Modelling of Atmospheric Nitrogen

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Environment Canada Environnement Canada

An Overview of this talk:

(1) What is an Air Quality Model?
  a. Overall Definition/Description
  b. Limitations
  c. Components of an Air-Quality Model
  d. Evaluation of Air-Quality Models

(2) Nitrogen in Air-Quality Models
  a. The Sources of Nitrogen Emissions
  b. Gas-Phase Smog Chemistry
  c. Inorganic Particle Chemistry
  d. Deposition of Nitrogen

(3) Air-Quality Models and Government Policy
  a. Overall Framework and Decision Making
  b. Scenario Runs – their role for policy advice
  c. Some examples from recent Air-Quality Model Applications.

What is an Air-Quality Model?

a. Overall Definition / Description:

A mathematical description

of the chemical and physical state of the atmosphere,

and of how that state is changing with time,

expressed as computer code.

What is an Air-Quality Model?

a. Overall Definition / Description:

Implications of this definition:

If …

…your theory of how the atmosphere works is “good enough”,

…your knowledge of the what’s being added to
the atmosphere is “good enough”, and

…your methods of converting the above into computer code
are “good enough”, and

,,,you have a big *and* fast enough computer to run the model, then

…you can predict the future.

What is an Air-Quality Model?

a. Overall Definition / Description:

Implications of the implication:

(a) An air-quality model can be used to ***forecast*** air pollution.

e.g. is there going to be bad pollution day tomorrow?

(b) An air-quality model can be used to ***predict what will happen*** if we change the amount or type of stuff we add to the atmosphere.

e.g. 1 Based on current emitting activities and predictions of future activities, will air pollution be better or worse in 2015?

e.g. 2: If a policy is put in place to control emissions, how effective will this policy be?

What is an Air-Quality Model?

b. Limitations:

Reality Check: How good ARE the theory, knowledge, methods, used to do air-quality modelling?

Short Answer:

"Good enough" that simulations from air-quality models have become a key ingredient in the scientific basis for the setting of government air-pollution policy,

BUT

Not *so* good that they are the *only* ingredient in setting that policy.

What is an Air-Quality Model?

b. Limitations:

<u>Reality Check:</u> How good ARE the theory, knowledge, methods, used to do air-quality modelling?

Longer Answer:

Each component of an air-quality model must be evaluated using laboratory observations, or using simple problems where the solution is already known.

The entire model must be evaluated using observations taken in the real atmosphere, for the location(s) where the model is being used.

→ This allows us to <u>quantitatively</u> state the model’s accuracy.

What is an Air-Quality Model?

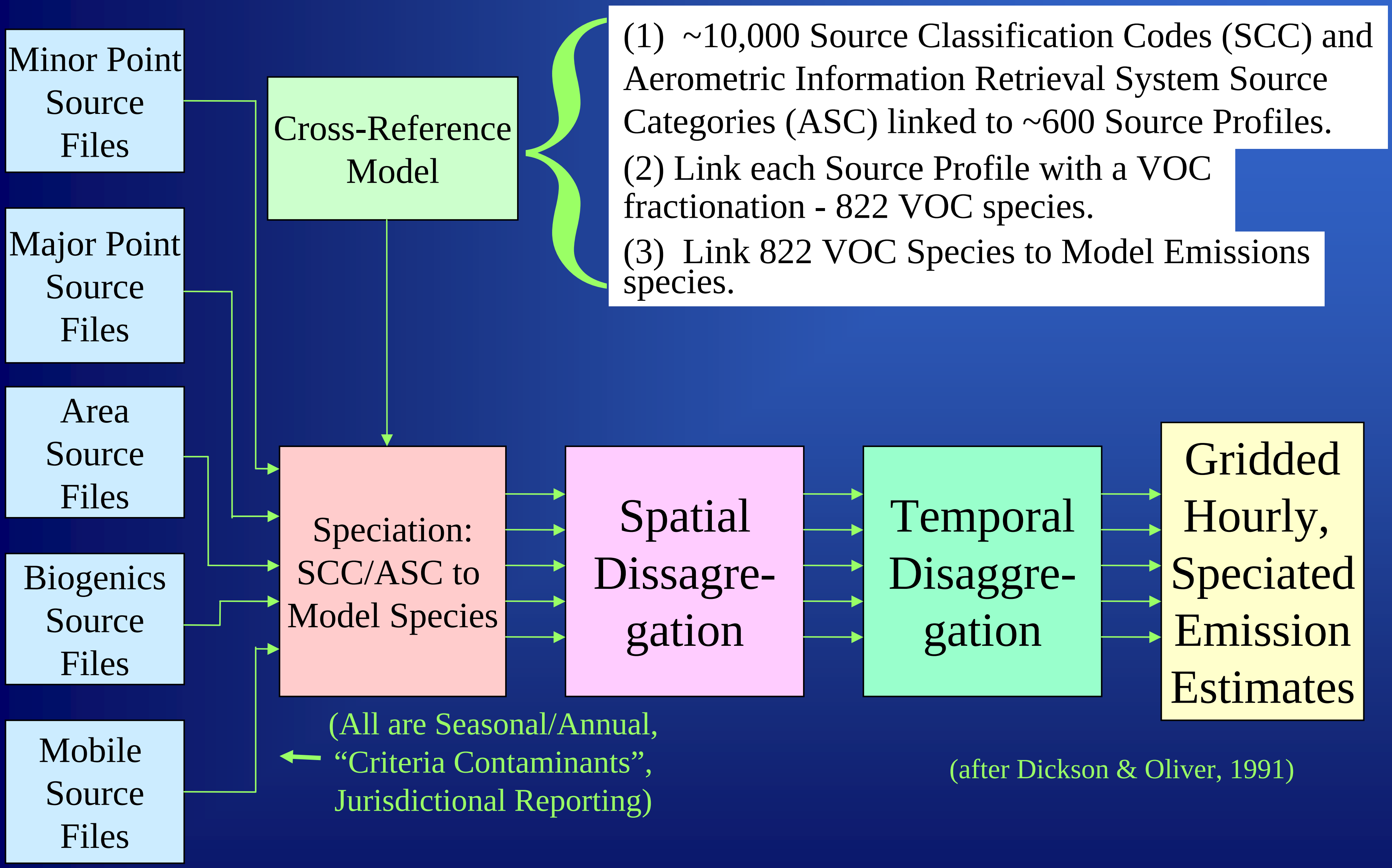
c. Components of a (comprehensive, “unified atmosphere”) air-quality model:

Emissions	What goes into the model
Advection	How winds transport stuff
Diffusion	How turbulence transports stuff
Gas-Phase Chemistry	Reactions between gases
Particle Chemistry	Reactions forming or within particles
Aqueous Chemistry	Reactions and transport within clouds
Particle Microphysics	Particle creation and interaction
Deposition	Removal on surfaces (plants, buildings, etc.)

There are different ways of doing these processes!

Some Examples:

Emissions: A Typical Emissions Processing System



Minor Point Source Files

Major Point Source Files

Area Source Files

Biogenics Source Files

Mobile Source Files

Cross-Reference Model

(1) ~10,000 Source Classification Codes (SCC) and Aerometric Information Retrieval System Source Categories (ASC) linked to ~600 Source Profiles.

(2) Link each Source Profile with a VOC fractionation - 822 VOC species.

(3) Link 822 VOC Species to Model Emissions species.

Speciation: SCC/ASC to Model Species

Spatial Dissagregation

Temporal Disaggregation

Gridded Hourly, Speciated Emission Estimates

(All are Seasonal/Annual, "Criteria Contaminants", Jurisdictional Reporting)

(after Dickson & Oliver, 1991)

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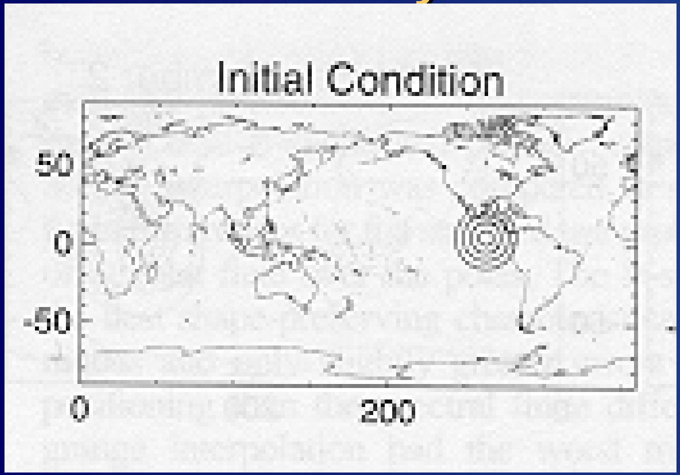
Emissions:

Most of the emissions are treated as “area sources”; the mass of each chemical being emitted within each square of a model grid is added up, and is assumed to be uniformly released into the bottom of the model atmosphere within that grid-square. Usually a boundary condition on diffusion.

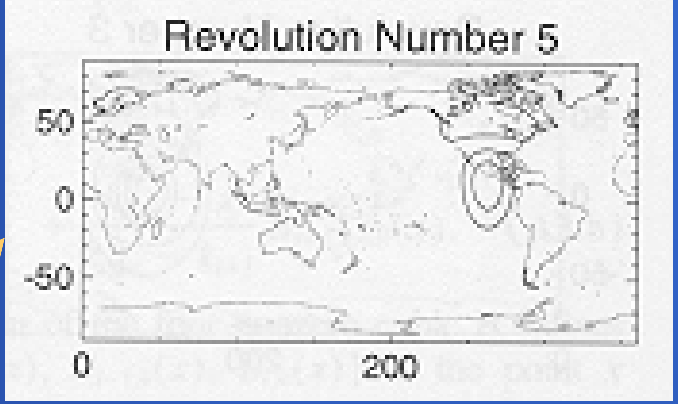
For large single sources (big stacks), the plume will be distributed vertically upon emission, according to formulae that make use of the temperature of the emissions, the temperature of the air, the stability of the atmosphere, etc.

Advection: the transport of pollutants by winds

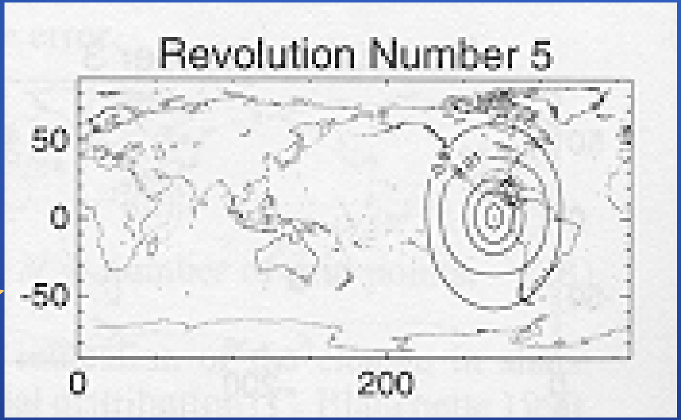
Start off with an initial “bulls-eye”


Initial Condition

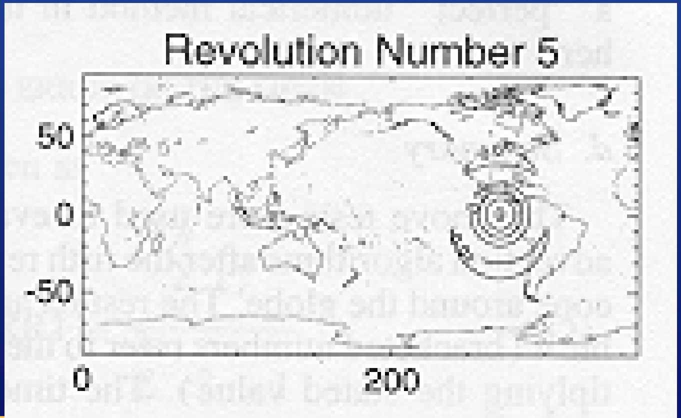
Spectral Leapfrog Finite Difference


Revolution Number 5

Semi-Lagrangian w. cubic Lagrange interpolation


Revolution Number 5

Semi-Lagrangian w. cubic Spline interpolation


Revolution Number 5

Create a pure rotational wind field and blow the bulls-eye around the earth 5 times.
Should look the same as at the start…

Vertical diffusion: mixing of pollutants due to atmospheric turbulence.

