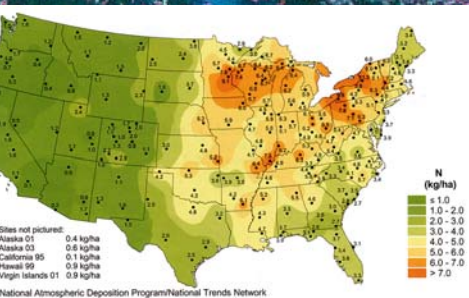


Background

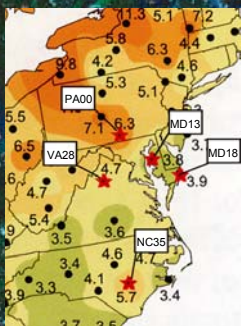
Measurements in precipitation samples from the **National Atmospheric Deposition Program (NADP)** have focused on soluble inorganic forms of nitrogen (as nitrate and ammonium) since the program began in 1978. Some researchers reported that dissolved organic nitrogen (DON) compounds are also present in precipitation and may comprise up to 30% of the total nitrogen wet deposition. Based on these reports, TN and DON data are needed to assess the total deposition of nitrogen into watersheds to determine environmental impacts and pollutant sources. In order to investigate this for NADP samples, the Central Analytical Laboratory (CAL) developed a method to measure total nitrogen (TN) using in-line persulfate digestion via Lachat Instruments Quick Chem 8000 series flow injection analyzer. DON is measured by subtracting the inorganic nitrogen (nitrate-N and ammonium-N) concentrations from the TN concentration. This method was applied to NADP National Atmospheric Deposition Program (NADP) National Trends Network (NTN) samples from 5 sites in the Chesapeake Bay watershed. Samples were collected following the normal NTN weekly sampling protocol and analyzed at the CAL. When excess sample was available it was refrigerated and TN analysis was performed as time allowed. In addition, subsamples were sent to the Lachat Laboratory, University of Maryland Center for Environmental Science at Frostburg, MD for interlaboratory comparison for ~ 2 years.



Samples Analyzed

Dr. Castro requested samples from five NTN sites in the area of the Chesapeake Bay watershed for his nitrogen research. Samples were split at the CAL prior to shipment to the Lachat Laboratory, University of Maryland Center for Environmental Science at Frostburg, MD. Results between the two laboratories were compared for these five sites.

| | | |
|-----------------------|--------|---------------------------------------|
| Dec. 2002 to May 2003 | (n=18) | Wye |
| Nov. 2002 to May 2003 | (n=21) | Assateague Island NS, Woodcock |
| Dec. 2002 to May 2003 | (n=19) | Clinton Crops Research Station |
| Dec. 2002 to May 2003 | (n=22) | Arendtsville |
| Nov. 2002 to May 2003 | (n=39) | Shenandoah National Park, Big Meadows |



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Results

DON was measured in samples obtained from five NADP sites in the Chesapeake Bay watershed. Weekly precipitation samples from the NTN were shipped to the CAL following their normal protocol (samples were shipped and stored at ambient temperature until processed). When excess sample was available, it was refrigerated until it could be split and shipped to Dr. Castro's lab.

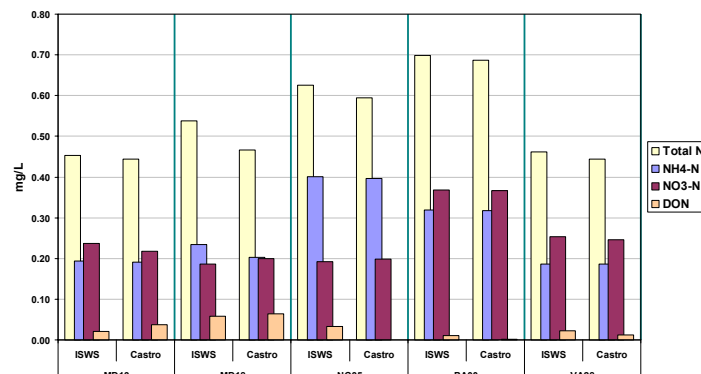
At the CAL, samples were refrigerated until TN and $\text{NH}_4\text{-N}$ analysis were performed. The samples were filtered with a 0.45 μm Gelman Acrodisc IC, 13 mm syringe filter immediately prior to TN and $\text{NH}_4\text{-N}$ analysis. Since nitrate is stable in these samples, nitrate-N values from NTN analyses were used in the calculation. NTN ammonia values were not used due to potential problems with stability, and $\text{NH}_4\text{-N}$ was determined immediately prior to the TN measurement using a different flow injection analyzer.

