Ammonia:
A Particulate Matter Precursor

Dr. Julia Lester, ENVIRON International

Agricultural Air Quality Task Force
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Overview

- Ammonia – what it is, why do we care
- The pollutant / regulatory cycle
- Estimating ammonia emissions
- Ammonium aerosol particulates – PM$_{2.5}$
- Ammonia regulations – current and proposed
- Emission Reduction Credits: PM equivalency
- Summary
What Happens to Emitted Ammonia?

PM$_{2.5}$ Formation

- Ammonia is the source of the predominant base compound in the atmosphere (ammonium – NH$_4^+$)
- Acids are formed by reaction of combustion by-products
  - NO$_2$ + OH $\rightarrow$ HNO$_3$
  - SO$_2$ + 2OH $\rightarrow$ H$_2$SO$_4$
- Under the right conditions, ammonium will join with gaseous acids (e.g. sulfuric and hydrochloric acids)
  - 2NH$_3$(g) + H$_2$SO$_4$ $\rightarrow$ 2(NH$_4$)SO$_4$ (aerosol)
  - NH$_3$(g) + HNO$_3$(g) $\leftrightarrow$ NH$_4$NO$_3$(PM) (solid and aerosol)
- Acid formation generally slower than aerosol formation
- Ammonium sulfate, then ammonium nitrate
The Pollutant / Regulatory Cycle

Emission Factors
Emission Models
Inventories

Emissions

Ambient

Effects

Monitoring
Modeling
(all scales)

Standard setting
Air Quality Plans
Regulations
Source Categories

- Livestock agriculture
- Fertilizer usage
- Motor vehicles (3-way catalysts)
- Native soils
- Industrial (including ammonia slip)
- Domestic (biologic and residential uses)
- Wild animals

Ways to estimate emissions:
- historical: emissions = EF x activity
- latest: emissions models (multi-component)
Could It Get Any More Complicated?

Goal: Emission models for whole systems, multiple pollutants, for a variety of management practices and meteorological conditions

Fertilizer Application

- Emissions affected by soil, rainfall, meteorological conditions
- Seasonal and diurnal patterns

Source: Battye and Barrows (EPA 2004)
Emissions Models

From Regional Inventories (e.g., WRAP) . . .

. . . to Single Farm Emissions

And many more . . .
Agricultural Ammonia Emissions: An Inventory View (by County)

2002 Ammonia Emissions from Animal Agricultural Operations

Legend
Ammonia Emissions (Tons)
- 0
- 0 - 249
- 250 - 499
- 500 - 999
- 1,000 - 4,999
- 5,000 - 11,999
- Greater than 12,000

Eastern Research Group, Inc.
18 April 2005
Agricultural Ammonia Emissions:
A Modeling View (36-km grid)

Source: WRAP
PM$_{2.5}$ Non-Attainment Areas

Counties Exceeding New NAAQS Levels, Based on 2003-2005 Monitoring Data

Legend
- County with monitor exceeding:
  - red: both annual and 24-hour PM$_{2.5}$ standards
  - yellow: ONLY the 24-hour PM$_{2.5}$ standard
  - orange: ONLY the annual PM$_{2.5}$ standard

Number of Counties
- 55
- 69
- 17
- Total Counties Exceeding: 141

- Data from AQS 7/10/2006
- Data completeness computed per CFR 7/10/2006

ENVIRON
Agricultural Ammonia Emissions: A Modeling View (12-km grid)

Source: WRAP
Ammonia as a PM Precursor

- A necessary, but not sufficient precursor
  - Wetter conditions with limited mixing conducive to ammonium aerosol production
  - Sulfuric acid will preferentially react with any available ammonia first
  - ammonium nitrate will be formed if additional ammonia available and conditions are conducive

- Limiting reactant: Ammonia or Acids?

Source: After Pandis (2003)
Example: South Coast Air Basin PM$_{2.5}$

2001

2005

2005 MATES-III Annual PM$_{2.5}$

- Anaheim
- Los Angeles
- Diamond Bar
- Fontana
- Rubidoux
Example: San Joaquin Valley

- 2006 PM10 Plan:
  - SJV is ammonia-rich, NOx (nitrate) limited area
  - Regional ammonia controls unlikely to be effective; NOx control is preferred strategy (supported by California Regional Particulate Air Quality Study (CRPAQS) modeling)

<table>
<thead>
<tr>
<th>Summary of findings</th>
<th>Primary</th>
<th>Secondary</th>
<th>Effective control option</th>
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<tbody>
<tr>
<td>Geologic and Construction</td>
<td>PM10</td>
<td>ROG</td>
<td>Yes</td>
</tr>
<tr>
<td>Mobile exhaust, tire and brake wear</td>
<td>PM10</td>
<td>ROG</td>
<td>Yes</td>
</tr>
<tr>
<td>Vegetative burning</td>
<td>PM10</td>
<td>ROG</td>
<td>Yes</td>
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<tr>
<td>Organic Carbon (stationary and area)</td>
<td>PM10</td>
<td>NOx</td>
<td>No</td>
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<tr>
<td>Ammonium Nitrate</td>
<td>PM10</td>
<td>Ammonia</td>
<td>Yes</td>
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<tr>
<td>Ammonium Sulfate</td>
<td>PM10</td>
<td>SOx</td>
<td>No</td>
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<tr>
<td></td>
<td></td>
<td>Ammonia</td>
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</tr>
</tbody>
</table>

Source: SJVAPCD 2006 PM10 Plan Public Workshop
Ammonia Regulations

- South Coast AQMD – 1997, 2003 AQMPs
  - Rule 1133.2 (2003) for co-composting
  - Rule 1127 (2004) for dairies
  - Proposed: PAR 1127.1 (poultry, swine)
- San Joaquin Valley APCD – 2006 PM10 Plan
  - None currently or planned
- Idaho – lawsuit settlement
  - Permit by rule: dairies with > 100 tons/year ammonia (~1600 to 5100 cows, depending on dairy type)
  - Requirements (July 2006): registration, BMPs
  - Compliance: BMP scoring system
Other Regulatory Drivers

- Ammonia and ammonium aerosol deposition
- Visibility Impairment
  - Light scattering of aerosol particulate and associated water
Emission Reduction Credits (ERCs)

- PM$_{10}$ ERCs for New Source Review (NSR) offsets
  - Supply limited in South Coast and San Joaquin
    - SJV: $12K/ton/year (2005), now ~$50K/ton/year
    - SC: $70K/lb/day (2005), now ~ $200K/lb/day (!!!)
- Way to realize ammonia reduction benefits of biomass renewable energy and GHG reduction projects?
- USDA and CEC PIER Grant: Feasibility Analysis
  - Emission reduction quantification / verification
  - PM equivalency of ammonia reductions methodology development
  - Equivalency determination – case studies
  - ERCs and other applications: opportunities / barriers
Proof of Concept -- IEUA

- Ammonia Reductions: 0.45 tons/day (165 tons/year)
- PM$_{10}$ Model Results (primary PM$_{10}$ reduction of 1 ton/day)

☑ Draft PM Equivalency Methodology (PM$_{10}$ and PM$_{2.5}$)
- Equivalency metric(s) analysis (underway)
- Feasibility Assessment (2008)
Summary

- Atmospheric aerosol chemistry understood better, but PM “isopleths” with NOx, VOC, and ammonia are rare
- Transition from EFs to emission models
  - Several emission models now available or under development
  - More data (field and lab) and peer review needed
- New PM$_{2.5}$ standard may increase consideration of ammonia regulations
- Ammonia deposition and visibility issues may lead to additional ammonia reduction programs
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