Total & Organic Nitrogen in Precipitation

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Abstract

Total soluble nitrogen (TN) measurements in precipitation samples from the National Atmospheric Deposition Program (NADP) were determined by flow injection analysis from samples received in 2004 and 2005. Other researchers have reported the presence of significant levels of organic nitrogen (ON) in precipitation; therefore, a study was undertaken to measure TN and ON in precipitation samples from selected NADP sites. Organic nitrogen levels were determined using the formula ON = TN – (NO_3-N + NH_4-N). Precipitation samples for this study were collected from the Atmospheric Integrated Monitoring Network (AIRMoN) and the National Trends Network (NTN). Samples from the AIRMoN are obtained within 24 hours of a precipitation event, are immediately refrigerated, and remain chilled during shipment to the NADP Central Analytical Laboratory (CAL) in Champaign, IL. Samples from the NTN are kept at ambient temperature in the field for up to a week and then shipped to the CAL. At the CAL, these samples were analyzed within seven days for inorganic nitrogen as ammonium and nitrate by flow injection analysis and ion chromatography, respectively, and for TN by flow injection analysis. The TN method detection limit was determined to be 0.008 mg/L N. Complete conversion to TN by organic and inorganic nitrogen compounds was determined by including three quality control standards (QCS) every twelve samples during analysis. The recovery in 2005 for a 2.0 mg/L N sulfanilamide digestion QCS was found to be 77.8% ± 1.2 (typical recovery for this compound by this method is 80.5%). Four additional QCS, containing ammonium and nitrate in varying amounts, were also used with concentrations of 0.050, 0.199, 0.730, and 1.00 mg/L N. The percent recoveries for these QCS were 103.4% ± 6.7, 98.8% ± 2.9, 98.9% ± 1.3, and 99.8 ± 1.4, respectively. Seasonal data from 2004 and 2005 will be presented for an AIRMoN site in east central Illinois. Recent ON results for the eight site AIRMoN network will also be presented as well as the effects of sample filtration on TN measurements.

Method

Analysis: Nitrogen compounds are oxidized in-line to nitrate using an alkaline persulfate digestion at 90°C with additional energy supplied by ultraviolet light. After digestion, the nitrate is then passed through a cadmium column, quantitatively reducing it to nitrite. The nitrite is then reacted with sulfanilamide, under acidic conditions, to form a diazonium ion. This ion is coupled with N-(1-naphthyl)ethylenediamine dihydrochloride (NED) to produce a pink dye that absorbs at 540 nm and is proportional to the total nitrogen concentration. This method will recover nearly all forms of nitrogen, including nitrate and nitrite, thus it is termed total nitrogen. Nitrate and nitrite are not recovered in the conventional Kjeldahl nitrogen method.

Equipment: The total nitrogen method is applied using a Lachat Quik-Chem Flow Injection Analyzer 8000+ Series, an eight channel proportioning pump, Lachat Sample Preparation Module A30X11 with UV-254 nm light, Lachat Total Nitrogen Reaction Manifold including a cadmium reduction column, 8 cm tubular membrane (debubbler), Lachat's Omnion® software V 3.0, and Lachat's XYZ Autosampler.

Method Range: 0.008 – 2.00 mg N/L; Six standards prepared from potassium nitrate and calculated as KNO_3-N were prepared to construct calibration curve from 0.00 – 2.00 mg N/L.

Method Detection Limit: Calculated as 0.008 mg/L N (based on multiple analyses of the CAL's "Faux Rain" 10th percentile laboratory control standard where n=16 and target concentration = 0.06 mg/L N).

Quality Control: Five different quality control standards (QCS) are used to verify the method's accuracy and precision. The CAL prepares in-house simulated rain quality control standards that are used on all instruments. In addition, other QCS are prepared weekly and analyzed to validate the method and check the persulfate digestion. The five QCS are listed below. A 1.0 mg/L N nitrite (NO_2^-) check standard was also analyzed to check cadmium column efficiency. Our system yielded 100.6% recovery using this check standard.