Most AQ models use some variation of K-theory:

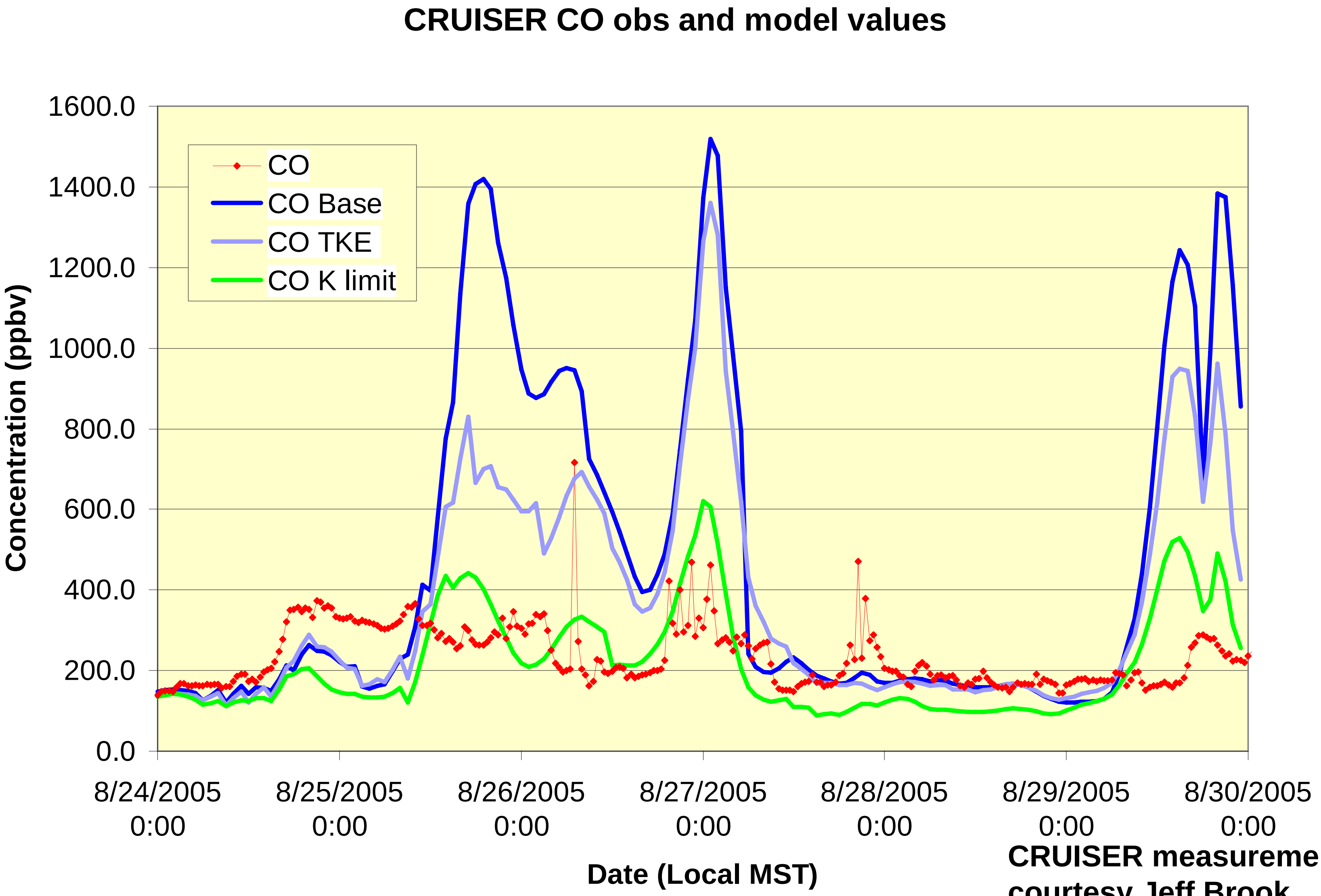
“The change in concentration over time due to turbulence
Equals the change with height of the product of
constant and the change in concentration with height.”

… the constant (K) is a function of
atmospheric stability, TKE theory, etc.

K is provided by the meteorological model, though some AQ models recalculate it. AURAMS’ K’s come from the GEM weather forecast model.

→The details of how K is calculated have a VERY big impact on AQ model accuracy (more so than a met model). Some examples…

Three different methods of doing diffusion (blue, purple and green lines, vs measurements (red).



CRUISER measurements courtesy Jeff Brook

Gas-Phase Chemistry:

Two parts to this in an air-quality model:

(1) A Reaction Mechanism

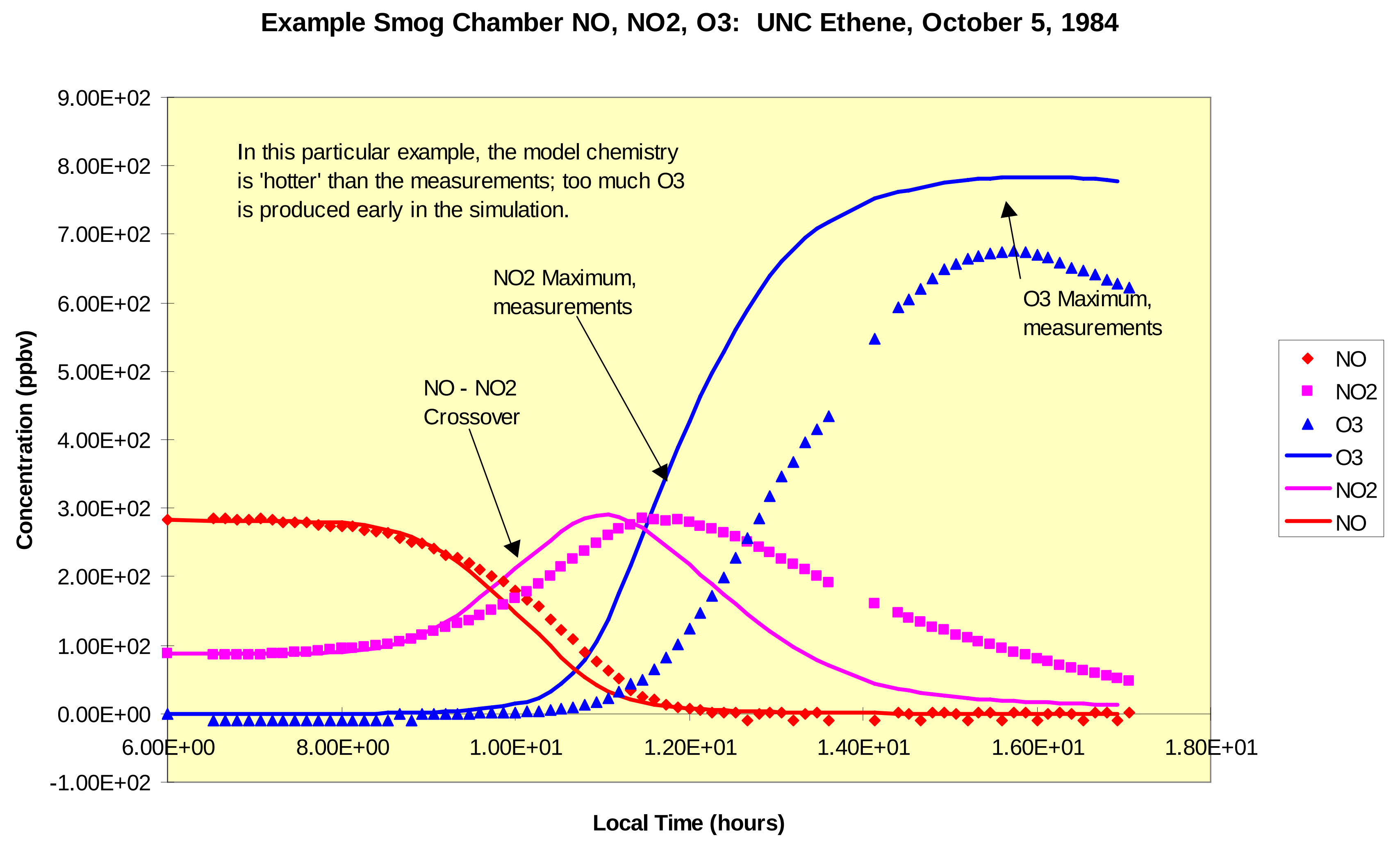
(2) A Numerical Integration Method

The reaction mechanism describes the temperature, light and pressure dependant reactions between gases.

The numerical integration method uses this information and a set of starting concentrations to predict future concentrations of the gases in the mechanism.

Due to the large number of hydrocarbon compounds in the atmosphere, there are a LOT of possible reactions, so the mechanisms in models must be simplified → different methods For doing this, so different reaction mechanisms have been Developed. All must be tested against laboratory experiments.

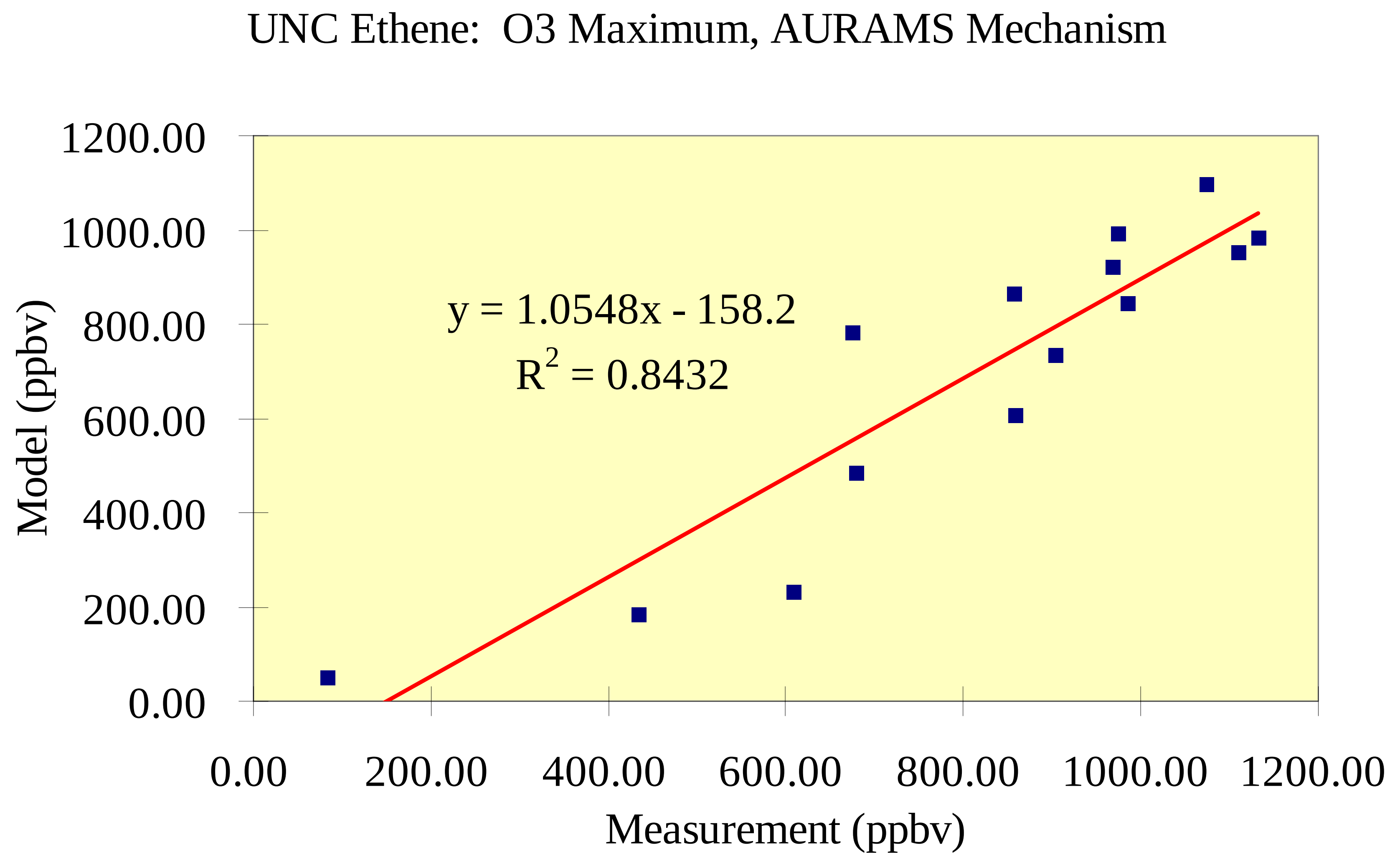
Comparisons to individual experiments: a check on mechanism's ability to follow time-trends, etc.



Example Smog Chamber NO, NO2, O3: UNC Ethene, October 5, 1984

In this particular example, the model chemistry is 'hotter' than the measurements; too much O3 is produced early in the simulation.

Statistical comparisons: how well does the mechanism predict the maximum ozone concentration, for several experiments?



