Ammonia:
A Particulate Matter Precursor

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Agricultural Air Quality Task Force

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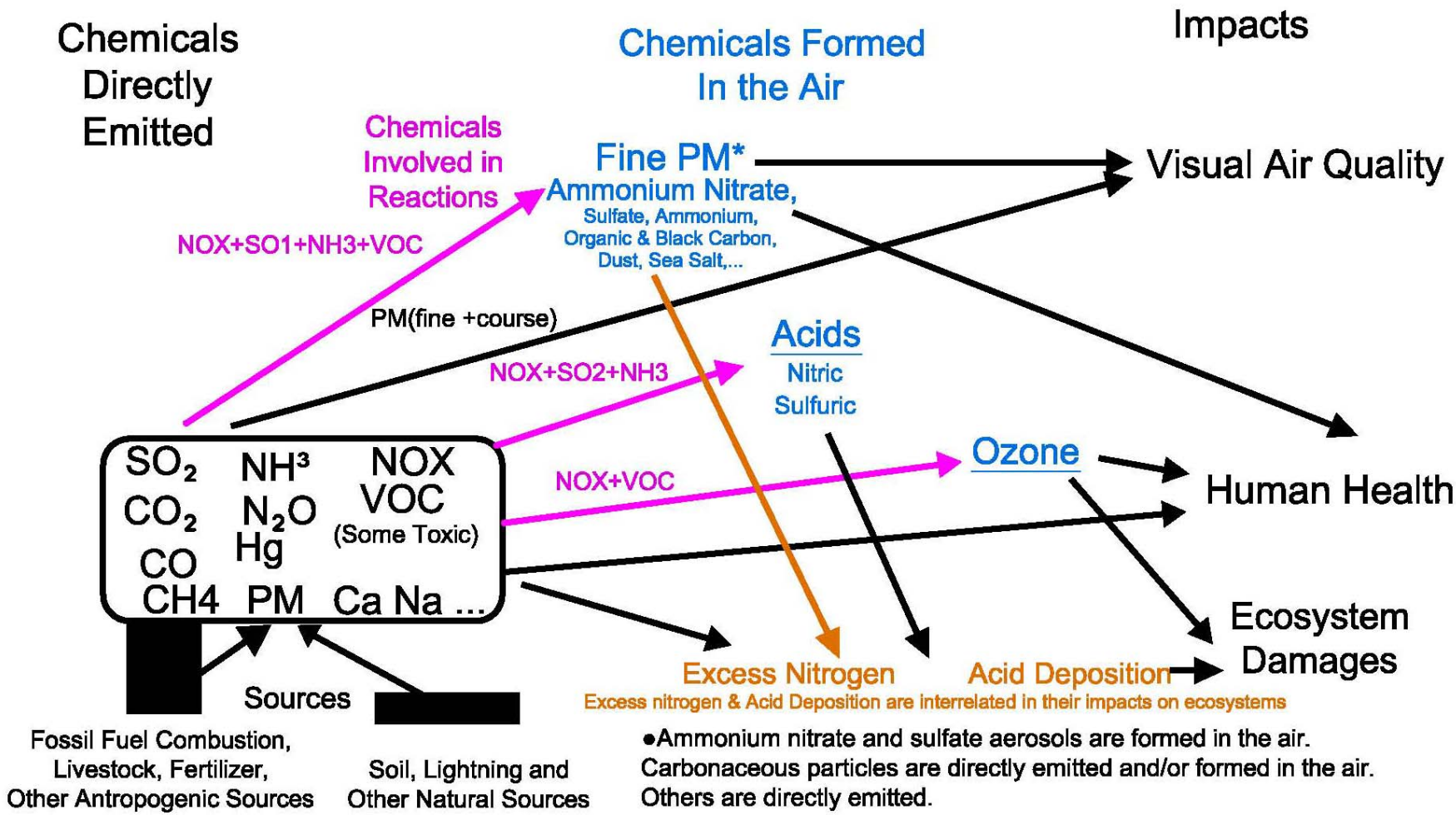
Overview

- 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?



Source: Summary of Environmental Defense Forum (2004)

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$PM_{2.5}$ 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
  - $NO_2 + OH \rightarrow HNO_3$
  - $SO_2 + 2OH \rightarrow H2SO_4$
- Under the right conditions, ammonium will join with gaseous acids (e.g. sulfuric and hydrochloric acids)
  - $2NH_3(g) + H_2SO_4 \rightarrow 2(NH_4)SO_4$ (aerosol)
  - $NH_3(g) + HNO_3(g) \leftrightarrow NH_4NO_3(PM)$ (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

Monitoring
Modeling
(all scales)