Quality Control Standard	Compound	Concentration (mg/L N)	Recovery (%)	Std. Dev. (%)	n
Lowest Calibration Standard	NO_3^-	0.050	103.4	6.7	40
CAL's simulated rain 25th percentile QCS (FR25)	NO_3^-/NH_4^+	0.199	98.8	2.9	38
CAL's simulated rain 75th percentile QCS (FR75)	NO_3^-/NH_4^+	0.730	98.9	1.3	39
Mid-point Calibration Standard	NO_3^-	1.00	99.8	1.4	37
Sulfanilamide Digestion Check Standard (typical recovery for this compound by this method is 80.5%)	NH_2-C_6H_4-SO_2-NH_2	2.00	77.8	1.2	52

Note: All AIRMoN samples are obtained within 24 hours of a precipitation event, are immediately refrigerated, and are shipped chilled to the CAL. Samples are immediately refrigerated at 4°C upon arrival and are analyzed within seven days for inorganic nitrogen, as ammonium and nitrate, and total nitrogen.

Reference:

-QuikChem® Method 10-107-04-3-A, Lachat Instruments, Milwaukee, WI 53218

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Background

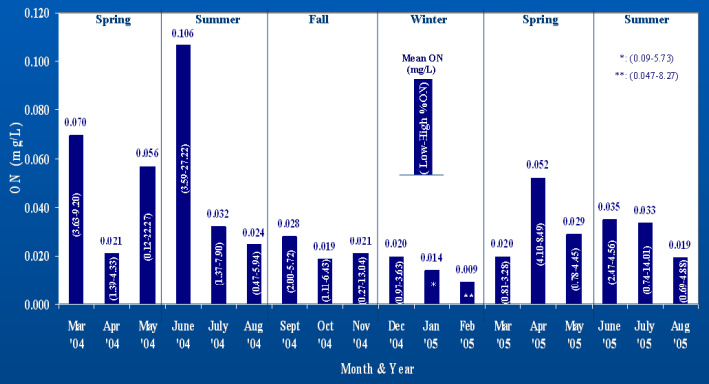
Nitrogen measurements in NADP NTN and AIRMoN precipitation samples have focused on inorganic-N measured as nitrate and ammonium. Nitrogen wet-deposition researchers usually assume that the levels of other forms of N such as the organic-N fraction in these samples are low. It is also anticipated that ON levels in NTN or AIRMoN samples may be low due to degradation and losses of these nitrogen sources prior to analysis. Although the chemical stability of these forms of nitrogen in NADP samples is unknown, we feel that the addition of total N measurements adds value to the networks since they can be used to better estimate the TN wet-deposition component and to estimate the contribution of other forms of nitrogen present in these samples for environmental assessments.

Purpose

1. Investigate the seasonal trends of dissolved organic nitrogen (ON) at one NADP AIRMoN site in east central Illinois (IL11) for 2004 and 2005
2. Evaluate effects of filtration on total nitrogen measurements
3. Study the effect of Hurricane Dennis in the transport of ON through the eastern United States using NADP NTN samples that were refrigerated immediately after filtration
4. Determine TN and ON levels in samples from AIRMoN

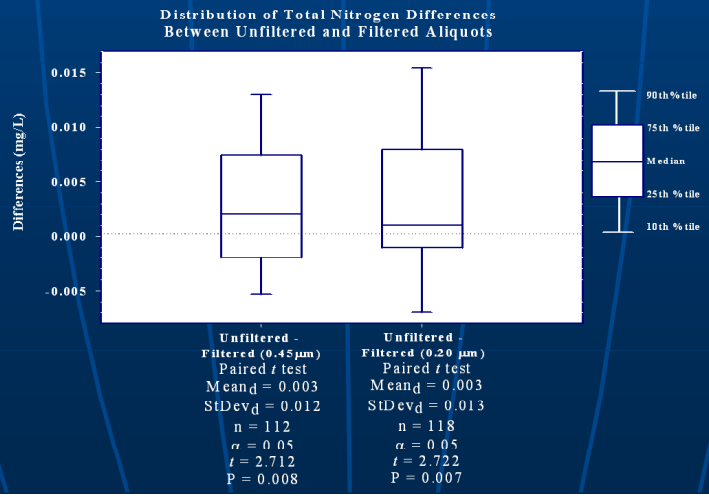
AIRMoN IL11 ON Data: March 2004-August 2005

Data were categorized by collection date into months and meteorological seasons.