Particle Chemistry: Organic and Inorganic Reactions

Organic: Organic gases react, some of the products of the reactions may be liquids or solids at atmospheric temperatures. These products can coat existing particles.

The reactions may continue once the initial coating has been formed.

Organic particle formation is still “poorly understood”; many of the theories currently used in air-quality models tend to predict organic particle concentrations that are lower than measurements.

Particle Chemistry: Organic and Inorganic Reactions

Inorganic: some kinds of particles will be composed of very high concentration acid and base solutions (sufficiently high so that some components may crystallize out of the solution).

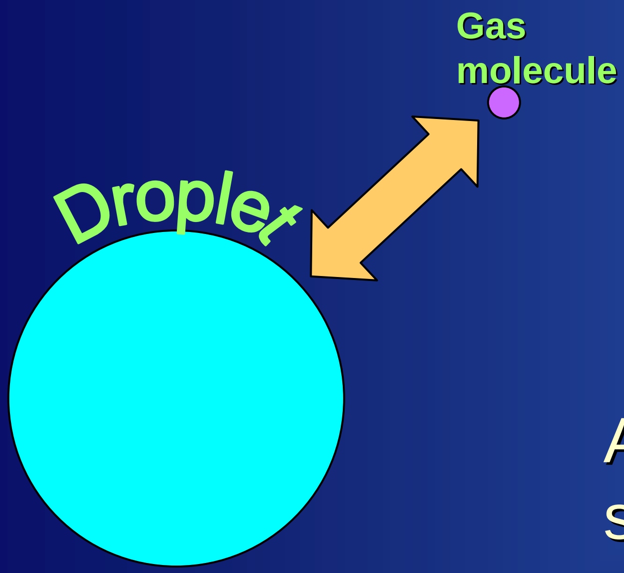
Main starting ingredients will be sulphuric acid, ammonia gas, nitric acid gas, water, and sometimes sea-salt.

Depending on the relative amounts of these, different strengths of solution will form, with differing composition.

All reactions (gas, particle and aqueous-phase) are temperature-dependant, but this dependence can be extreme for inorganic particle reactions (5 degree change in temperature = 6x change in particle mass concentration, for some components).

Aqueous Chemistry: reactions between gases and clouds (cloud droplets or rain-drops).

Much lower concentrations than particles!



A set of temperature-dependant equilibrium reactions

+

(and this is very important)

A set of catalytic reactions that convert sulphur dioxide gas to sulphuric acid

Acid Rain: if sulphur dioxide gas and rain or cloud drops are present, you get a little sulphuric acid. If you add the catalysts (ozone, hydrogen peroxide and Iron or manganese particles), you get a <u>lot</u> of sulphuric acid.

Another important cloud process: aerosol “scavenging”:

(1) Aerosol activation: within the cloud (between the droplets), the humidity is very high. Some kinds of particles will take up large amounts of water and become cloud droplets. This is another way in which pollutants can enter cloud water.

(2) Below-cloud: falling rain, snow, etc., impact particles as they fall, and some of these particles will become attached to the falling object. Falling rain, snow, etc. are one way in which pollutants are removed from the atmosphere.

Deposition: Different ways of handling this, for particles and gases.

Both make use of a "deposition velocity"; an equivalent speed at which the gas molecules or particles are travelling when they hit the ground.

For gases, the deposition velocity depends on turbulence, molecular diffusivity, the <u>type of surface on which the gas is being deposited, and the chemical interactions between the gas and the surface.</u>

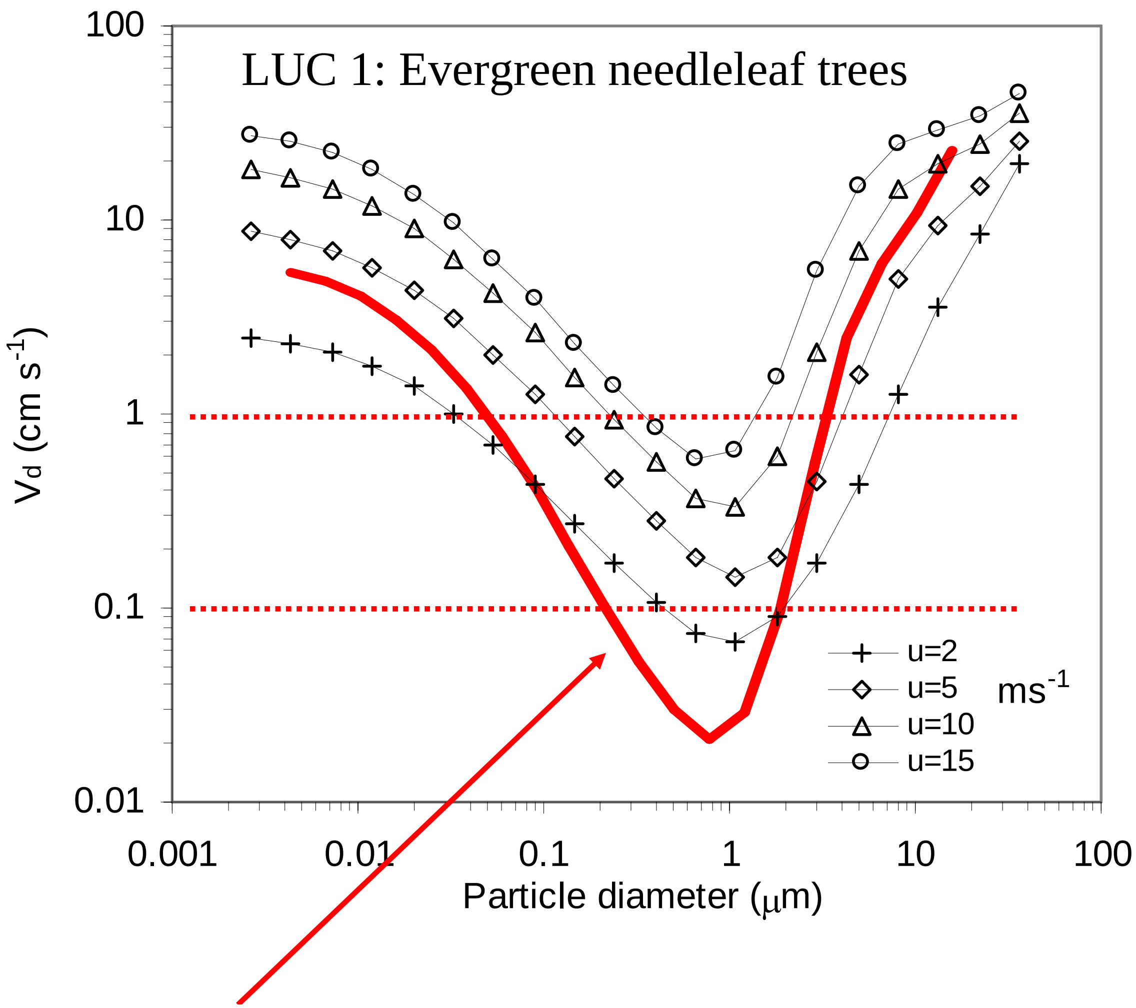
e.g. is the surface wet or dry, is the surface vegetated, what kind of vegetation, etc.

Deposition: Different ways of handling this, for particles and gases.

Both make use of a “deposition velocity”; an equivalent speed at which the gas molecules or particles are travelling when they hit the ground.

For particles, the deposition velocity depends on turbulence, The size and density of the particle, viscosity of the air, collisions between particles while falling, type of surface, etc.

Typical variation of deposition velocity with particle size and wind speed (Zhang et al, 2001):



Results from most existing models

What is an Air-Quality Model?

d. Evaluation of Air-Quality Models

Put all of the above into a set of computer codes, add in some meteorological model forecasts, and predict the air pollution over the next few days. How well did we do?

Alternately, run the model using past meteorology and emissions as a “base case” for policy-related emissions scenario runs. How well did the model perform for the base case?

d. Evaluation of Air-Quality Models

Two ways to do this:

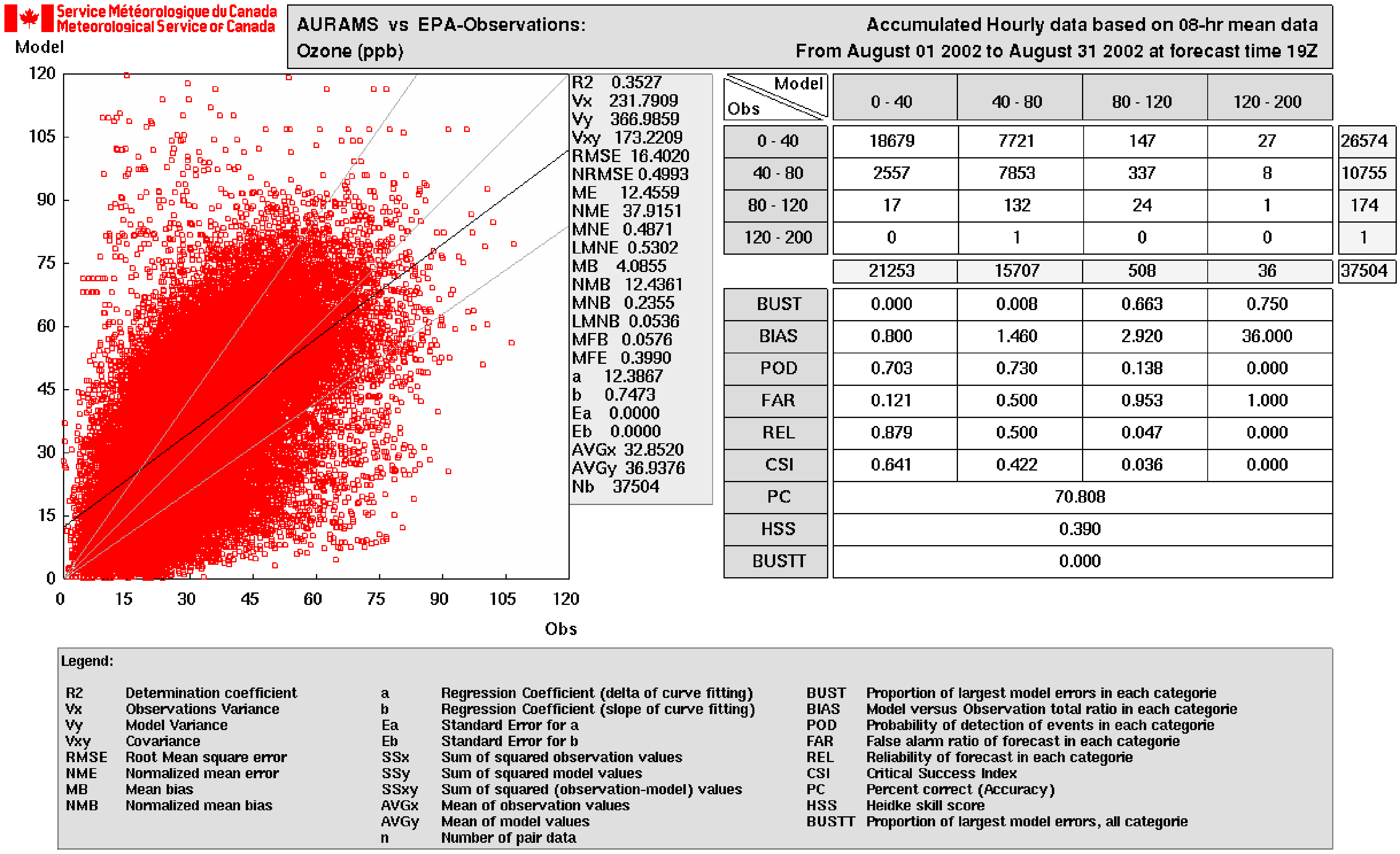
(1) Monitoring networks: 24 hour average concentrations of some chemical species, measured at stations positioned over a large area.

→Average the model results for the same locations over 24 hours, compare to observations.

