Ambient Ammonia

Air Quality and Health Impacts

Dr. Randy Martin
Utah State University
Dept. of Civil & Env. Eng./Utah Water Research Laboratory
Logan, UT
(435)797-1585
rmartin@engineering.usu.edu

Outline

I. Gaseous Ammonia – what is it?
II. Health & Welfare Issues
III. Sources & production
IV. Case Study: Cache Valley, UT/ID
V. Current Ammonia Air Quality Regulations
VI. Summary

What is Ammonia?

(the nerdy, chemistry stuff)

- NH_3
  - MW = 17.0306 g/gmol (for comparison, MW_{air} = 29.87)
  - Major species in the biogeochemical nitrogen cycle
  - Water soluble, especially as water becomes more acidic
    - *natural rainwater pH ≈ 5 – 5.5*
  - Most abundant base (pH) gas in the atmosphere
  - Slow gas-phase oxidation (to N_2 or N_2O)
    - *lifetime with OH, $\tau_{NH3/OH} \approx$ 72 days*
  - Readily reacts with gaseous nitrate & sulfate to form suspended particulate matter (esp. $PM_{2.5}$) and very depositional (wet or dry)
    - *Exists as ammonium (NH_4^+) in liquid and solid phases*
    - *$\tau_{PM/Deposition} \approx$ few hours - few days*

Ambient Ammonia Health and Welfare Effects

- Human Health Issues
  - *Primarily wet tissue (i.e. eyes, nose, throat) irritation and damage*
    - *corneal and skin burns/blistering, intraocular pressure (glaucoma), coughing, pulmonary and laryngeal edema, chest pains, pinky/frothy sputum*
  - *Human Health Regulations:*
    - *OSHA PEL 8-hr: 50 ppm (35 mg/m^3)*
    - *ACGIH recommends…*
      - *8-hr exposure limit: 25 ppm (17 mg/m^3)*
      - *15-min exposure limit: 35 ppm (27 mg/m^3)*
    - *NIOSH gives IDLH (Immediate Danger to Life and Health) level as 300 ppm (215 mg/m^3)*
    - *CDC gives a 5 min. LCLo (Lethal Concentration - Low) as 5000 ppm (3.6 g/m^3)*

Health and Welfare Effects (*cont.*)

- Animal Health Issues
  - *Similar to human effects (eyes, nose, throat irritation/damage)*
    - *Swine:*
      - *reduced weight gain of 12-32% at NH_3 levels of 50-100 ppm*
      - *increase stress, lowered resistance to infectious disease*
      - *recommend levels below 20 ppm (others suggest 10-15 ppm)*
    - *Cattle:*
      - *pulmonary effects most prominent (reduced lung function)*
      - *decreased mucociliary transport*
    - *Poultry:*
      - *reduced body weights at 25 ppm*
      - *respiratory irritation, predisposition to infectious disease, and cornea/conjunctiva inflammation (keratoconjunctivis) at 50 ppm*
- Welfare Issues
  - *Excess NH_3/NH_4^+ deposition can lead to enhanced water body eutrophication (excessive nutrients, in the case, nitrogen, N)*
    - *excessive plant growth (i.e. algal blooms → reduced dissolve oxygen)*
  - *Soil acidification via microbial nitrification of NH_3 to nitrate (NO_3^-)*
  - **Contributes to fine particle formation (more on this next slide!)**

NH_3 & Particulate Matter ($PM_{2.5}$)

Gaseous NH_3 readily converts gaseous acids, esp. sulfuric and nitric acids to fine particles (≤ 2.5 μm):

$NH_{3(g)} + H_2SO_{4(g,l)} \rightarrow NH_4HSO_{4(s,\ l)}$ (ammonium bisulfate)

- if excess NH_3 is available…

$NH_{3(g)} + NH_4HSO_{4(l)} \rightarrow (NH_4)_2SO_{4(s,\ l)}$ (ammonium sulfate)

- Irreversible reactions, stable at most atmospheric conditions -

- if additional excess NH_3 is still available…

$NH_{3(g)} + HNO_{3(g)} \leftrightarrow NH_4NO_{3(s)}$ (ammonium nitrate)

- Equilibrium reaction, shifts right (NH_4NO_3) at low temp. & high humidity -
(i.e.) change for 25°C to 0°C results in a shift of ≈100x towards NH_4NO_3

It can be seen that the control of ammonium-based PM may ultimately be based on NH_3 controls

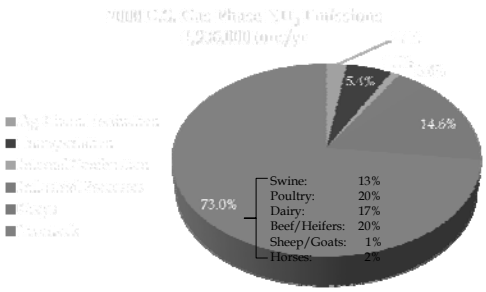
Particulate Matter ($PM_{2.5}$)