Effects

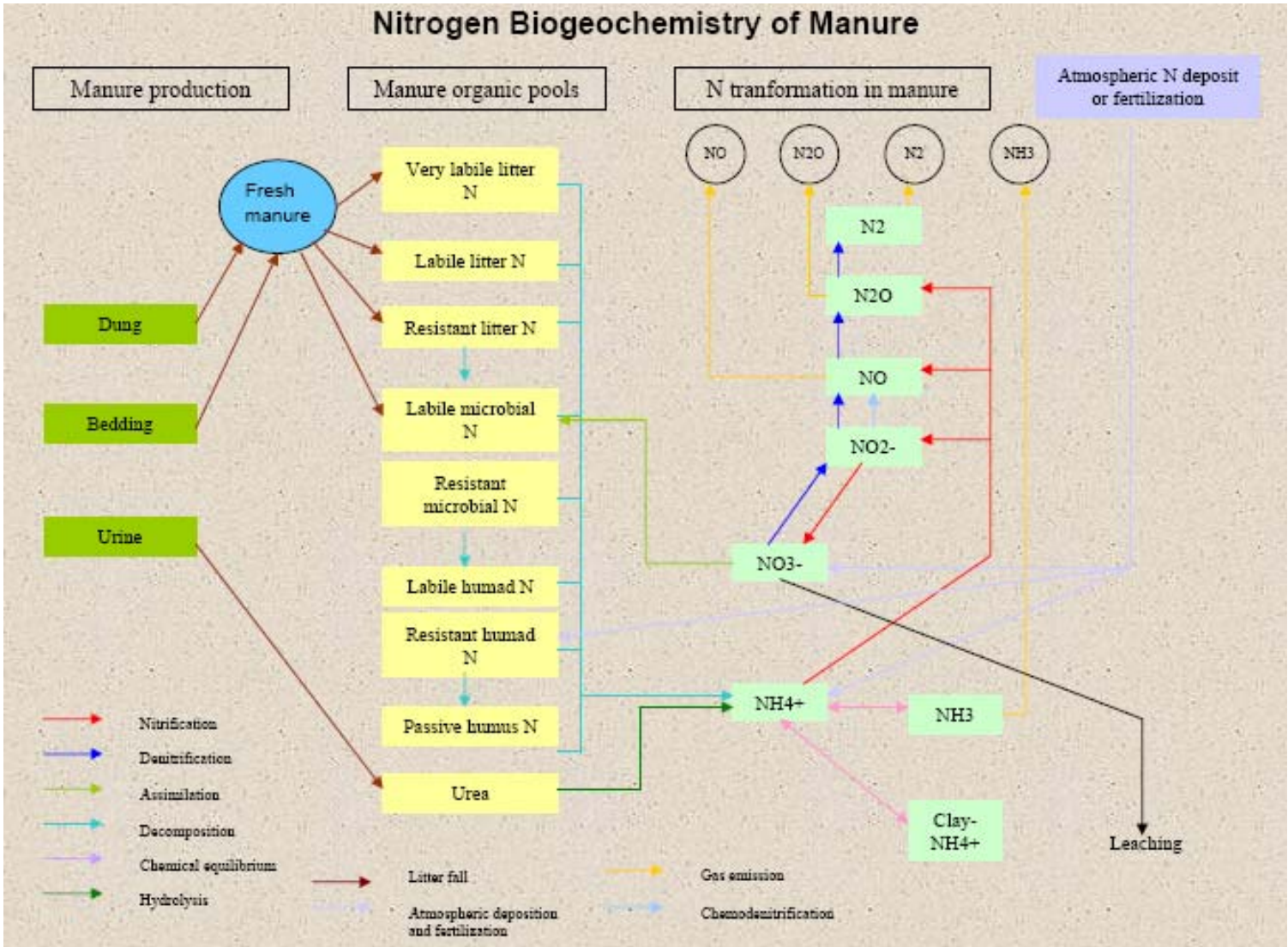
Standard setting
Air Quality Plans
Regulations

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?



Source: William Salas, CARB Dairy Symposium 2006

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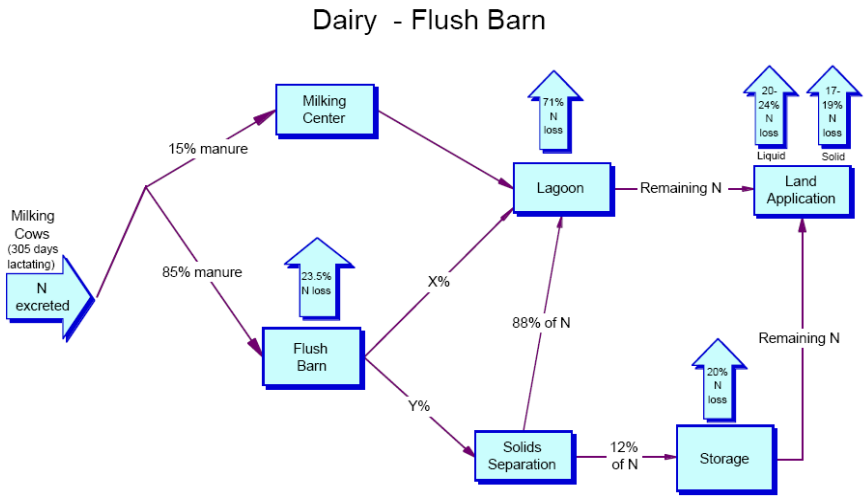
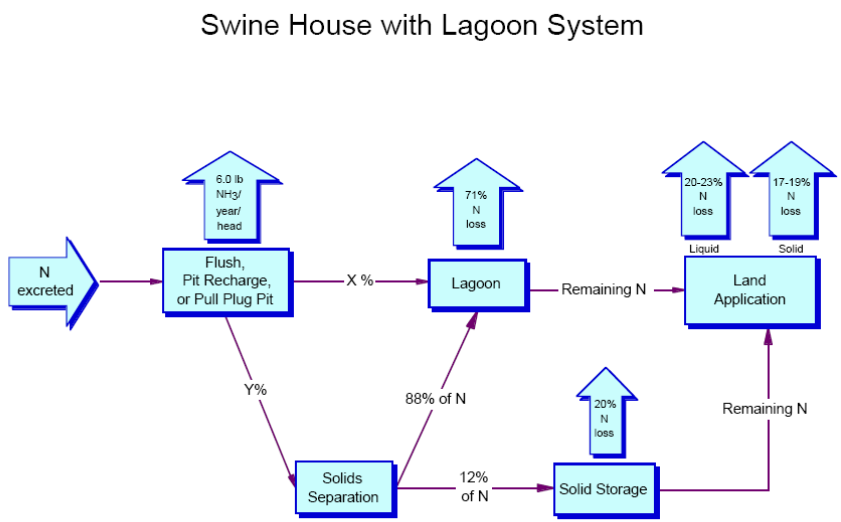
CAFO Nitrogen Sources





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

Source: EPA Ammonia NEI Report (2004)