Some examples: Ozone and $PM_{2.5}$ over Canada, 2002:

d. Evaluation of Air-Quality Models

August 1 to 31, 2002, Ozone



AURAMS vs EPA-Observations: Ozone (ppb)

Accumulated Hourly data based on 08-hr mean data
From August 01 2002 to August 31 2002 at forecast time 19Z

R2	0.3527
Vx	231.7909
Vy	366.9859
Vxy	173.2209
RMSE	16.4020
NRMSE	0.4993
ME	12.4559
NME	37.9151
MNE	0.4871
LMNE	0.5302
MB	4.0855
NMB	12.4361
MNB	0.2355
LMNB	0.0536
MFB	0.0576
MFE	0.3990
a	12.3867
b	0.7473
Ea	0.0000
Eb	0.0000
AVGx	32.8520
AVGy	36.9376
Nb	37504

Model / Obs	0 - 40	40 - 80	80 - 120	120 - 200	
0 - 40	18679	7721	147	27	26574
40 - 80	2557	7853	337	8	10755
80 - 120	17	132	24	1	174
120 - 200	0	1	0	0	1
	21253	15707	508	36	37504
BUST	0.000	0.008	0.663	0.750	
BIAS	0.800	1.460	2.920	36.000	
POD	0.703	0.730	0.138	0.000	
FAR	0.121	0.500	0.953	1.000	
REL	0.879	0.500	0.047	0.000	
CSI	0.641	0.422	0.036	0.000	
PC	70.808				
HSS	0.390				
BUSTT	0.000				

Legend:

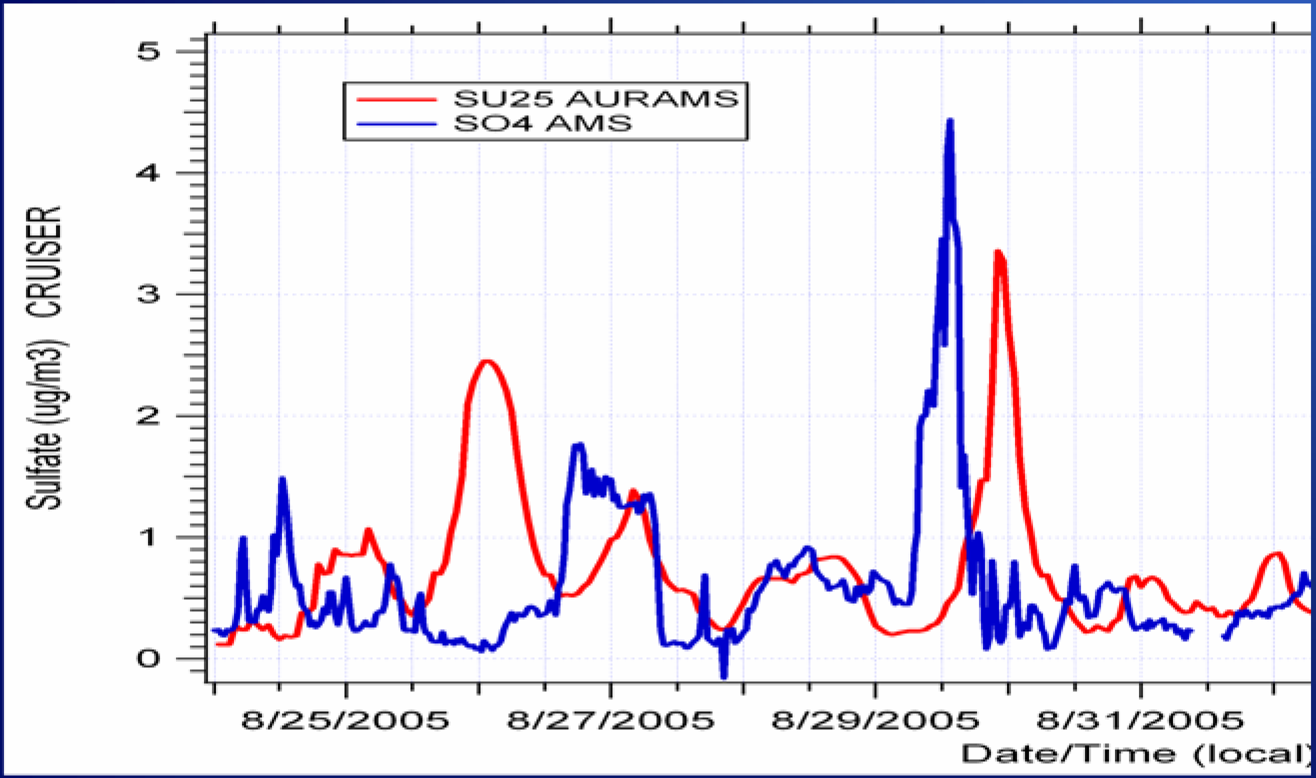
R2	Determination coefficient	a	Regression Coefficient (delta of curve fitting)	BUST	Proportion of largest model errors in each categorie
Vx	Observations Variance	b	Regression Coefficient (slope of curve fitting)	BIAS	Model versus Observation total ratio in each categorie
Vy	Model Variance	Ea	Standard Error for a	POD	Probability of detection of events in each categorie
Vxy	Covariance	Eb	Standard Error for b	FAR	False alarm ratio of forecast in each categorie
RMSE	Root Mean square error	SSx	Sum of squared observation values	REL	Reliability of forecast in each categorie
NME	Normalized mean error	SSy	Sum of squared model values	CSI	Critical Success Index
MB	Mean bias	SSxy	Sum of squared (observation-model) values	PC	Percent correct (Accuracy)
NMB	Normalized mean bias	AVGx	Mean of observation values	HSS	Heidke skill score
		AVGy	Mean of model values	BUSTT	Proportion of largest model errors, all categorie
		n	Number of pair data		

Comparison courtesy S. Cousineau,AQMAD

d. Evaluation of Air-Quality Models

The other method: measurement “intensives”.

Studies in which more detailed measurements are made over a smaller region, to understand the chemical processes that occur in that region.



e.g. PrAIRie2005 particle sulphate, 80km from Edmonton, AURAMS model vs CRUISER AMS.

CRUISER data courtesy J. Brook.

(2) Nitrogen in Air-Quality Models

a. The Sources of Nitrogen Emissions
b. Gas-Phase Smog Chemistry
c. Inorganic Particle Chemistry
d. Deposition of Nitrogen

The Sources of Nitrogen Emissions:

Three places nitrogen gets into an air-quality model:

(1) As a by-product of the high temperatures of combustion and the mixture of oxygen and nitrogen that makes up most of the atmosphere:

$$N_2(g) + O_2(g) \xrightarrow{\text{(heat)}} 2\ NO(g)$$

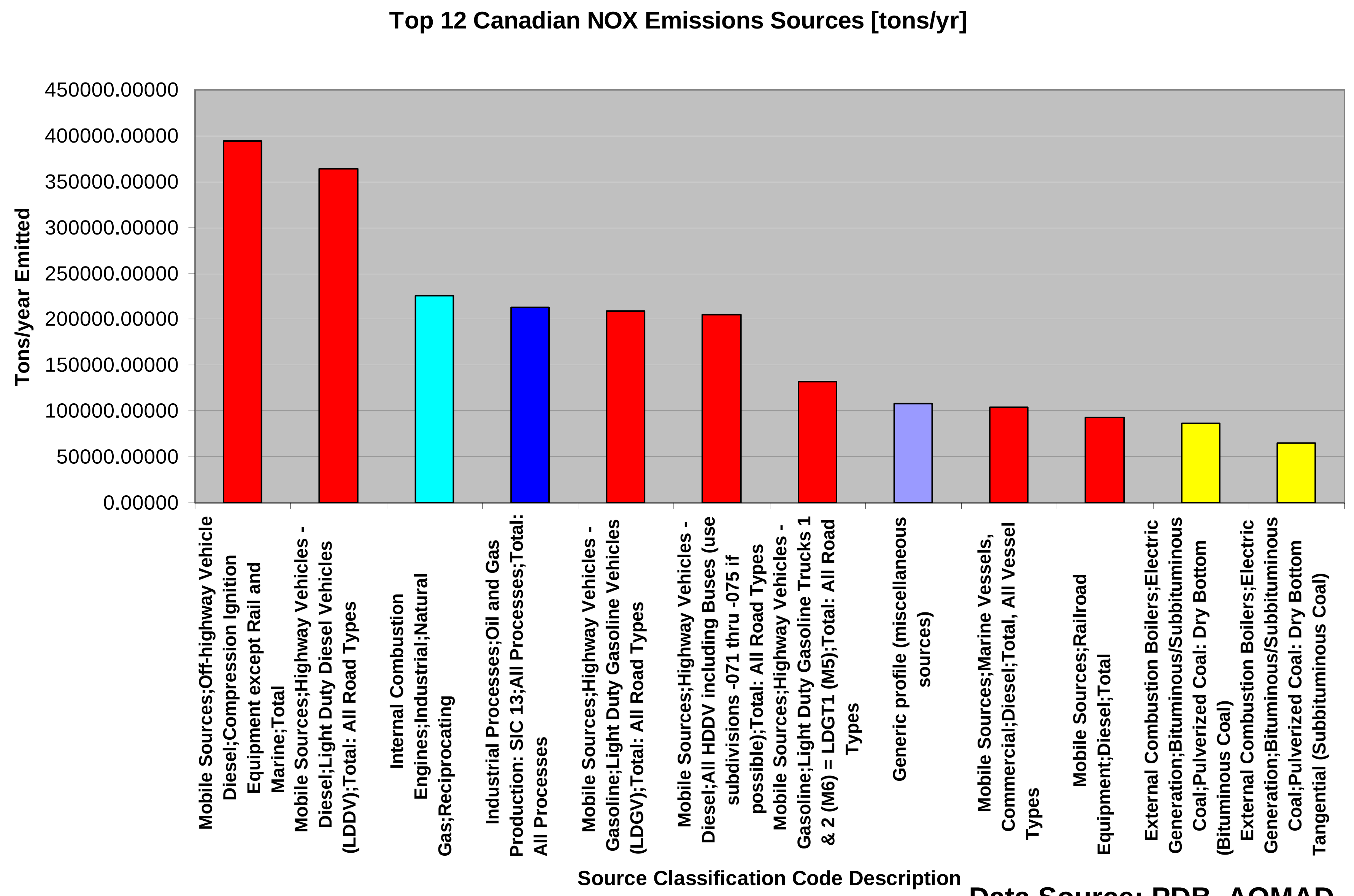
(2) From the application of fertilizers and biological processing of animal waste.

$$NH_3(g)$$

(3) As part of organic gases emitted by human activities (e.g. amides, amines, etc.)

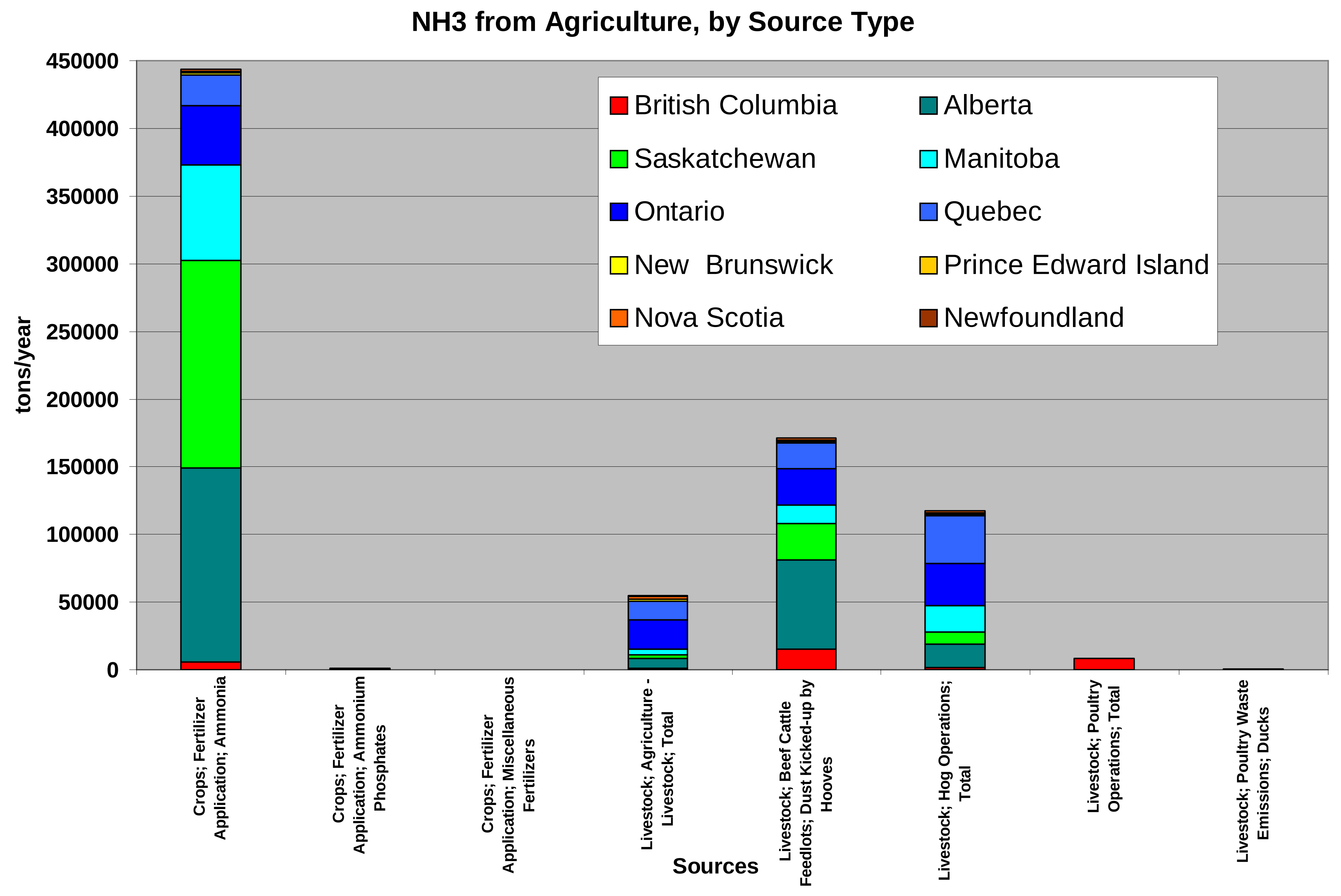
(1) Nitrogen Monoxide, NO(g):