- $PM_{2.5}$ = all particulate matter suspended in the ambient air which is less than or equal to 2.5 μm in aerodynamic diameter
  - *approx. 1/40th diameter of a human hair*
- National Ambient Air Quality Standards (NAAQS)
  - 24-hr Standard: 35 μg/m³
    - *reported at the 98th percentile (maximum) value for a given year*
    - *(e.g.) if 100 24-hr concentrations are collected, the 3rd highest $PM_{2.5}$ concentration is used*
    - *averaged over 3 consecutive years*
  - Annual Standard: 15 μg/m³
    - *annual avg is the mean of a year's four quarterly avg's*
    - *averaged over 3 consecutive years*

Particulate Matter ($PM_{2.5}$)

1. Human Health Issues
   - *able to penetrate deep into the respiratory tract/lung tissue*
   - *Pope et al. (2002) reported 8% increase in lung cancer risk for every 10 μg/m³ increase in $PM_{2.5}$*
2. Responsible for visibility reduction episodes (haze)
3. Deposition of particulate material on sensitive materials
   - *potential to change nutrient/chemical balance in soil and water environments*
   - *erosion/corrosion/staining of structures and statuary*

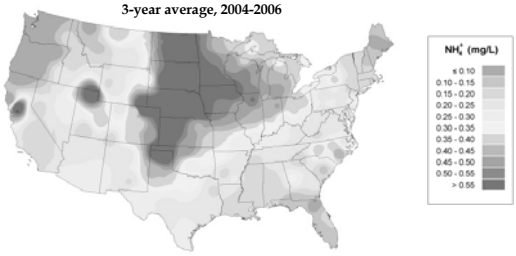
Gas-Phase Ammonia Sources



(adapted for USEPA, 2003, 2004, and Moore, 2007)

National Acid Deposition Program NH_4^+ Map

3-year average, 2004-2006

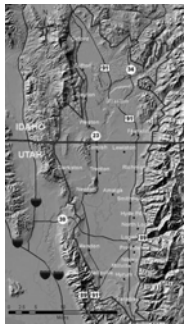


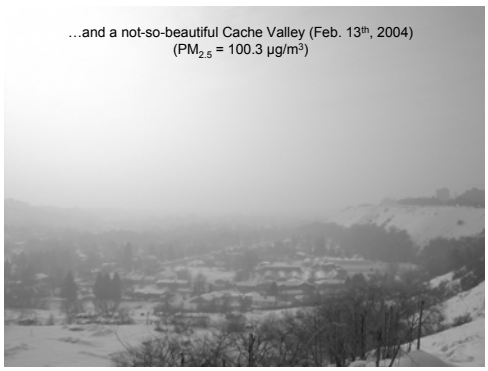
Agricultural Gaseous Ammonia Production

- Majority of ammonia emissions from animals originate from a mixture of feces and urine:
  - *Nitrogen excreted in urine as urea, $CO(NH_2)_2$ (mammals), uric acid, $C_5H_4O_3N_4$ (poultry), and undigested protein (manure)*
  - *Urea and uric acid converted to NH_3/NH_4^+ by the enzyme Urease which is present in the manure*
    - *requires "intimate" contact with the urine & feces*
    - *rapid conversion (hours - few days)*
    - *enzyme activity also influenced by pH and temperature*
    - *gaseous NH_3 favored at neutral to basic pH's*
  - *Complex undigested proteins (manure) converted by microbial activity*
    - *slow conversions (months - years)*
    - *affected by temperature, pH, and moisture*
- Ammonia is also released through volatilization during waste storage, transport, and disposal
  - *(i.e.) solid or liquid waste or fertilizer application*

Cache Valley, UT/ID *(a case study)*

- Flat-bottomed valley on SE Idaho, N. UT
  - *ele, 1340 m asl, surrounding mountains to 3040 m*
  - *approx. 1440 km²*
- Population ≈110,000 (>85,000 vehicles)
- Agriculturally dominated economy
  - *$189 million in 2004*
  - *≈106,000 cattle, 7400 sheep, 7500 swine, 1.5 million poultry*
- **Unacceptably high wintertime $PM_{2.5}$**
  - *recorded 24-hr values as high as 137.5 µg/m³*
  - *Cache Valley has been reported as having the nation's worst air pollution on a number of winter days (EPA's AIRNow website)*
  - *3-yr of 98th % 24-hr avg (2005-2007) = 40.4 µg/m³*
    - *Cache Valley 3-yr avg as high as 63.7 µg/m³*

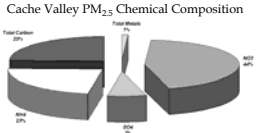




Cache Valley $PM_{2.5}$, the why?