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Fertilizer Application

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

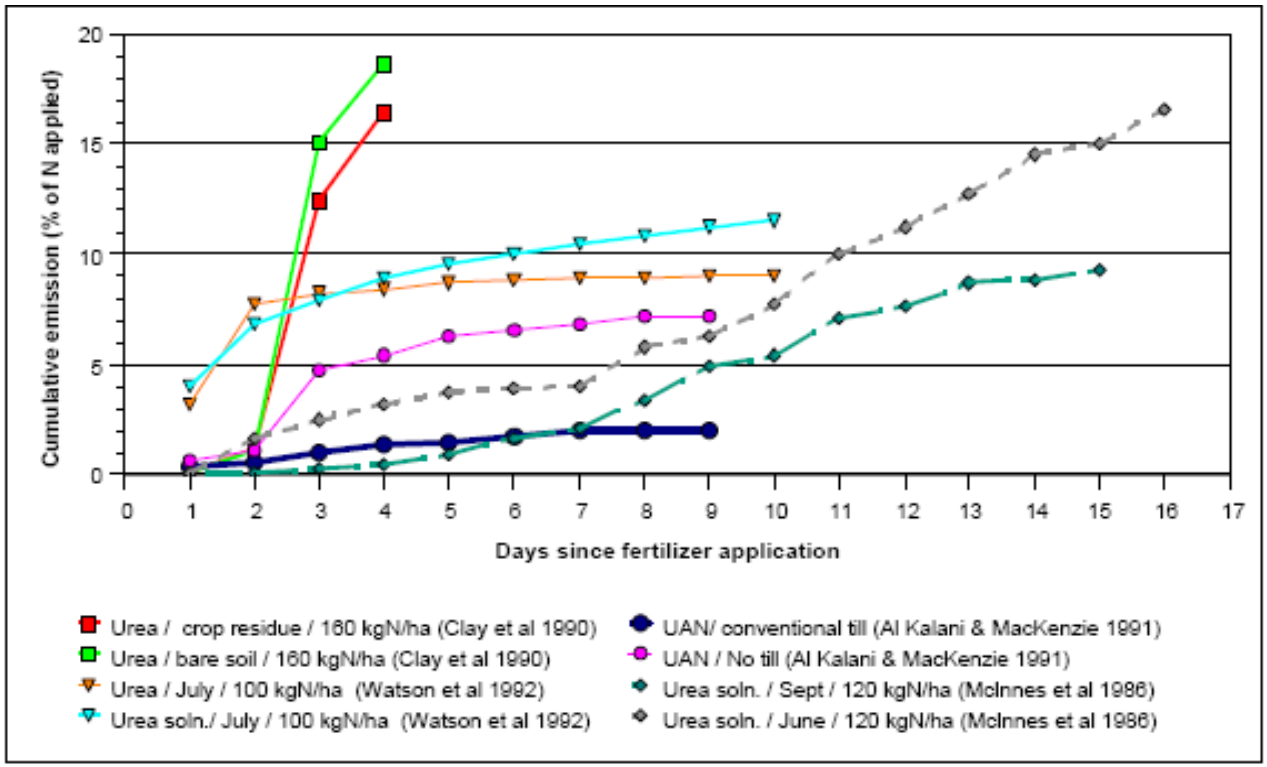

Figure 10. Cumulative NH_3 emissions after fertilizer application.

Source: Battye and Barrows (EPA 2004)

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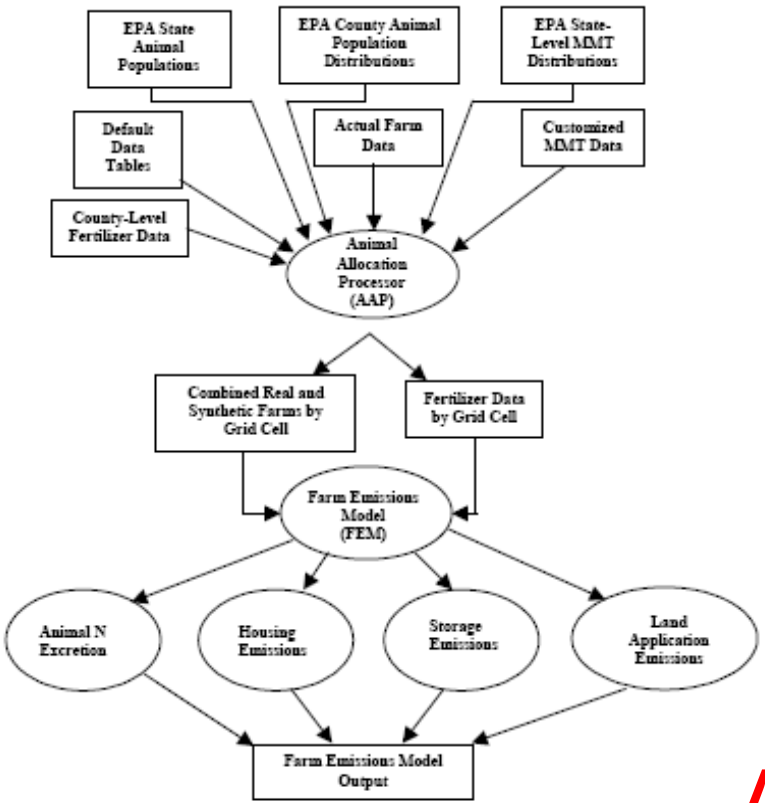
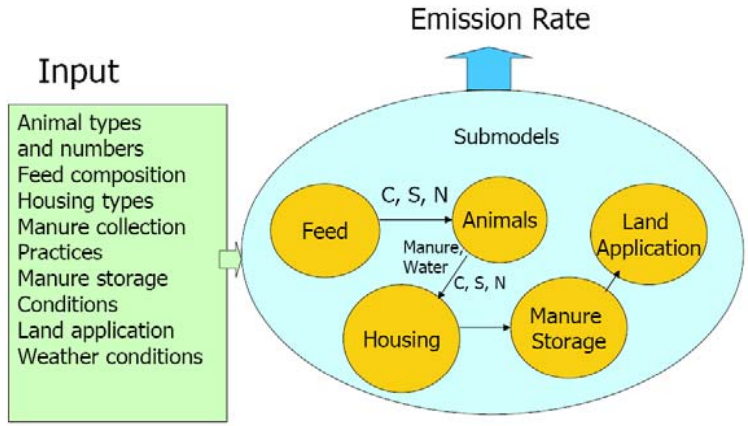
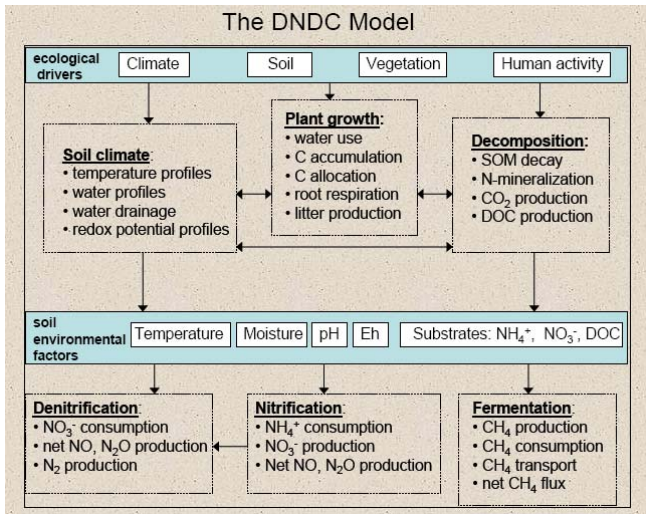
Emissions Models

