Ammonia Flux Calculations Across the Air-Water Interface Using Hourly Air and Water Ammonia Observations at an Over-Water Site on the Chesapeake Bay

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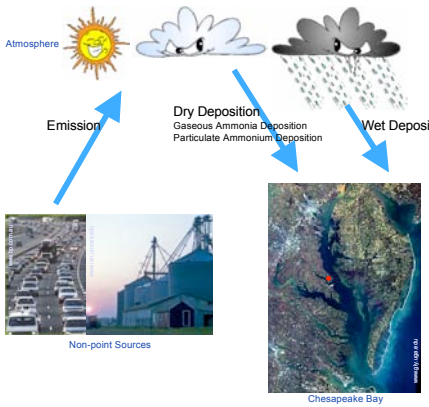
ABSTRACT

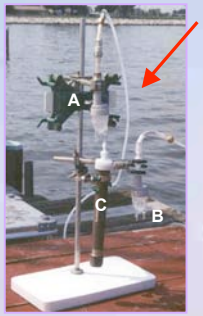
Atmospheric deposition represents approximately 25% of the total nitrogen loading to the Chesapeake Bay, and ammonia(um) represents about 1/3 of this flux.[1] In this study, ammonia(um) fluxes across the air-water interface were calculated using hourly atmospheric and surface-water measurements to investigate the temporal variability of ammonia(um) deposition directly to the Chesapeake Bay. A two-channel mist chamber collection system was used to collect hourly gas-phase ammonia and particulate ammonium concentrations at an over-water site on the Patuxent River with concurrent water measurements to calculate hourly air-water fluxes of ammonia and ammonium. Measurements were made on two separate dates in the summer of 2004. On July 29th, the net flux into the bay ranged from 74 to 440 μg NH_3-N m^{-2} day^{-1} over an 8 hour time period, and on August 4th the net flux into the bay ranged from 119 to 1210 μg NH_3-N m^{-2} day^{-1} over a 6 hour time period. Gas-phase deposition dominated the overall deposition although particulate ammonium concentrations were usually larger by an average of 89%. The dominant factors for the large variability in the fluxes were the variation in gas-phase NH_3 and its larger gas-phase exchange coefficient.

Atmospheric Ammonia Cycle



Nitrogen loading contributes to eutrophication of the Chesapeake Bay.[2] Atmospheric ammonia deposition is estimated to account for 10% of this nitrogen loading. However, current monitoring programs do not routinely monitor gas-phase ammonia concentrations and therefore may underestimate the true flux of ammonia from atmospheric deposition. In this study we measured hourly gas-phase and particulate phase ammonia/um concentrations at an over-water site with concurrent measurements of ammonia/um in the surface water. A deposition model was then used to calculate the dry-depositional flux of ammonia/um to the surface waters.

Ammonia Collection Equipment



Atmospheric Ammonia

- Parallel mist chambers, A & B, were set up on the end of a pier over the Patuxent River
- Chamber A collected particulate ammonium (Denuder C removed gas-phase ammonia)
- Chamber B collected total ammonia/um (gas-phase ammonia and particulate-phase ammonium).
- Gas-phase ammonia concentrations were calculated by difference

Aqueous Ammonia

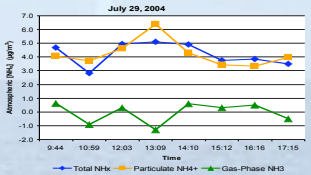
- Surface water samples were collected by bucket and immediately filtered to remove biological material.