Top sources of NOx (=NO + NO_2, mostly NO on emissions), in Canada:

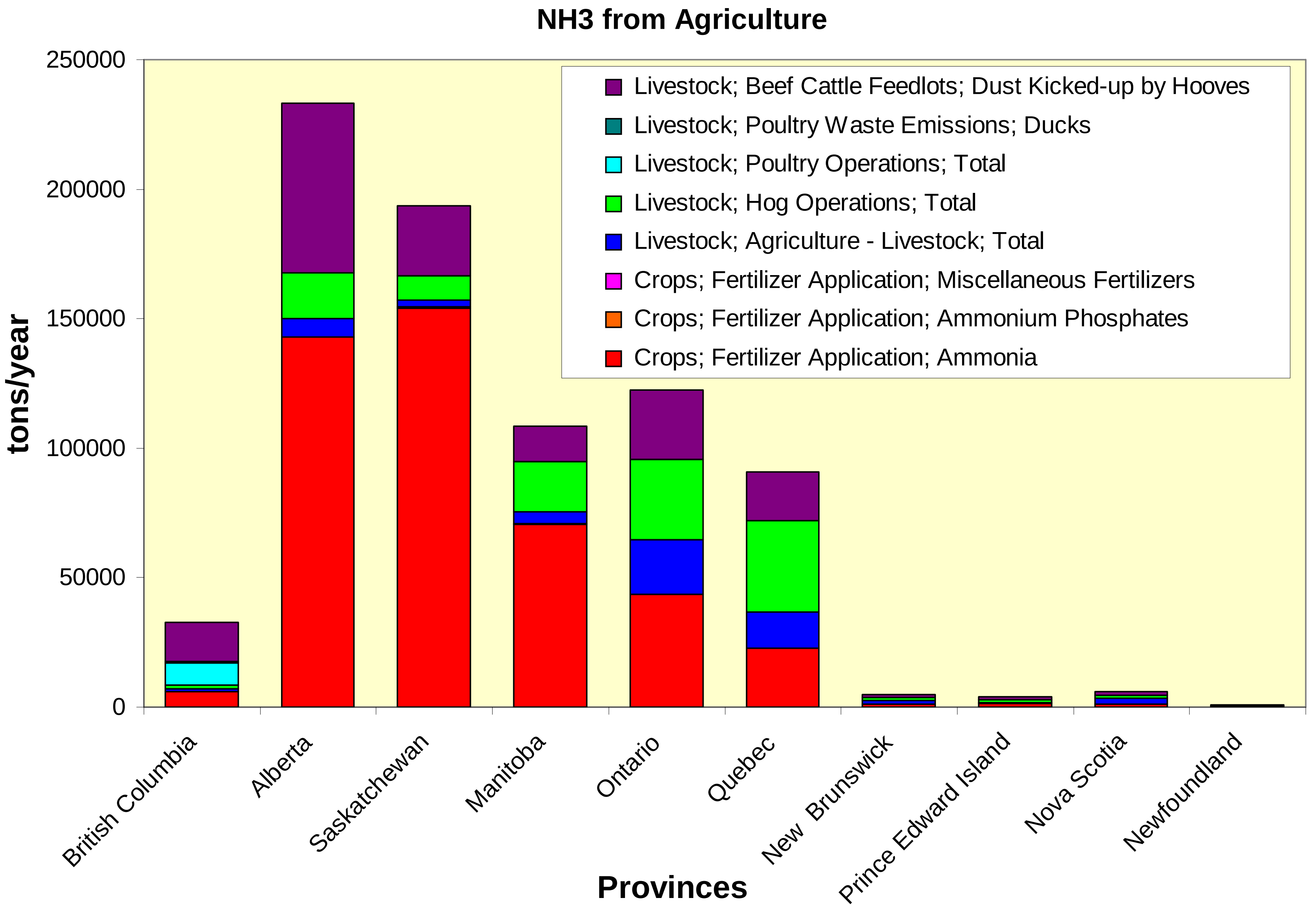


Data Source: PDB, AQMAD

(2) Ammonia Gas, NH_3:
Mostly from the agricultural sector (PDB 2000/2001 inventory):



(2) Ammonia Gas, NH_3: Arranged from West to East, by province.



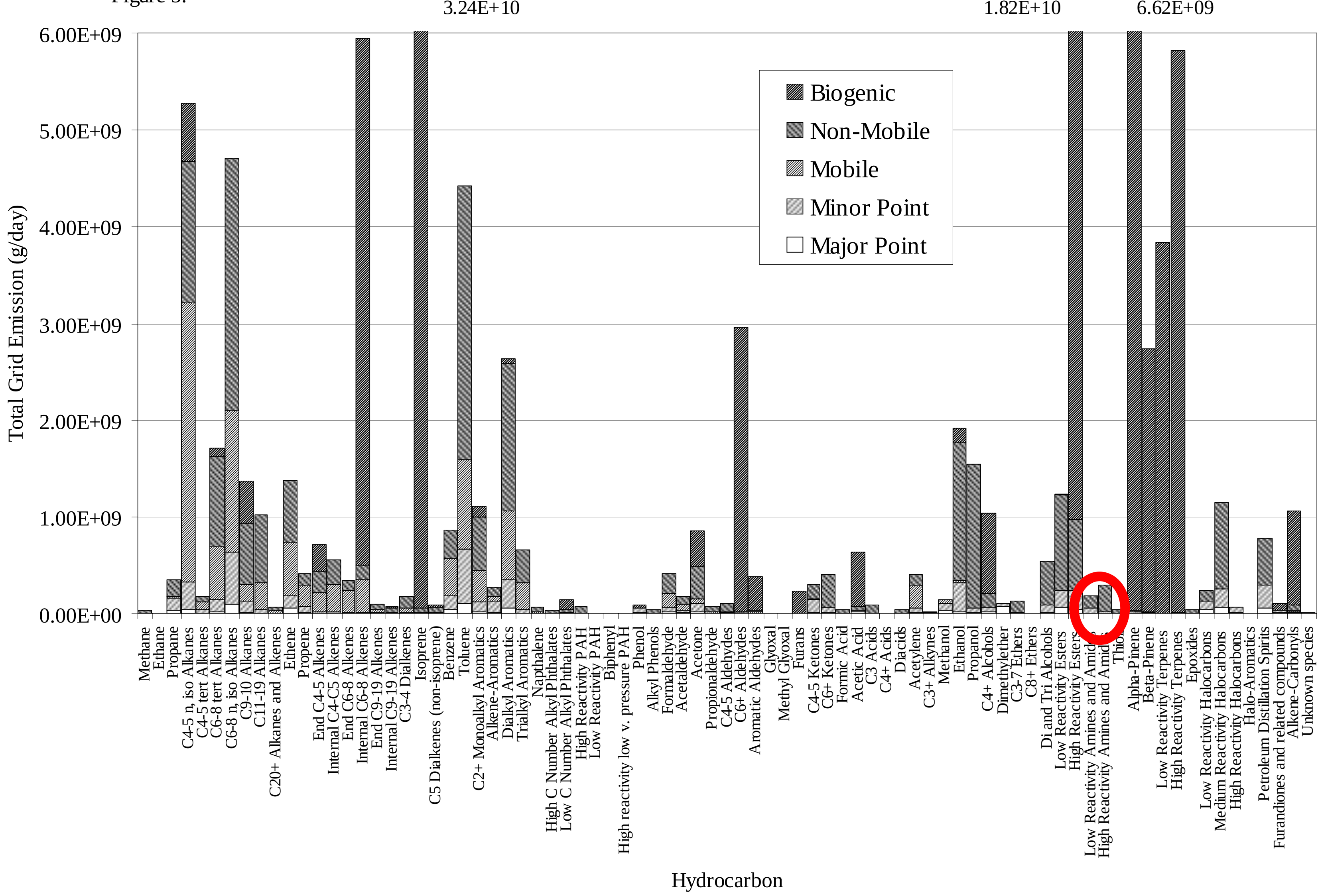
(2) Ammonia Gas, NH_3:

As a point of interest: The federal government has a major initiative underway, the National Agri-Environmental Standards Initiative (NAESI), one part of which will result in a much improved ammonia emissions database for modelling. ➔ see poster by Carrie Lillymann for details.

(3) As part of organic gases emitted by human activities (e.g. amides, amines, etc.)

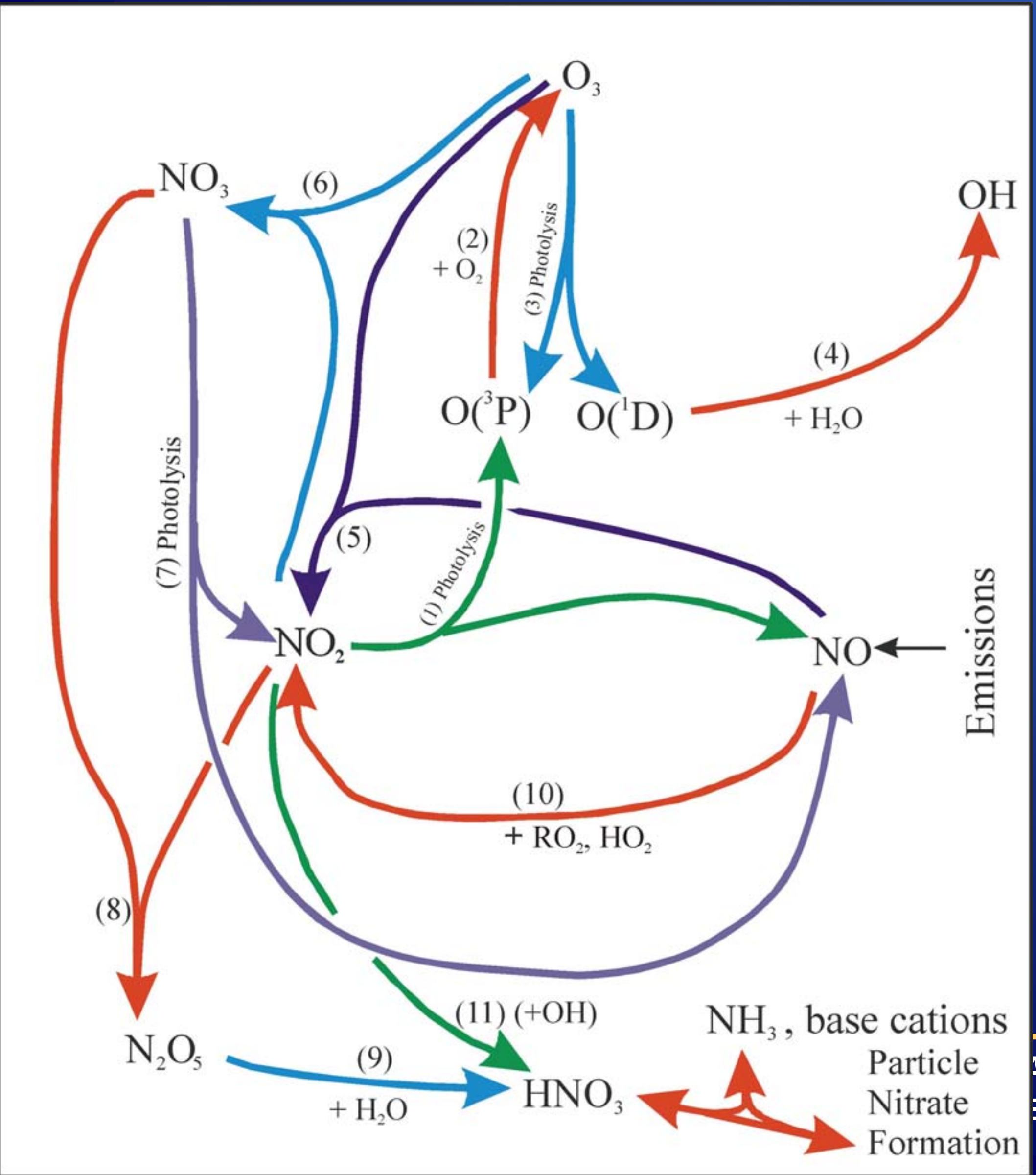
e.g. Eastern North America, 80 groups of VOCs, amines and amides circled.