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





. . . to Single Farm Emissions



And many more …

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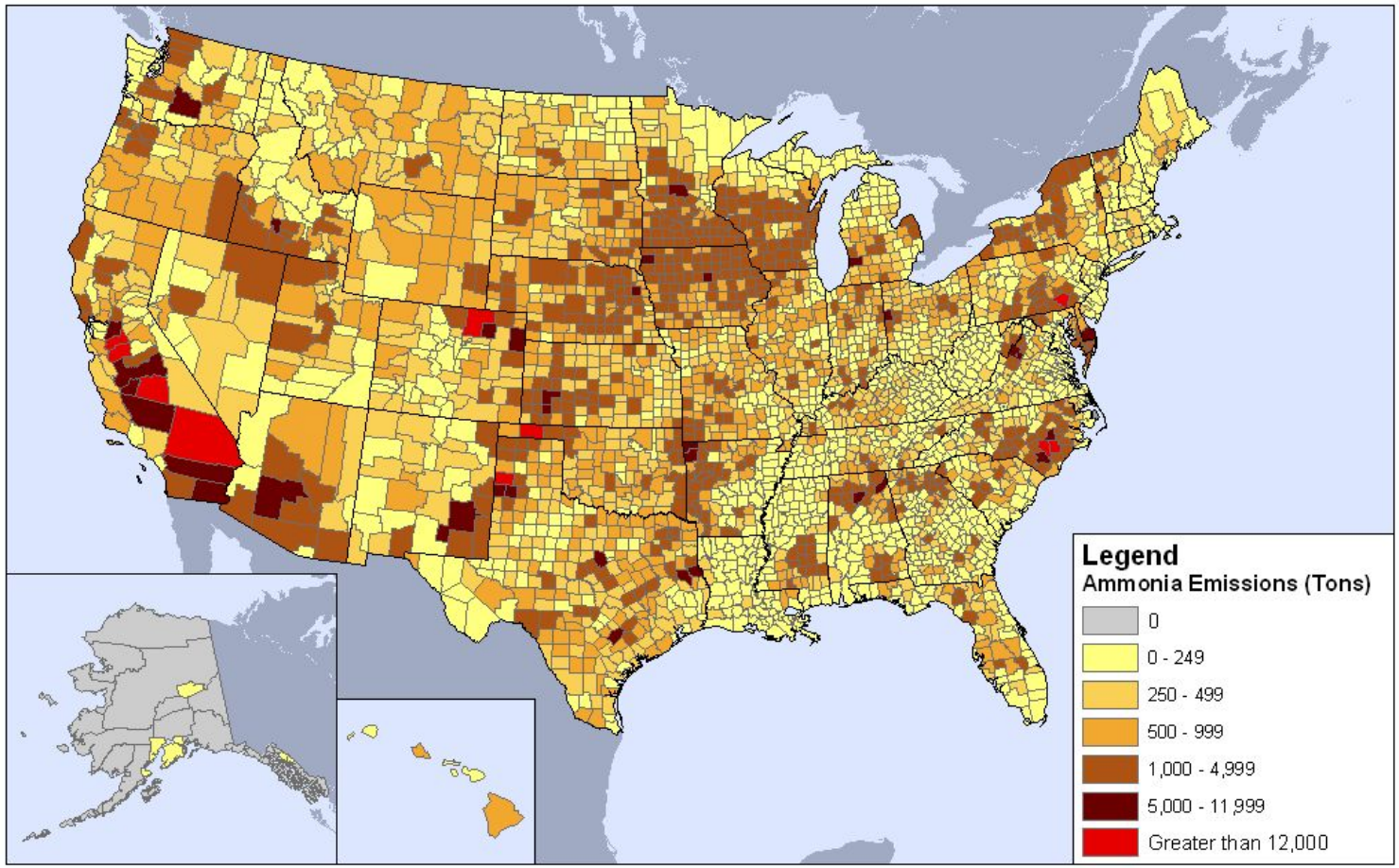
Agricultural Ammonia Emissions: An Inventory View (by County)