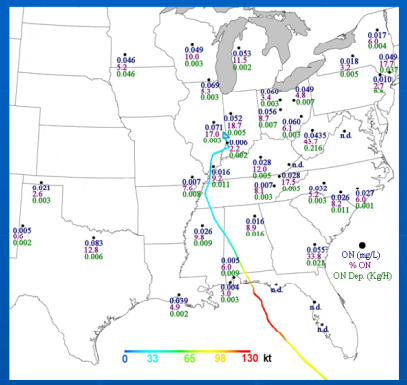
Effects of filtration on TN measurements

A study was undertaken to determine if sample filtration causes a change in the total nitrogen concentration. IL11 AIRMoN samples from 2004 and 2005 were analyzed unfiltered and filtered by a 0.45µm or 0.20µm Supor® (PES) Membrane Pall IC Acrodisc® 13 mm syringe filter to determine the effect of filtration on TN concentration. Each filter is rinsed with approximately 5 mL deionized water (18.0 mΩ-cm resistivity) and flushed with 2 mL sample to equilibrate the filter before the sample is filtered for analysis.



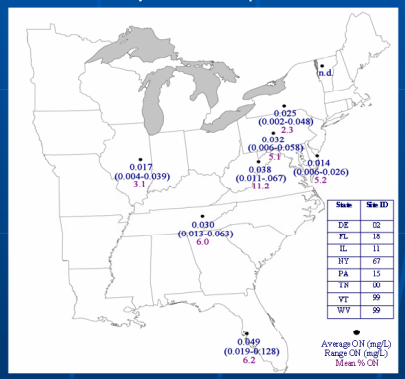
Hurricane Dennis effects on transport of ON

Hurricane Dennis arrived near Pensacola, Florida as a category 4 hurricane on July 10, 2005 and traveled northwest toward Illinois. Dennis stalled over Illinois as a tropical depression on July 12, 2005 and finally dissipated on July 13, 2005. A study was undertaken to investigate if Hurricane Dennis carried and deposited ON over the eastern United States as it traveled northwest. Eastern United States samples were chosen from the NTN for the week of July 5, 2005-July 12, 2005. Samples were filtered through a 0.45µm filter upon arrival and stored at 4°C until analysis. Samples were analyzed within seven days for inorganic nitrogen, as ammonium and nitrate, and total nitrogen.



AIRMoN Study: Dates 7/8/05 - 8/21/05

The NADP Atmospheric Integrated Monitoring Network has eight sites scattered throughout the eastern United States. In July and August 2005 the CAL has analyzed AIRMoN samples with sufficient volume for total nitrogen.



Conclusion

Although there is concern about the stability of ON or other nitrogen species in precipitation samples, we feel that the measurement of TN in AIRMoN or NTN samples can be used to better estimate the total wet-deposition of nitrogen across the U.S. for environmental assessments. We feel this method is sound and can meet the needs of the NADP for measurements using current sample protocols or by designing targeted experiments tailored to minimize degradation and to identify other nitrogen species in samples from sites across the U.S. (esp. central and western states).

1. Our ON data from the IL11 AIRMoN site for 2004-2005 ranged from 0-27% ON. The average was <5% ON for 201 samples analyzed from this site. Data did not not show a clear seasonal trend.
2. Differences between decanted, unfiltered samples and those filtered through 0.2 µm and 0.45 µm Supor® filters were found to be minimal. Unfiltered samples had a slight positive bias of 3 ppb when compared to samples filtered through a 0.2 µm or a 0.45 µm filter. No clear preference for pore size could be determined after analyzing over 100 samples using each pore size.
3. NTN samples were collected the week that Hurricane Dennis hit the gulf coast and traveled into the central states for TN analysis. Samples were filtered (0.45 µm), then an aliquot was removed (from samples with sufficient volume to allow subsampling), and were refrigerated immediately. ON levels ranged from 0 to 43.7% with an average of 8.5% in 38 samples. ON values were >10% in 10 of 38 samples. No clear connection was apparent between higher ON values and the storms trajectory.
4. TN and ON measurements from AIRMoN sites may be of value since samples are collected, refrigerated, and shipped to the CAL within 26 hours of a precipitation event. Samples from 8 AIRMoN sites were collected over a 6-week period from July-August 2005. The average %ON levels ranged from 0-11.2% (by site). West Virginia (WV99) exhibited the highest %ON in the AIRMoN network with a mean of 11.2% during this period.