Figure 5.



(2) Nitrogen in Air-Quality Models

b. Gas-Phase Smog Chemistry

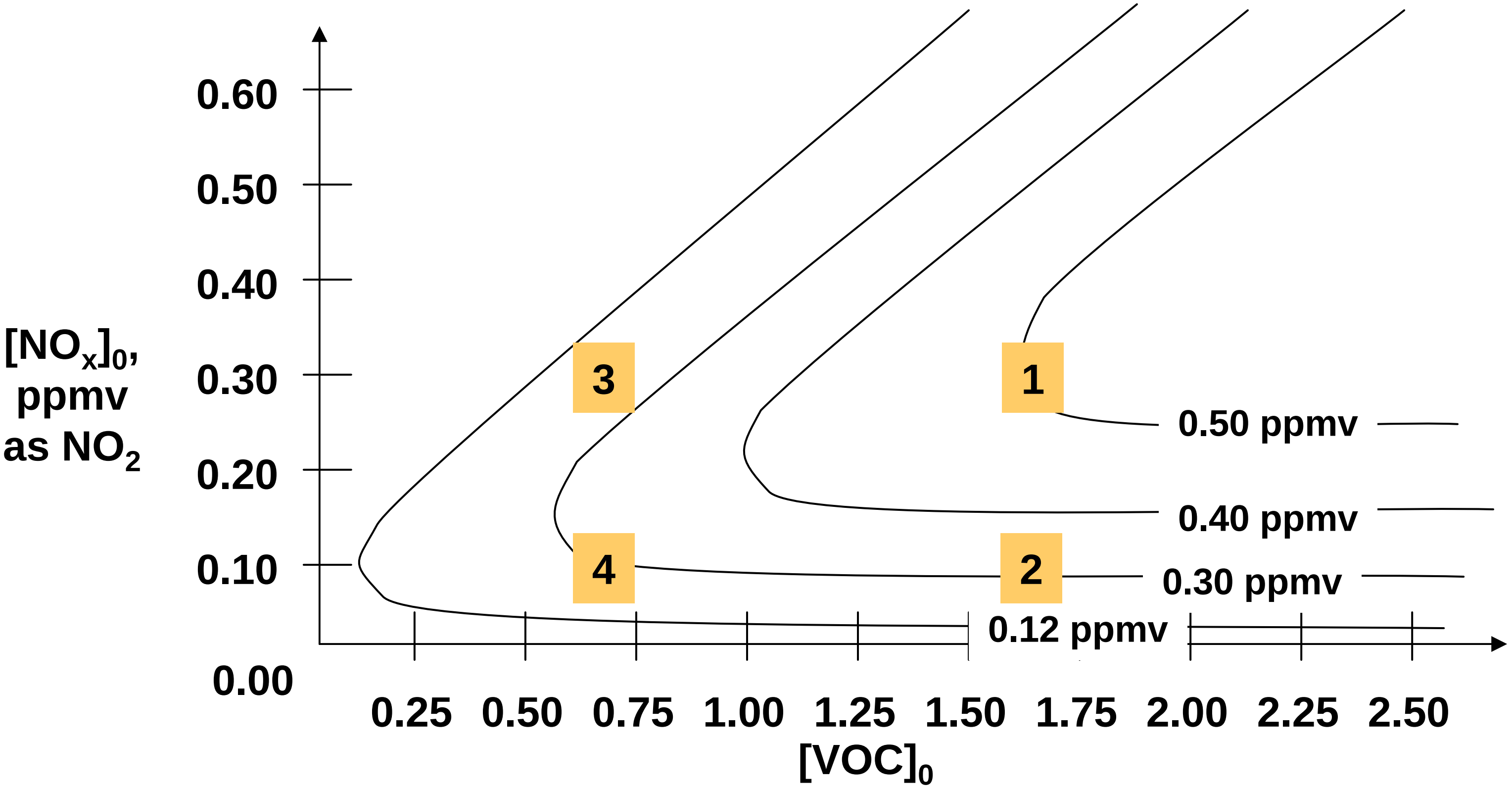


Depending on temperatures, amount of emissions, etc., NO emissions can either increase or decrease ozone.

NO ends up as HNO_3, or organic nitrates.

Some NO_2 gets stored temporarily in organic compounds such as Peroxyacetylnitrate (PAN).

EKMA plot – a contour map of ozone concentrations that occur for different initial concentrations of NO_x and VOC at a fixed temperature and irradiation level.



Suppose your atmospheric conditions are similar to “1”. You could reduce O_3 by reducing *either* NO_x or VOC. If you are at “3”, reducing NO_x will actually increase O_3, and but reducing VOC will reduce O_3. If you are at “2”, reducing VOC will have no effect on O_3, but reducing NO_x will reduce O_3.

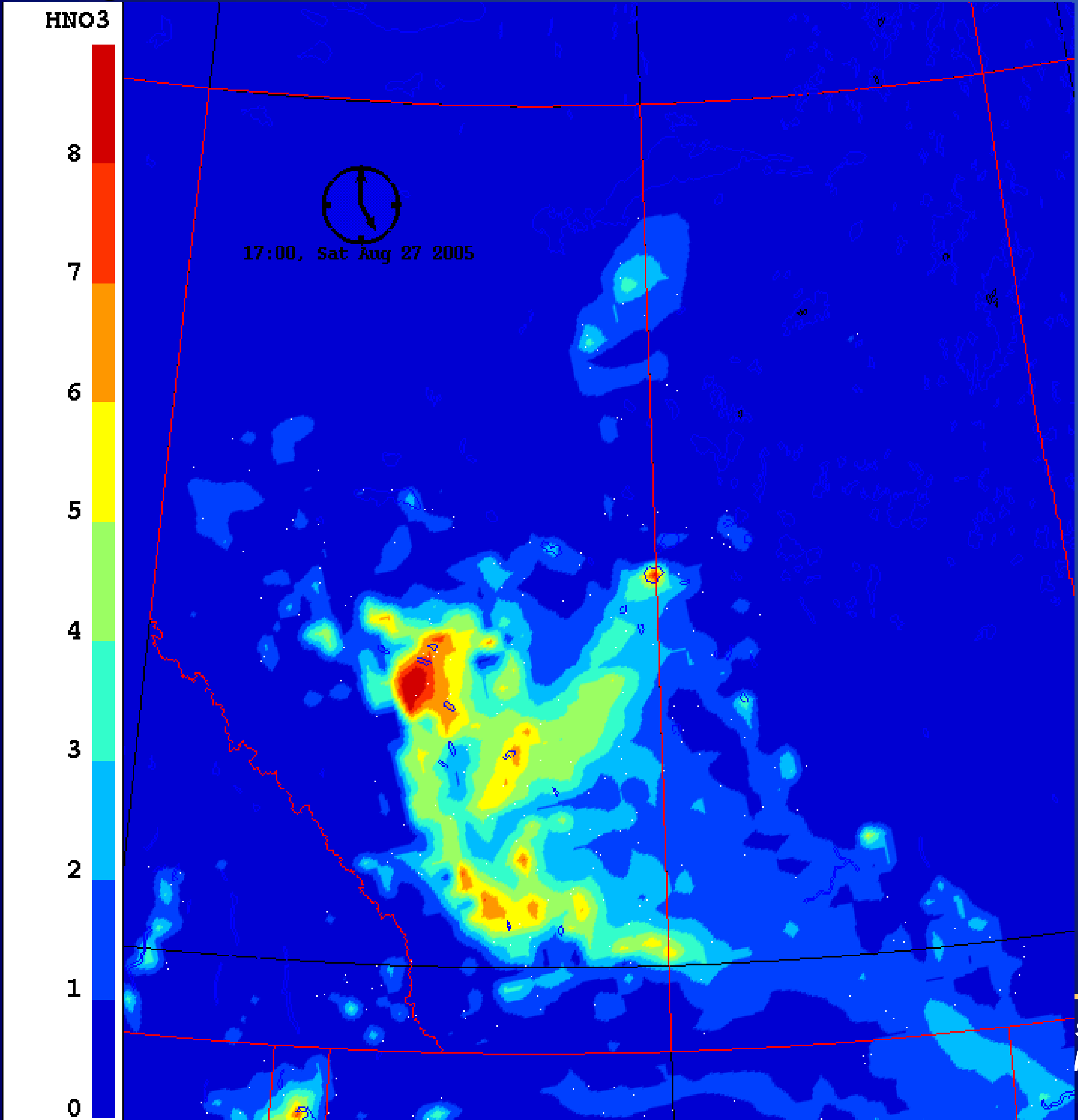
“2”: Reduce NO_x, get a big drop in O_3. Reduce VOC, little change in O_3. NO_X Limited! Rural

“3”: Reduce NO_x, get an increase(!) in O_3. Reduce VOC, get decrease in O_3. VOC Limited! Urban

If the $[VOC]_0/[NO_x]_0$ ~ 1 to 2, then NO→ NO_2, and the formation of O_3 is *limited* by the VOCs.

If the $[VOC]_0/[NO_x]_0$ ~ 20, then O_3 can’t accumulate further due to its reaction with Alkenes, removal of NO_2 by free radicals, etc.

An example: NOx titration of Ozone over Edmonton, Using the EC AURAMS model



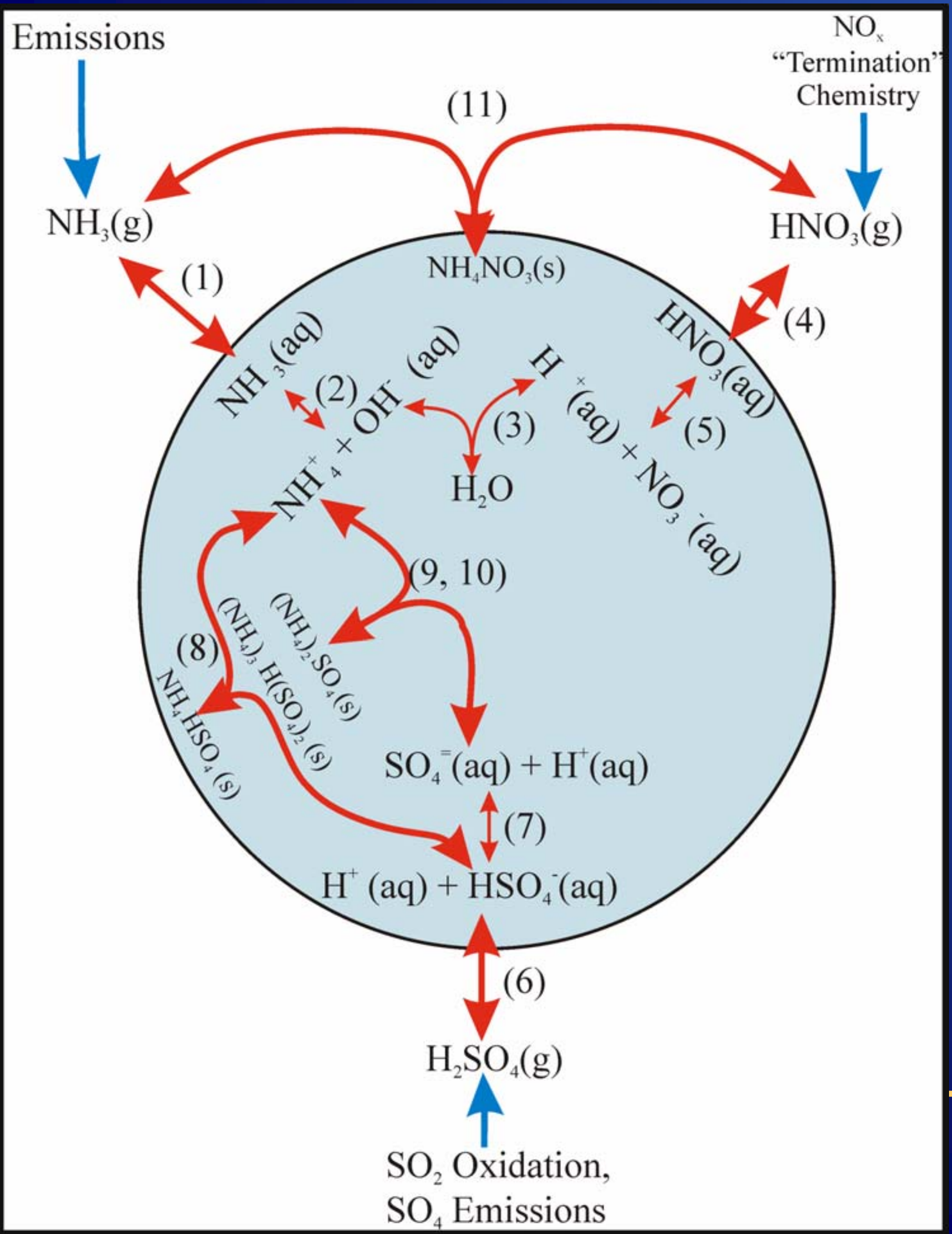
HNO_3 concentration

O_3 concentration

O_3 is removed in the cities by titration, and HNO_3 is created downwind.

