



Schematic of experimental Nitrotrain instrument showing the four converters: TNx (850°C) and NOy converters (315°C) are placed at 10m. The NOx and photolytic NOx converter are located in the modified Teledyne API Model 501y analyzer box.

Nitrotrain constructed and tested in Gainesville, FL prior to site installation. Calibration gas was delivered to each channel separately at a range of concentrations to confirm that no cross-contamination was occurring. All four converters accurately converted NO2 at high and mid-level concentrations. As expected, the photolytic NOx detector did not detect NPN, but the NOx Mo did. NOy convertor captured NH3 at 50% efficiency.

Results



- Study spans 4 months with ~2000 co-located and valid observations
- Includes winter and spring months with cold and warm temperatures.
- Artifact (cold temperature inlet adsorption of NH_3) is very apparent in MARGA.
- Differences in inlet heights and meteorological conditions have significant impact on agreement between the two systems.
- Excellent performance between co-located MARGA systems.
- Very good agreement with co-located PFA SO_2 analyzer strongly supports MARGA accuracy and comparability across different detection methods.
- Tracking between Nitrotrain and MARGA systems looks very good.
- Nitrotrain baseline drift or baseline shift may be a calibration issue and may affect perceived low-bias (~20%).
- Good agreement between integrated methods.

Reference

EPA/600/R-14/182 'Measurements of Atmospheric NH_3 , NOy/Nox, and NO_2 and Deposition of Total Nitrogen at the Beaufort, NC CASTNET Site (BFT142)' August 2014

Mishoe, K. Puchalski, M., Beachley, G. Rogers, C., Baumgardner, R. CASTNET's Enhanced NOy Analyzer. Poster session presented at: NADP2014: The Global Connection of Air and Water.; 2014 Oct 21-24; Indianapolis, IN.