2002 Ammonia Emissions from Animal Agricultural Operations



Eastern Research Group, Inc.
18 April 2005

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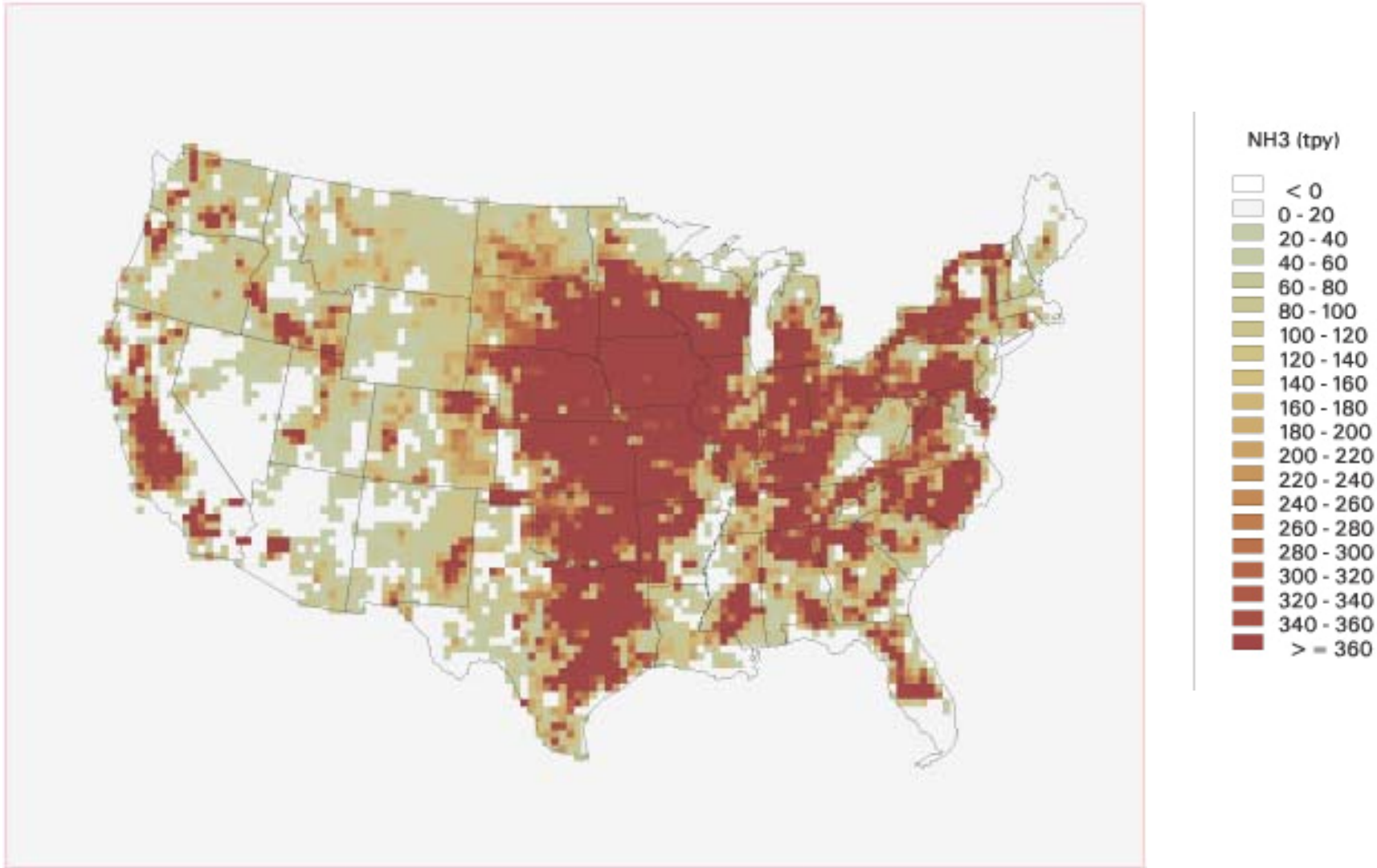
Agricultural Ammonia Emissions: A Modeling View (36-km grid)



Source: WRAP

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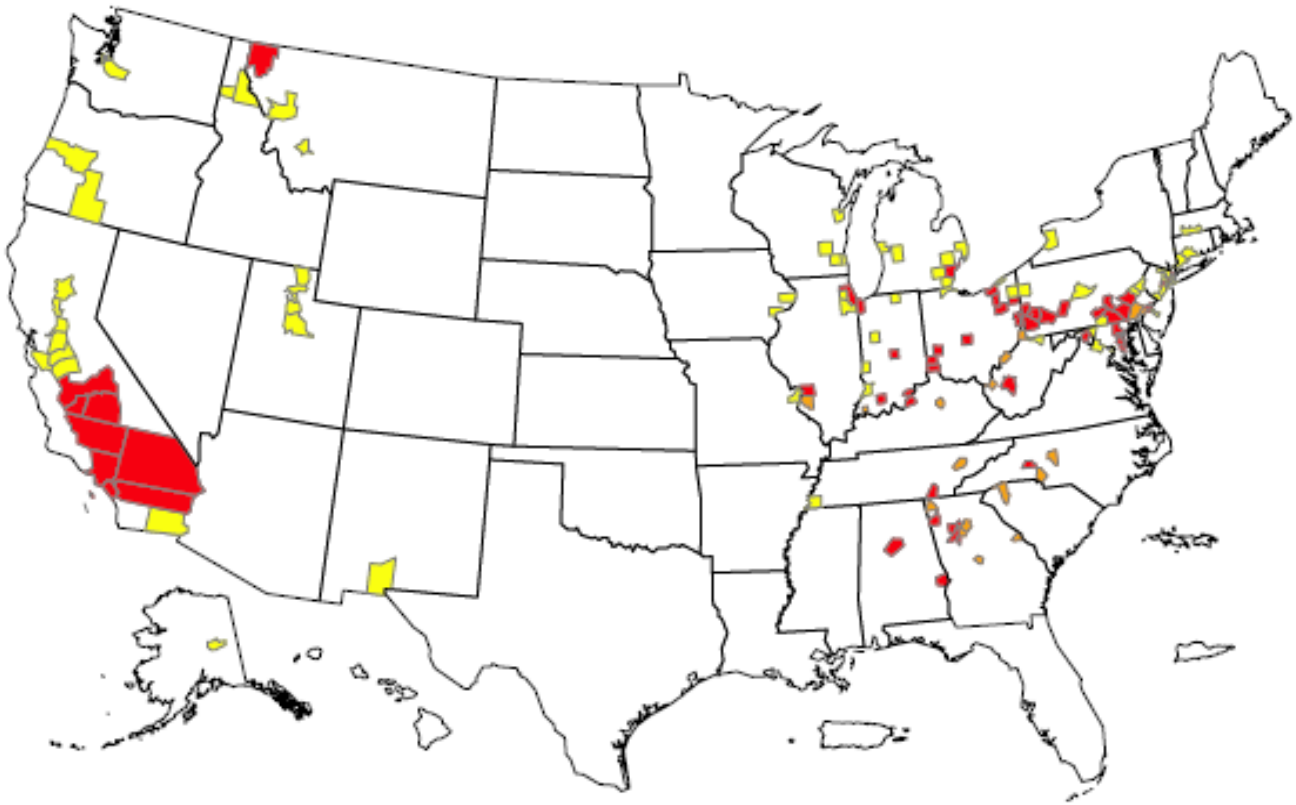
$PM_{2.5}$ Non-Attainment Areas