(2) Nitrogen in Air-Quality Models

c. Inorganic Particle Chemistry



This schematic shows the main components of the inorganic heterogeneous system that includes sulphate (SO_4), nitrate (NO_3) and ammonium (NH_4).

Note that, within the particle, ammonium nitrate ($NH_4NO_3(s)$), ammonium bisulphate ($NH_4HSO_4(s)$), ammonium sulphate ($(NH_4)_2SO_4(s)$), and letovicite ($(NH_4)_3H(SO_4)_2(s)$) are all present.

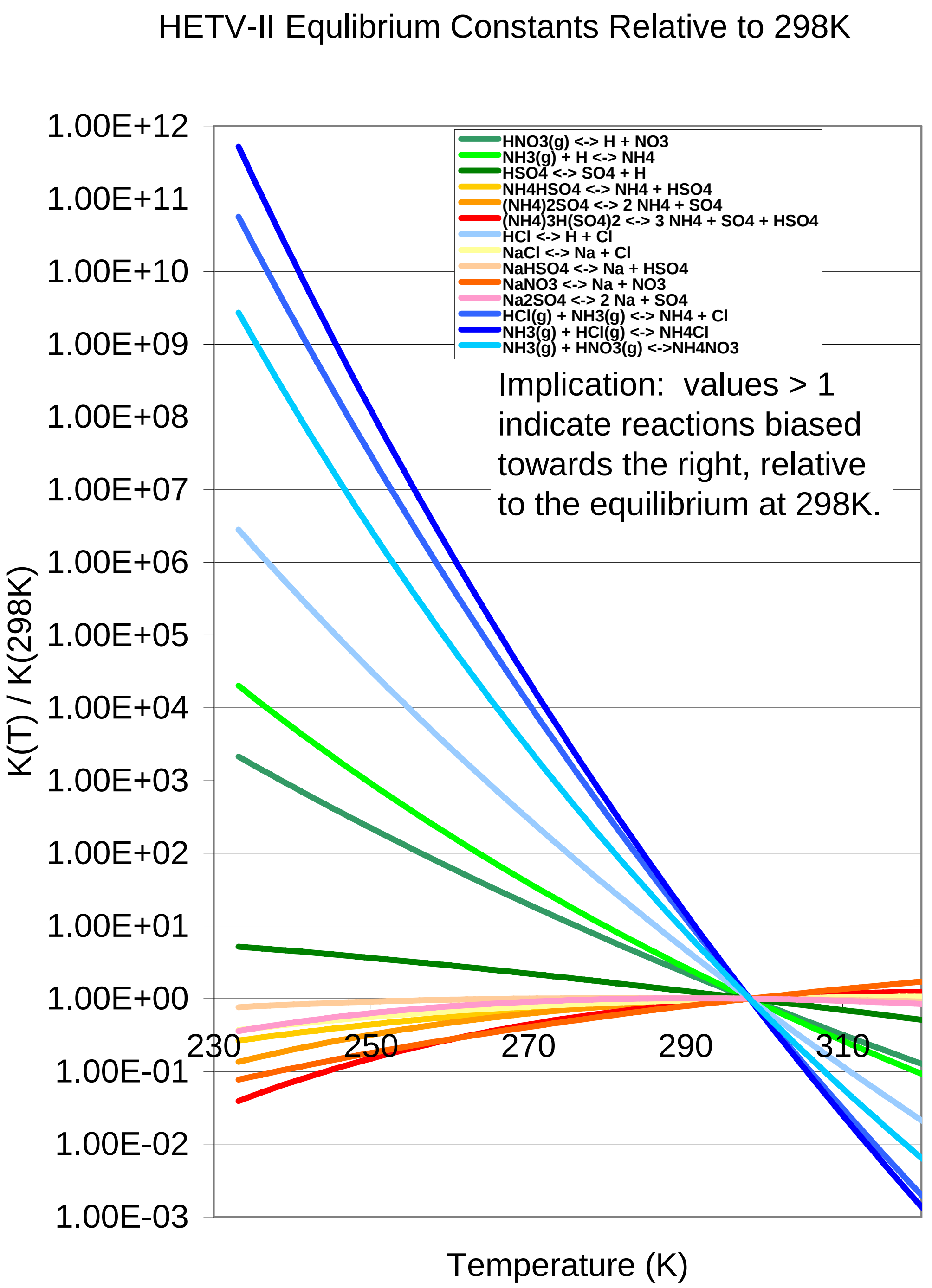
The reactions are sometimes VERY temperature dependant!

(2) Nitrogen in Air-Quality Models

c. Inorganic Particle Chemistry

e.g. particle ammonium nitrate formation is about **<u>1000x</u>** more efficient at 273K than at 298K. Particle nitrate ion formation is about **<u>20x</u>** more efficient at 273K than at 298K.

There will be a test on this idea at the end of the lecture.☺



Implication: values > 1 indicate reactions biased towards the right, relative to the equilibrium at 298K.

(2) Nitrogen in Air-Quality Models

d. Deposition of Nitrogen

NOx, inorganic nitrogen acids, organic nitrates and Peroxynitrates: all have different deposition velocities (composition based, but usually values inferred from chemical properties; few direct measurements of the deposition velocities of these species.

Nitrogen is also deposited as particles (e.g. ammonium nitrate, nitrate ion, ammonium ion, etc.)

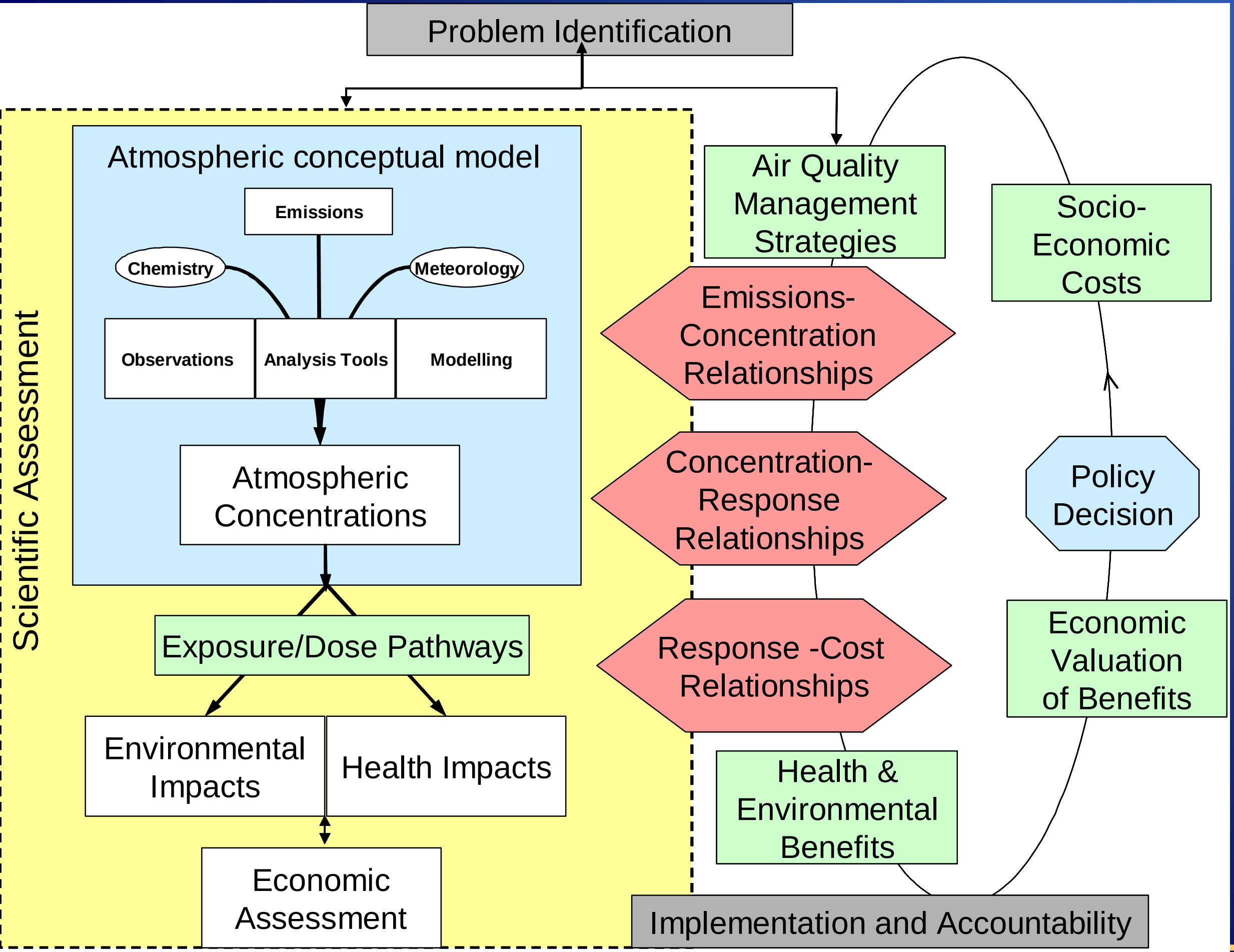
This deposition can be tracked to get total masses, and is usually irreversible.

(3) Air-Quality Models and Government Policy

a. Overall Framework and Decision Making
b. Scenario Runs – their role for policy advice
c. Some examples from recent Air-Quality Model Applications.

(3) Air-Quality Models and Government Policy
a. Overall Framework and Decision Making

Models are part of a larger process to assess air-quality science and provide scientific advice to policy-makers.



A lot of other factors go into policy decisions aside from modelling!

Sketch courtesy J. Brook, EC.

(3) Air-Quality Models and Government Policy

b. Scenario Runs – their role for policy advice

After a problem has been identified (e.g. links between human health issues and $PM_{2.5}$ or ozone, or links between emissions of SO_2 and acid precipitation), the question asked by the policy community is “what can be done about it?”

However, atmospheric chemistry is complex and “non-linear”; a change in the emissions of one component does not necessarily have the same effect everywhere.

Models can be used to provide some information on these effects. → change the emissions and run the model; how do all of the components change? Compare to a base case in which no emissions have changed: a “scenario run”.

(3) Air-Quality Models and Government Policy

c. Some examples from recent Air-Quality Model Applications.

e.g. Do some projections for the years 2010 and 2020

“Base”: emissions projected using assumptions based on legislation already passed in the US and Canada.

“Control”: emissions projected using assumptions based on legislation being debated in the US and Canada.

Percent differences between scenario emissions of primary PM2.5 and PM precursors on the AURAMS domain for three pairs of scenarios. A positive value indicates an increase in emissions in going from the first scenario to the second scenario of the pair.

Emitted **Pollutant**	**2010B Vs. 2020B**			**2010B Vs. 2010C**			**2020B Vs. 2020C**		
	Can.	U.S.	Dom.	Can.	U.S.	Dom.	Can.	U.S.	Dom.
$PM_{2.5}$	10.9	0.1	2.1	-0.6	0.0	-0.1	-0.9	0.0	-0.1
SO_2	-9.7	-5.1	-5.6	-12.2	-25.2	-23.9	-15.1	-34.1	-32.3
NO_x	-8.7	-17.9	-17.2	-5.3	-10.4	-10.0	-7.2	-16.6	-15.9
VOC	8.7	1.0	1.7	-4.5	0.0	-0.5	-5.4	0.0	-0.6
NH_3	0.0	4.7	4.3	0.0	0.0	0.0	0.0	0.0	0.0

NH_3 assumed to increase (not controlled), and NOx decreases, going from Base to Control.