Both sets of samples were analyzed by the Nutrient Analytical Services Laboratory at Chesapeake Biological Laboratory using the Berthelot Reaction.[3]

Atmospheric and Aqueous Results

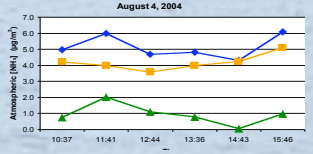
Atmospheric Ammonia Concentrations

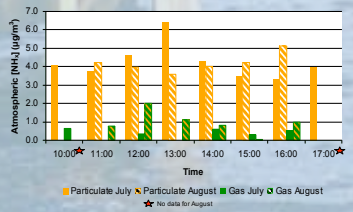
- Particulate NH_4^+ concentrations were greater than gas-phase NH_3 concentrations
- Most ammonia in particulate phase
- Difference resulted in three negative gas phase conc.; assumed to be zero



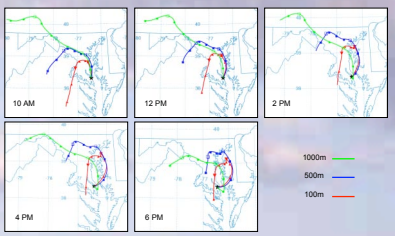
Aqueous Ammonia Concentrations

Aqueous ammonia concentrations of samples and blanks were below the detection limit of 0.2 μM for all cases and therefore a concentration of zero was used for flux calculations.





- Clear difference between gas-phase NH_3 and particulate NH_4^+
- Both days saw similar particulate concentrations (with exceptions of peaks)
- Larger variation in gas-phase concentration for August 4th compared to that of July 29th
- Greater gas-phase concentrations collected during westerly winds



Forty-eight hour back trajectory of air masses to Solomons Island on July 29, 2004.[4]

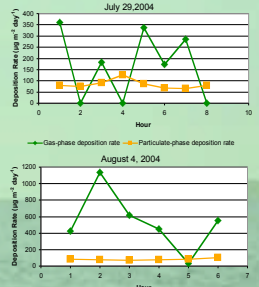
Meteorology

- Both July 29th and August 4th were mostly sunny with wind speeds between 1 to 3 m/s (roughly 2 to 7 mph)
- Wind northerly becoming easterly on July 29th and northerly becoming westerly on August 4th
- Back trajectories for July 29th show where wind masses at various heights were previous to flowing over Solomons Island.

Flux Calculations and Results

Net Exchange Flux = Gross Volatilization + Gross Dry Deposition[5]

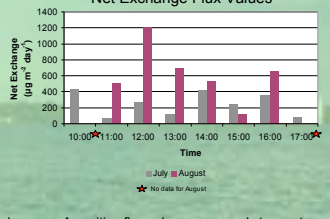
Deposition Rates by Species



Gross Volatilization = $V_e[NH_3]_{eq}$
Gross Dry Deposition = $-(V_e f_g[NH_x] + V_d(1 - f_g)[NH_x])$

where V_e = 6.5 mm/s and V_d = 0.23 mm/s

Net Exchange Flux Values



Although the total collected ammonia for each day consisted mostly of particulate NH_4^+, the two graphs above showed that the majority of the net exchange flux results from gas-phase deposition.

- A positive flux value corresponds to a net exchange from the air to the water
- Greater flux rates estimated for August 4th

CONCLUSIONS

Ammonia(um) was predominantly in the particulate phase for both days

Dry deposition was dominated by gas-phase deposition due to the greater gas-phase exchange coefficient

Flux estimates varied throughout the day, more so on August 4th, and ranged from 100 to 1200 μg m^{-2} day^{-1} for both days

These measurements and calculation show the temporal variability of ammonia/um dry deposition at an over-water site. The dry deposition of ammonia seems to be a significant source on nitrogen to the Bay and current sampling networks should include gas-phase ammonia and particulate-phase ammonium measurements to better constrain this source. EPA's CASTNET program[6] currently measures particulate ammonium but not gas-phase ammonia.

References

1. Castro, M.S.; Driscoll, C. T. Environmental Science & Technology, 2002. **36**(15): 3242-3249.
2. Chesapeake Bay Program, www.chesapeakebay.net.
3. Nutrient Analytical Services Laboratory, www.cbl.umces.edu/nasl/index.htm.
4. Graphics produced from the NOAA HYSPLIT Model www.arl.noaa.gov/ready/.
5. Larsen, R. K. III; Steinbacher, J. C.; Baker, J. E. Environmental Science & Technology, 2001. **35**(24): 4731-4738.
6. EPA's CASTNET program, http://www.epa.gov/castnet/overview.html.

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