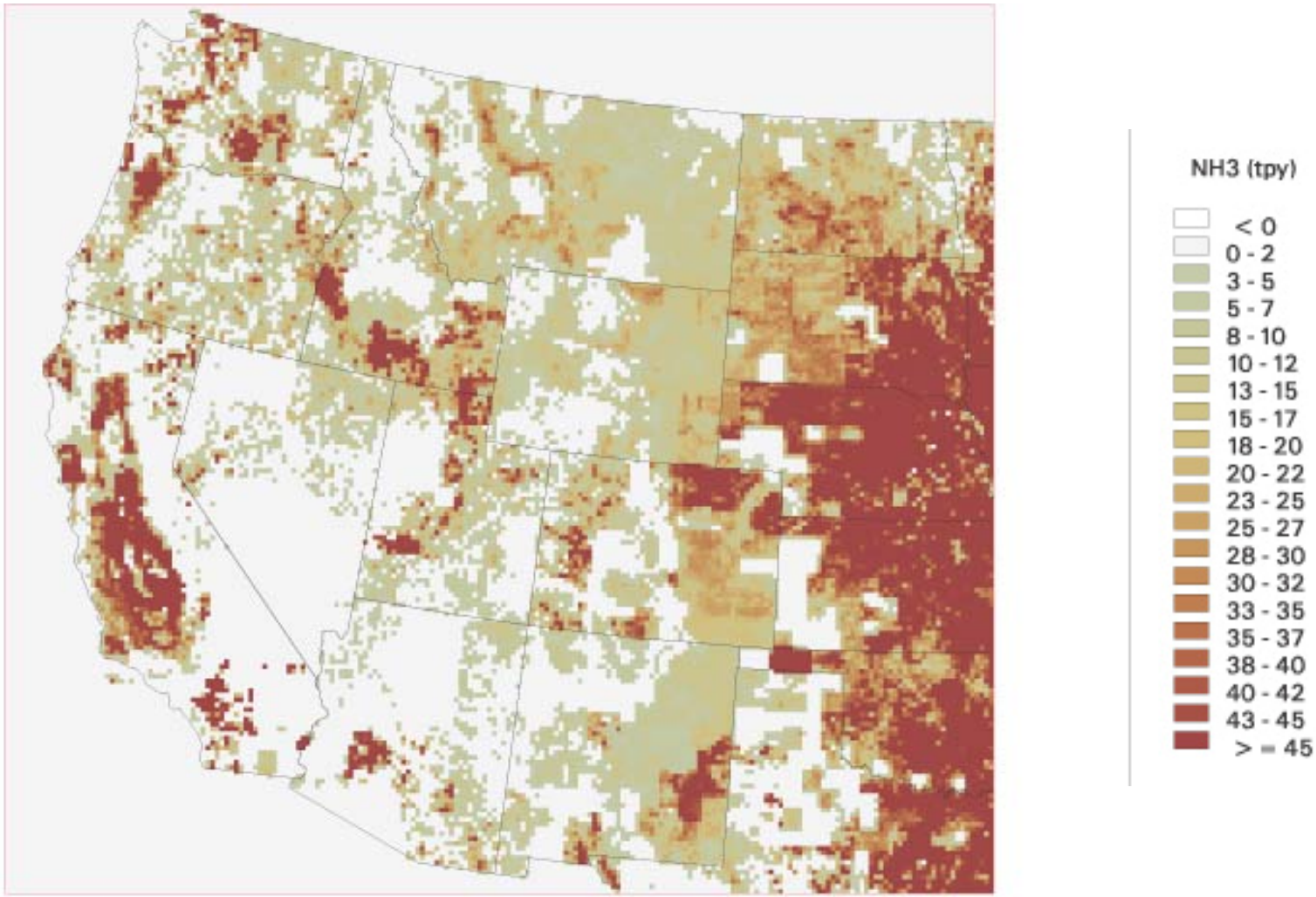
Counties Exceeding New NAAQS Levels, Based on 2003-2005 Monitoring Data



Legend	Number of Counties
County with monitor exceeding:	
both annual and 24-hour PM2.5 standards	55
ONLY the 24-hour PM2.5 standard	69
ONLY the annual PM2.5 standard	17
Total Counties Exceeding	141

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

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



Source: WRAP

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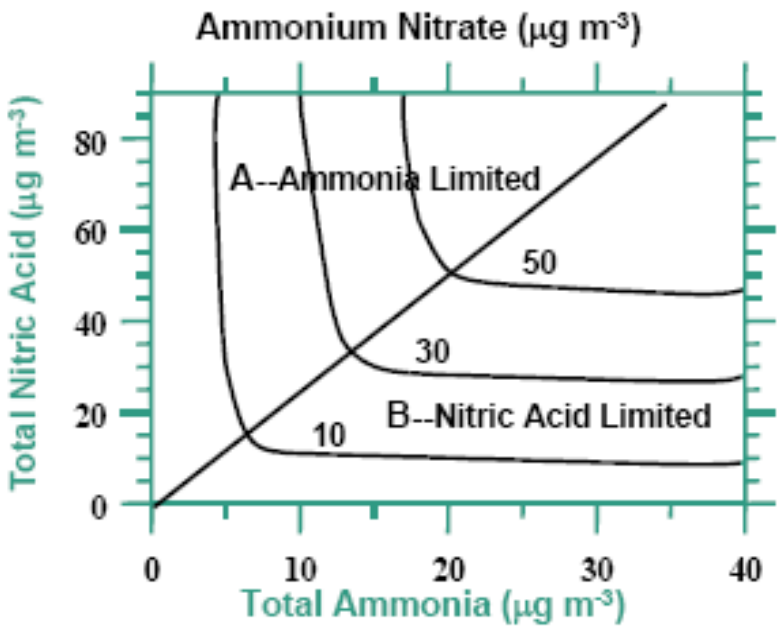
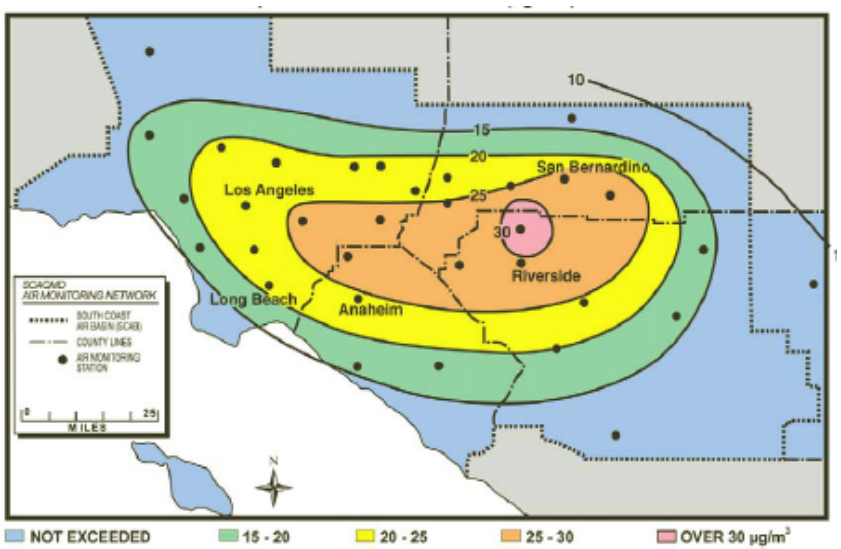
Ammonia as a PM Precursor

