Connecting atmospheric deposition of nitrogen to coastal water quality

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Questions

• How important is AD-N as a “new” N source?
• What are the origins & chemical forms of AD-N?
• What are the ecological impacts on specific coastal ecosystems?
• What are the spatio-temporal issues for monitoring and assessment?
Estimated contributions of AD-N* to "new" N inputs in estuarine, coastal and open ocean waters

- Baltic Sea ~30 % Elmgren et al. 2001
- North Sea (Coastal) 20-40% Holland et al. 1999
- W. Mediterranean Sea 10-60% Martin et al. 1989
- Waquoit Bay, MA >29% Valiela et al. 1996
- Narragansett Bay 12% Nixon 1995
- Long Island Sound >25% L. I. Sound Study 1996
- New York Bight 38% Valigura et al. 1996
- Barnegat Bay, NJ ~40% Moser et al. 2002
- Chesapeake Bay 30% Castro et al. 2002
- Rhode River, MD 40% Correll and Ford 1982
- Neuse R., NC ~35% Whitall et al 2003
- Pamlico Sound, NC 20->40% Paerl et al. 2002
- Sarasota/Tampa Bay, FL ~30% Sarasota Bay NEP 1996
- Mississippi River Plume > 5 % ?? Goolsby et al. 2000

* Includes estimates of wet and dry deposition, inorganics and organics
Why The Ecological Concern About AD-N in Coastal Waters?

- Many of these N-sensitive eutrophying waters are currently impacted by AD-N
Example: The Neuse R. Estuary-Pamlico Sound
Excessive N loading → eutrophication →
hypoxia → WQ/habitat decline

Neuse R Modeling & Monitoring Program (ModMon)
www.marine.unc.edu/neuse/modmon
Partners: UNC, ECU, Duke, NCSU, USGS, NCDENR, EPA,
Collaborators: NOAA-NOS, NASA, NADP, Weyerhaeuser
**Neuse River Estuary N Sources (at head of estuary)**

- **AD-N** (35%)
- **Runoff** (54%)
- **Pt. Sources** (11%)

### N Retention Values

<table>
<thead>
<tr>
<th>Source</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forest</td>
<td>0.95</td>
</tr>
<tr>
<td>Pasture</td>
<td>0.90</td>
</tr>
<tr>
<td>Crop</td>
<td>0.70</td>
</tr>
<tr>
<td>Urban</td>
<td>0.70</td>
</tr>
<tr>
<td>Other</td>
<td>0.70</td>
</tr>
</tbody>
</table>

- Runoff (excluding AD-N) and point source values from Valigura et al. 1996.
- Runoff values from Dodd et al. 1992.
Wet NO$_3^-$: 49%
Wet NH$_4^+$: 23%
Dry NH$_4^+$: 2%
Wet Organics*: 18%
Dry Organics???

*Estimate based on previous studies and limited data from this study; wet organics comprise approx. 20% of total wet N deposition.

Total AD-N for Neuse R. Estuary

Based on yearly averages from 1996-2002 data

*Whitall et al. 2003
*Walker et al. 2004
In Eastern NC, estuarine and coastal waters are getting more ammonium-rich. Why?
An possible increase in hypoxia may be one reason.

Data Sources: ModMon Project & NC DENR-DWQ

Fish kill data base: http://www.esb.enr.state.nc.us:80/Fishkill/fishkillmain.htm
Another reason: More ammonia is being emitted locally and regionally
National Atmospheric Deposition Program Data
Sampson Co. North Carolina (NC35)
Where are the hogs relative to the N sensitive waters?

Number of Hogs

- <1000
- 1000-9999
- 10000-34999
- 35000-99999
- >100000

prevailing wind direction
(from National Climatic Data Center)
PRINCIPAL NITROGEN AIRSHEDS FOR:
PAMLICO SOUND

DEVELOPED BY R. DENNIS, ATMOSPHERIC SCIENCES MODELING DIVISION:
ARL, NOAA, AND NIEH USA EPA
Why the Ecological Concern About Ammonium?