At the MD laboratory, samples were frozen when received and kept frozen until analysis. Samples were not filtered and $\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$, and TN were all run simultaneously using a multi-channel flow injection analyzer.

Since these samples were stored at ambient temperature for 1-3 weeks, then refrigerated prior to analysis, DON levels may have declined during collection and storage. The results may still be used to evaluate the underestimation of nitrogen in wet deposition (if any). Results available to date from the five sites indicate good average agreement between the two labs for TN, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and DON values. In some cases individual sample results varied widely between the two labs. This may be attributed to sample stability, and differences in method detection limits and sample handling. **The DON levels for individual samples ranged from <0 to 50%. Average DON levels for each of the five sites ranged from 2 to 11% of the TN.**

Additional work will continue at the CAL to optimize collection and analysis parameters for DON. The CAL plans to conduct additional analysis on samples from other areas of the country using on-site filtration and refrigeration as sample preservation techniques.

Mean Total [N] and Constituents, Measured at Two Labs, Across Five Sites



Principle of Method

Nitrogen compounds are oxidized in-line to nitrate using alkaline persulfate/UV digestion. After digestion, nitrate is quantitatively reduced to nitrite by passage of the sample through a copper-cadmium column. Nitrite is then determined by diazotization with sulfanilamide under acidic conditions to form a diazonium ion. Diazonium ion is coupled with N-(1-naphthyl) ethylenediamine dihydrochloride that absorbs at 540 nm. The method will recover nearly all forms of nitrogen. The method is calibrated with potassium nitrate and reported as mg/L Total Nitrogen (TN).

Equipment

Lachat Instruments Quick Chem FIA+ 8000 Series, PVC pump tubes; XYZ autosampler; 8 channel proportioning pump; total N (nitrate/nitrite) chemistry manifold; Lachat Sample Preparation Module A30X11 with UV-254 lamp; Cadmium Reduction Column; 8 cm tubular membrane (debubbler); and Omion Software V 3.0.

Method Differences

Inorganic measurement method:

CAL: nitrate was determined by ion chromatography and ammonium by flow injection colorimetry. Ammonia was determined same day as TN whenever possible, within 24 hours of the TN measurement.

MD Lab: nitrite, nitrate and ammonium were determined simultaneously by flow injection colorimetry using a multi-channel instrument.

TN digestion temperature:

CAL: digestion at 90°C
MD Lab: digestion at 105°C

Calibration Range

CAL: 0.05-2.00 mg TN/L; 6 standards at 0, 0.05, 0.20, 0.40, 1.00, and 2.00 prepared from potassium nitrate and calculated as $\text{KNO}_3\text{-N}$ were used to construct the calibration curve.
MD Lab: 0.05-5.00 mg TN/L; 6 standards at 0, 0.05, 0.10, 0.50, 1.00 and 5.00, which were prepared from a commercially available 1000 ppm potassium nitrate stock

Method Detection Limit

CAL: 0.01 mg TN/L (based on multiple analysis of the 0.05 standard (n=20))
MD Lab: 0.02 mg/L TN (based on multiple analysis of a blank, n=31)

Recovery

CAL:
Disodium EDTA: 1.00 mg/L as TN = 97.6% ± 0.064 (n=18)
Disodium EDTA: 0.10 mg/L as TN = 102.4% ± 0.013 (n=18)
Urea: 1.0 mg/L as TN = 100.8% ± 0.063 (n=13)
Urea: 0.10 mg/L as TN = 102.7% ± 0.016 (n=15)
Sulfanilamide: 2.0 mg/L as TN=79.4% (n=7)
MD Lab:
Disodium EDTA: 0.50 mg/L as TN = 98.15% ± 0.334 (n = 90)
Ammonium Chloride: 0.50 mg/L as TN = 98.15% ± 0.497 (n=70)

Quality Control

CAL: Quality control check samples were prepared by diluting commercially available NIST traceable Water Pollution Nutrient QC samples (VHG Labs) to obtain concentrations of 1.26 and 0.13 mg/L TN levels. In addition, synthetic rain samples prepared in-house for QC solutions for the NADP were analyzed to use for controls. The synthetic rain solutions represented 0.18 and 0.72 mg/L TN.
MD Lab: QCCS were prepared by diluting a commercially available 1000 ppm sodium nitrite stock solution to obtain a concentration of 0.20 mg/L TN.

References

"Determination of Total Nitrogen in Waters by In-line Digestion Followed by Flow Injection Analysis", Lachat Instruments/Hach Company, Loveland, CO 80539
CAL: Lachat Instruments QuikChem Method 10-107-04-3-A (revision August 2, 2001).
MD Lab: Lachat Method 10-107-04-1-P (revision October 21, 1998).

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