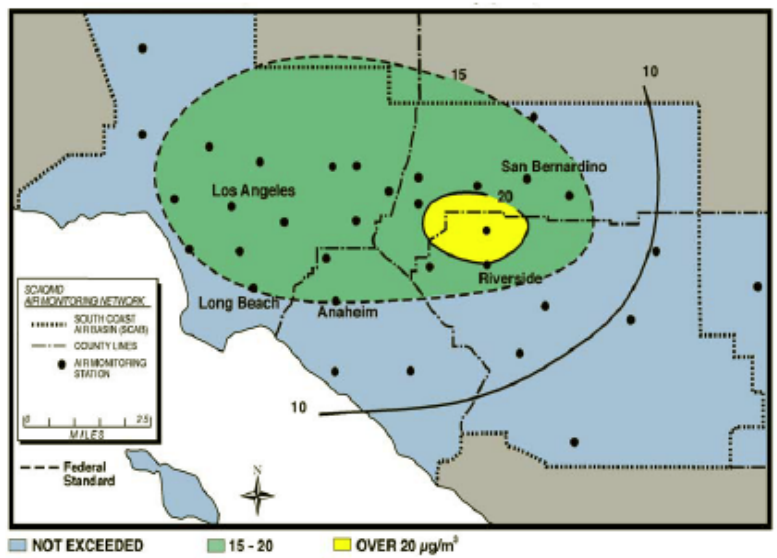
- A necessary, but not sufficient precursor
  - Wetter conditions with limited mixing conducive to ammonium aerosol production
  - Sulfuric acid will preferentially react with any available ammonia first
  - ammonium nitrate will be formed if additional ammonia available and conditions are conducive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



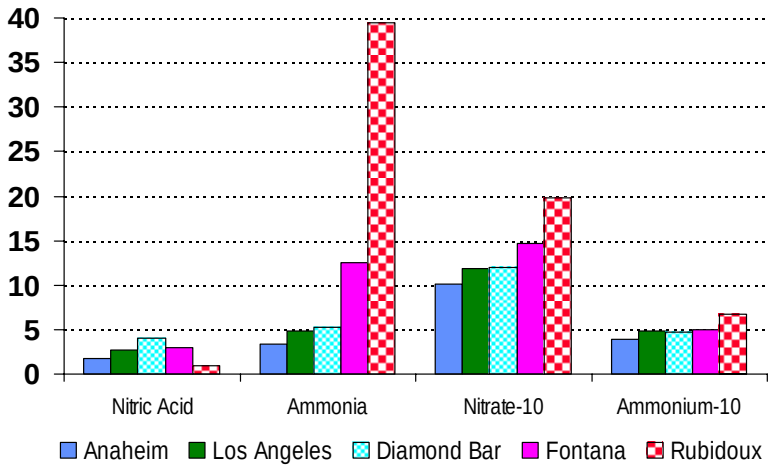
Source: After Pandis (2003)

Example: South Coast Air Basin $PM_{2.5}$

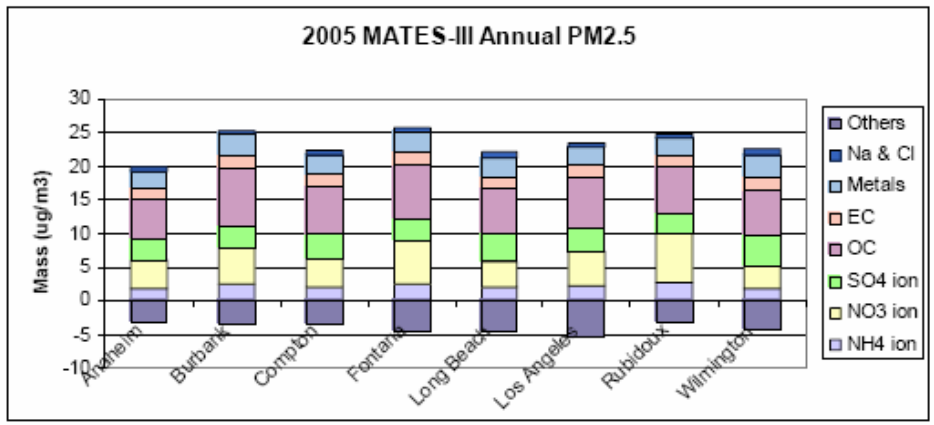




2001



2005



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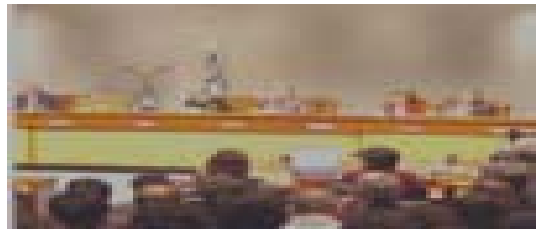
Example: San Joaquin Valley

- 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)

Summary of findings	Primary	Secondary	Effective control option
Geologic and Construction	PM10		Yes
Mobile exhaust, tire and brake wear	PM10	ROG	Yes
Vegetative burning	PM10	ROG	Yes
Organic Carbon (stationary and area)	PM10	ROG	No
Ammonium Nitrate		NOx	Yes
		Ammonia	No
Ammonium Sulfate		SOx	No
		Ammonia	No