1. Unfavorable wintertime meteorology
   - *Frequent high pressure systems (stagnant air)*
   - *Snow-covered surfaces (insufficient incoming solar radiation to break inversions)*
   - *Cold temperatures (well below 32°F) and higher humidity*
     - *strongly favors NH_4NO_3 particle formation*
2. Enclosed valley (inhibits atmospheric dispersion/drainage)
3. Abundant local sources of precursor compounds
   - *Vehicles → oxides of nitrogen (NO_x which forms the HNO_3)*
     - *older than typical vehicle fleet, greater % pickups & diesels*
     - *no vehicle I&M program*
   - *Agriculture → ammonia*

Cache Valley $PM_{2.5}$ Chemical Composition

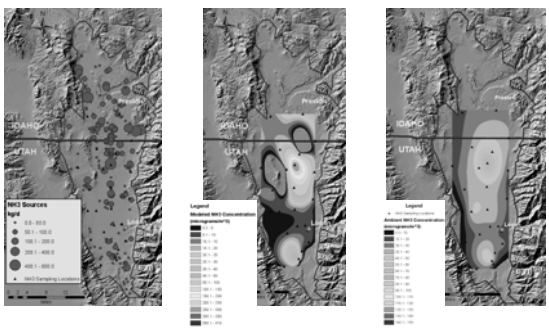


*** On high $PM_{2.5}$ concentration days, the ammonium nitrate (NH_4NO_3) fraction approaches 80-95%**

One important question….Where does all of the NH_3 come from?

Cache Valley NH_3 Maps

(sources vs. modeled vs. measured concentrations)



NH_3 Regulations

- No current NH_3 emission limits under the Clean Air Act or its Amendments
- Considered hazardous substances under the Comprehensive Emergency Response, Compensation, and Liability Act (CERCLA) and the Emergency Planning and Community Right-to-Know Act (EPCRA)
  - *If NH_3 emissions >100 pounds per day, reporting requirements would apply (NARA, 2005)*
- Some states may have initiated specific NH_3 emission regulations
  - *CA SB700*
  - *ID NH_3 Permitting Program*

Summary

- Agriculturally-derived NH_3 becoming increasingly important in regional and local air quality issues
  - *Especially photochemical formed $PM_{2.5}$ (AKA secondary PM)*
    - *Ammonium sulfate or ammonium nitrate dominance depends on local source abundance and photochemical potential*
  - *Nuisances odors may also become an more significant as the urban/rural interface continues to blur*
- Current and future regulations must be based on quantifiable, reliable, and defensible emission factors
  - *Historical emission estimates based on relatively few or limited application studies*
  - *Last decade has seen a dramatic increase in U.S.-based and process-centered emission studies*
    - *(i.e.) the National Air Emissions Monitoring Study (NAEMS), as well as numerous other investigations*

BIBLOGRAPHY

- Gay, S.W. and K.F. Knowlton. 2005. Ammonia Emissions and Animal Agriculture. Publication 442-110, www.ext.vt.edu/pubs/bse/442-110/442-110.html, accessed June 2008.
- Holland, R.E., T.L. Carson, and K.J. Donham. 2002. Animal Health Effects. In: Iowa concentrated Animal Feeding Operations Air Quality Study. Chapter 6.2. Iowa State University. www.ehsrc.uiowa.edu/CAFOstudy/CAFO_6-2.pdf, accessed June 2008.
- Moore, K. 2007. Derivation of Agricultural gas-phase Ammonia Emissions and Application to the Cache Valley. M.S. Thesis, Utah State University, Dept. of Civil and Environmental Engineering
- National Atmospheric Deposition Program (NRSP-3). NDAP Program Office, Illinois State Water Survey 2204 Griffith Drive, Champaign, IL, 61820, nadp@sws.uiuc.edu
- Pope III, C.A., R.T. Burnett, M.J. Thun, E.E. Calle, D. Krewski, K. Ito, G.D. Thurston. 2002. Lung Cancer, Cardiopulminary Mortality, and Long-term Exposure to Fine Particulate Air Pollution. Journal of the American Medical Association. 287: 1132-1141.
- U.S. EPA. 2003. National air quality and emissions trends report: 2003 special studies edition. EPA-454/R-03-005, September 2003.
- U.S. EPA. 2004. National emissions inventory – Ammonia emissions from animal husbandry operations. January 2004. http://www.epa.gov/ttn/chief/ap42/ch09/related/nh3inventorydraft_jan2004.pdf