Not all forms of N are used equally

\[ \text{NH}_3/_{4}{^+} \text{ vs. NO}_3^{-} \text{ vs. Organic N} \]
Nutrient Addition Bioassay Experiment, T1
Neuse River, July 2003

Chlorophyll a (µg L⁻¹)

Upstream
C, NH4, NO3, NH4 + NO3, P, NH4 + P, NO3 + P, NH4 + NO3 + P

CMAX
NH4 + NO3, NH4 + NO3 + P, NO3 + P

Downstream
C, NH4, NO3, NH4 + NO3, P, NH4 + P, NO3 + P, NH4 + NO3 + P

Ammonium is a preferred N source by phytoplankton
Looking into the green box: phytoplankton taxonomic group responses to specific forms of N enrichments by HPLC-ChemTax Analysis
Bogue Sound Bioassay

August, 1996

Concentration (mg m\(^{-3}\))

Chl a

Fucoxanthin

Alloxanthin

Zeaxanthin

Treatment

Control Nitrate Ammonium

Cryptophytes

cyanobacteria

diatoms

All phytos
Scaling up to the Ecosystem

Linkages Between Nutrient Inputs, Hydrology, Phytoplankton Community Composition, Grazing, Hypoxia and Fisheries Habitat

Nutrient and Hydrologic drivers

PHOTOPLANKTON COMMUNITY

FORM of Limiting Nutrient ($\text{NO}_3^-$, $\text{NH}_4^+$, DON)
Nutrient Ratios, Residence Time

Grazed Phytoplankton Species

Nuisance / Toxic Phytoplankton Species
Some Dinoflagellates
Cyanobacteria

Carbon Deposition (POC)

Grazing and Water Column Carbon Recycling

DECREASED $O_2$ Depletion Potentials

INCREASED $O_2$ Depletion Potentials

Nutrient Regeneration
Decomposition of POM

OXIC CONDITIONS

HYPOXIA ANOXIA

Mixing
PHYSICAL CONTROLS
Stratification

Scaling up to the Ecosystem
Seasonal Variability in ADN is also important
10 NRE Sites Pooled

Significantly higher than spring, fall and winter at $\alpha = 0.01$
Atmospheric N inputs can bypass the estuarine N “filter”
The Airshed Scale: Bypassing the Estuarine Filter & Influencing the Coastal Zone
Relative Importance of AD-N Flux to the Annual N Budget of NC Coastal Waters

Direct Deposition of AD-N to Coastal Waters (903 kg N/km²/yr)

Land Based N Flux to Coastal Waters (1877 kg N/km²/yr)

Land Based DIN Flux values for Southeastern U.S. region include AD-N deposition to land (Howarth et al. 1996), AD-N values from UNC-IMS 1990-2000 data (DIN+DON; where DON is estimated at 20% of DIN flux)
Spatial and temporal Issues: Implications for Monitoring

Estimated Annual Deposition (millimoles/meter²):

- Nitrate
- Ammonium

TOTAL OXIDIZED NITROGEN
2001 BASE - ANNUAL

January 1, 2001 1:00:00
Min = 3.08 at (27,1), Max = 16.38 at (22,24)

TOTAL REDUCED NITROGEN
2001 BASE - ANNUAL

January 1, 2001 1:00:00
Min = 0.95 at (27,1), Max = 39.68 at (16,4)
Finer grid: more accurate representation of ammonia hot spots

Ammonia Deposition: 36-km CMAQ

July 2001
z-J3a_b313.200107_36km.dep

Min~ 0.0000 at (139.39), Max~ 0.0073 at (124.49)

Nitric Acid Deposition: 36-km CMAQ

July 2001
z-J3a_b313.200107_36km.dep

Min~ 0.0000 at (118.94), Max~ 0.0039 at (117.71)

Finer grid: more accurate representation of urban hot spots

Ammonia Deposition: 12-km CMAQ

July 2001
y-J3a_b313.200107_12km.dep

Min~ 0.0000 at (118,150), Max~ 0.0128 at (164,77)

Nitric Acid Deposition: 12-km CMAQ

July 2001
y-J3a_b313.200107_12km.dep

Min~ 0.0000 at (175,81), Max~ 0.00083 at (144,146)
Spatial Heterogeneity of AD-N in the Neuse-Pamlico Sound System

Take-home message: 12-36 km grid is highly relevant

Annual Atmospheric N Deposition

- New Bern
- Pamlico
- Beaufort
- Cedar Island

<table>
<thead>
<tr>
<th>Site</th>
<th>kg N/ha</th>
</tr>
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<tbody>
<tr>
<td>New Bern</td>
<td>12</td>
</tr>
<tr>
<td>Pamlico</td>
<td>8</td>
</tr>
<tr>
<td>Beaufort</td>
<td>10</td>
</tr>
<tr>
<td>Cedar Island</td>
<td>4</td>
</tr>
</tbody>
</table>

20km
Conclusions

- AD-N is a significant source of N enrichment to coastal waters downwind of sources.
- AD-N impacts production and composition of phytoplankton. AD-N plays a role in eutrophication dynamics of these waters.
- Chemical forms of AD-N are important and ammonium is of growing concern.
- Spatial heterogeneity is important, from both monitoring and ecological effects perspectives.
- Impacts and management of AD-N should include local, regional, and global scales.
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