Source: SJVAPCD 2006 PM10 Plan Public Workshop

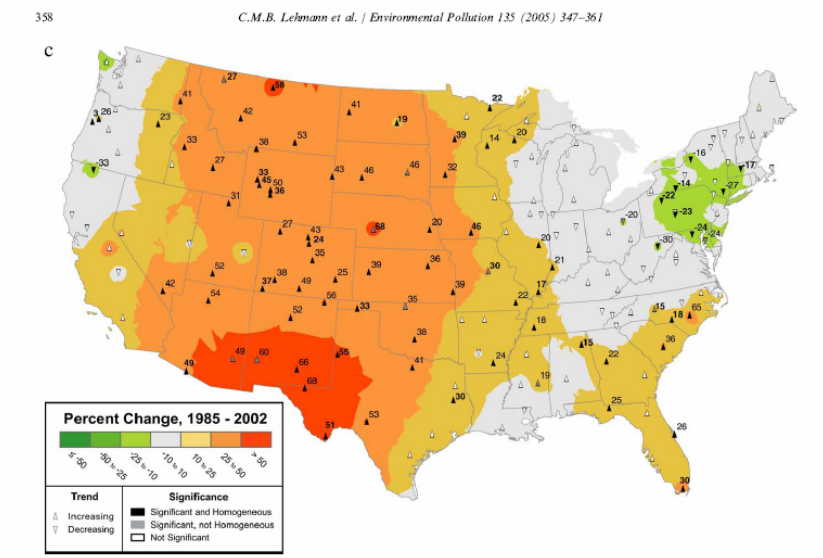
Ammonia Regulations

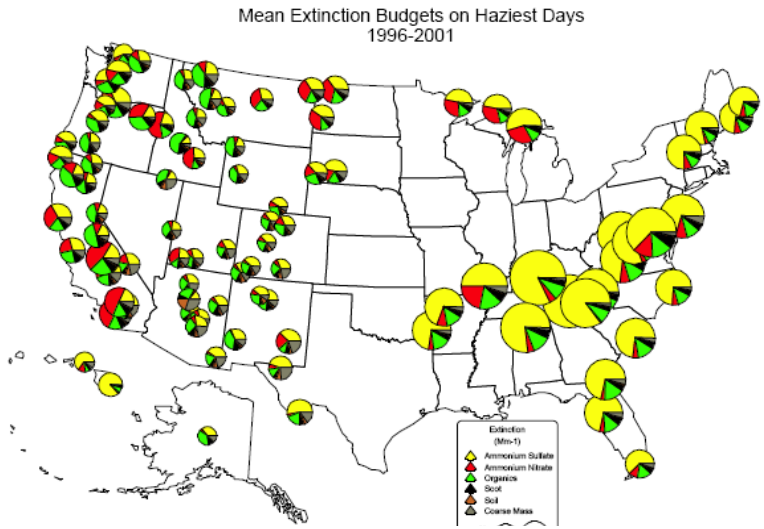


- South Coast AQMD – 1997, 2003 AQMPs
  - Rule 1133.2 (2003) for co-composting
  - Rule 1127 (2004) for dairies
  - Proposed: PAR 1127.1 (poultry, swine)
- San Joaquin Valley APCD – 2006 PM10 Plan
  - None currently or planned
- Idaho – lawsuit settlement
  - Permit by rule: dairies with > 100 tons/year 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





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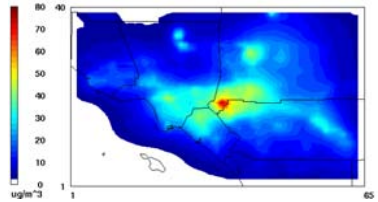
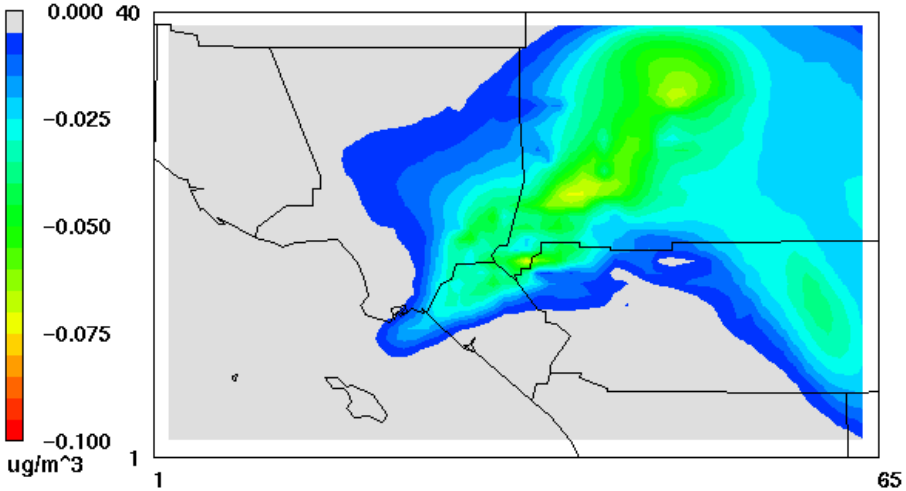
Emission Reduction Credits (ERCs)

- 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

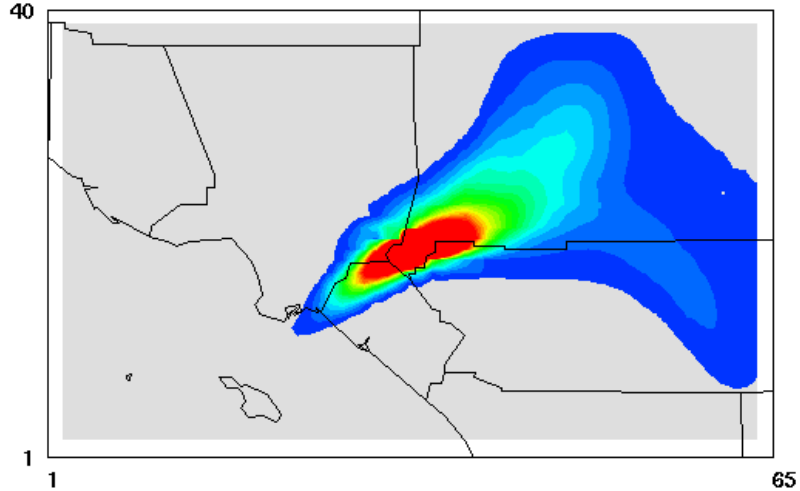
Proof of Concept -- IEUA



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



IEUA Ammonia Reduction Case



Primary PM Reduction Case

- ✓ 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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