Source: Canada – United States Transboundary PM Science Assessment, http://www.msc-smc.ec.gc.ca/saib, http://www.epa.gov/airmarkt/usca/index.html

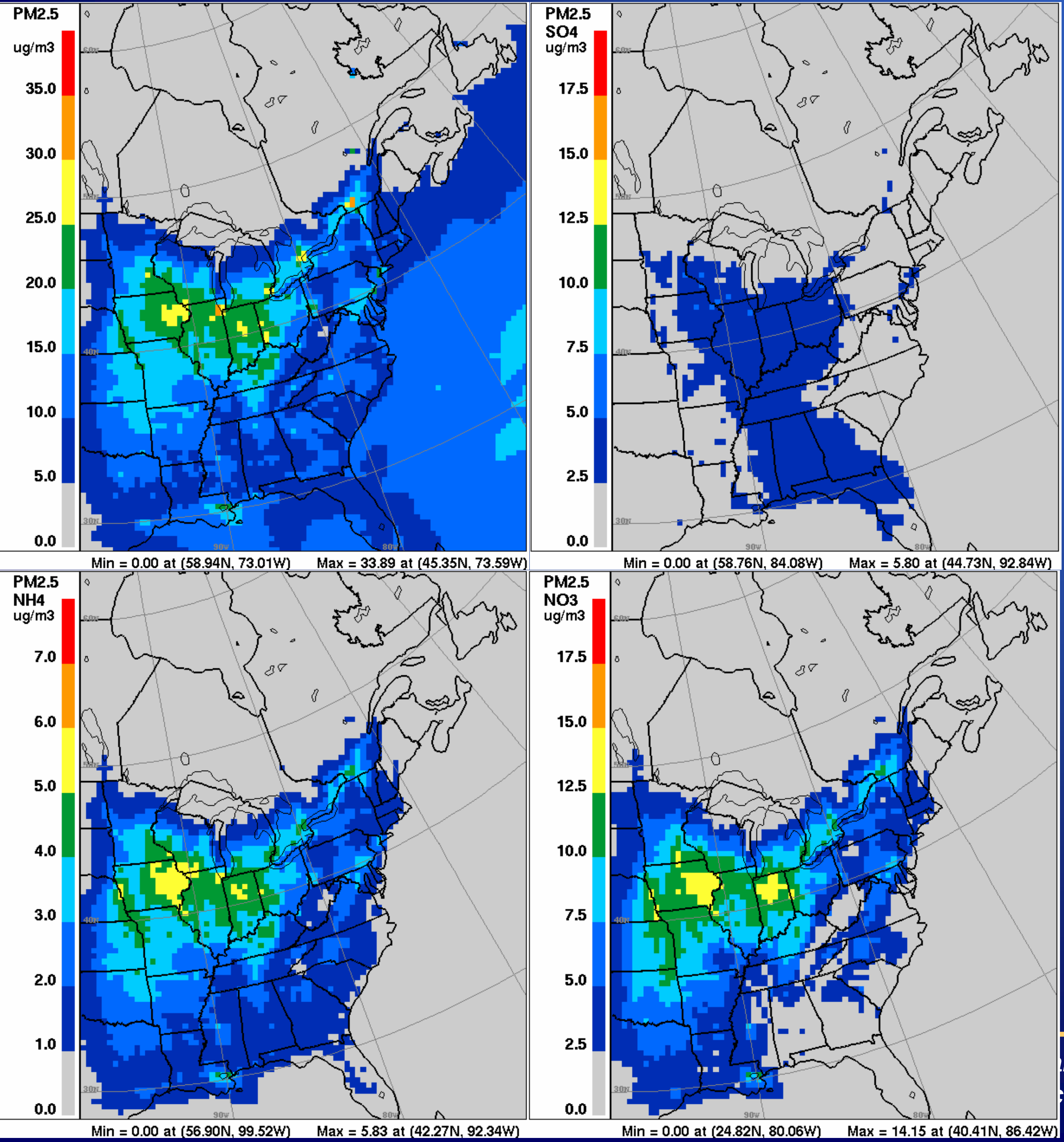
(3) Air-Quality Models and Government Policy

c. Some examples from recent Air-Quality Model Applications.

Run these simulations for summer (July 8-18, 1995 meteorology) and winter (Feb 7-15, 1998) meteorology.

Compare average $PM_{2.5}$ concentrations: how would these change if new legislation was enacted?

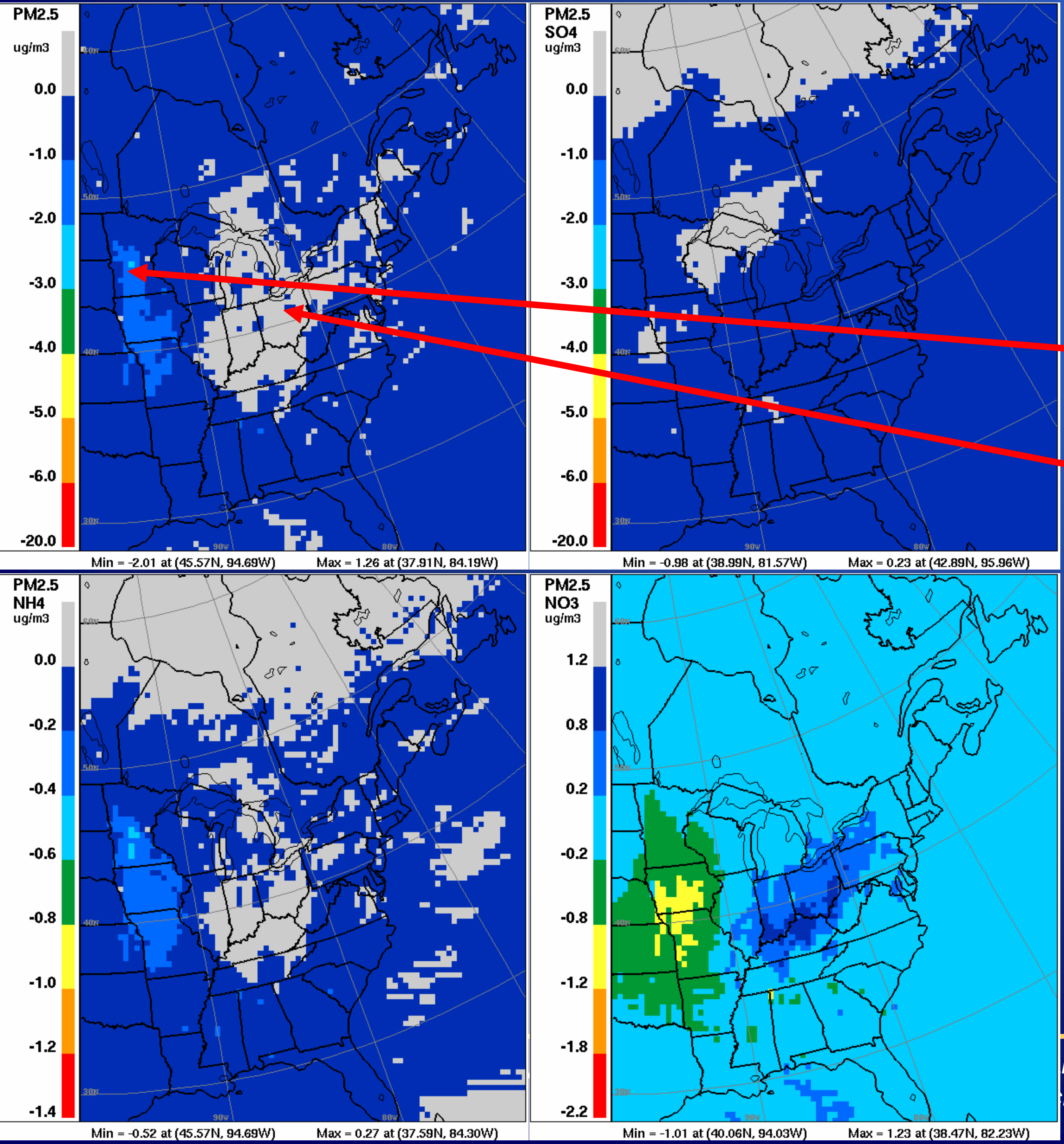
e.g. 2010 base case concentrations
in Eastern Canada, February…



<u>Average</u> PM$_{2.5}$ 7-15 February is close to CWS limit of 30 ug/m^3.

And a large part of that PM$_{2.5}$ mass is ammonium and nitrate.

This is the base case – if additional controls are enacted, what happens?



"Control"-"Base"; negatives mean PM decreased; positive means PM increased.

In some places, $PM_{2.5}$ decreases, in some places, $PM_{2.5}$ increases.

Both decreases *and* increases are associated with particle ammonium and nitrate.

How can a *decrease* in the emissions of some chemicals lead to an *increase* in the particle levels? (this the test at the end of the lecture ☺)

(1) The control scenario reduced SO_2, NO_x.

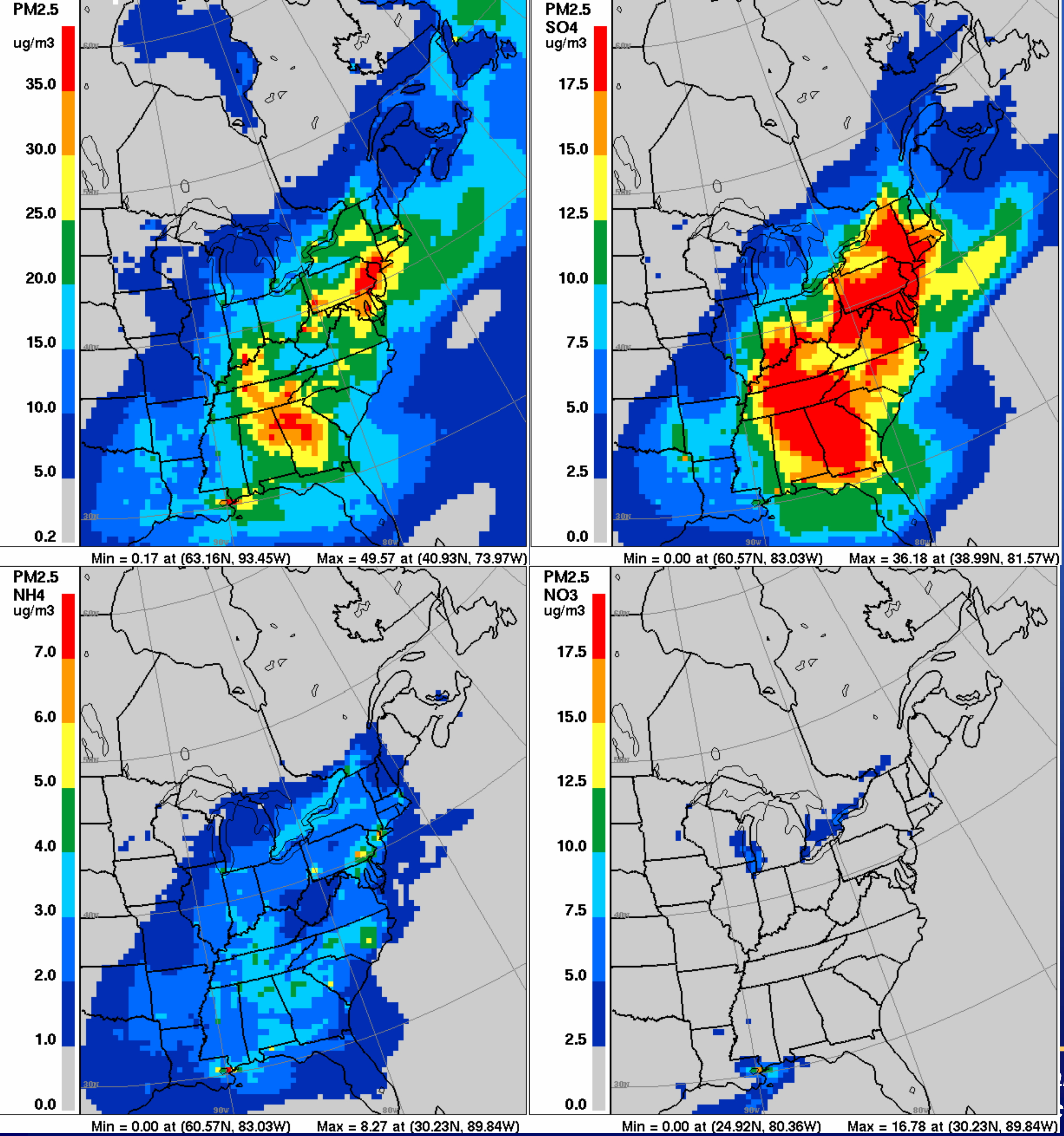
(2) Reducing SO_2 reduces particle sulphate, *but…*

(3) NH_3 is the same in base case and control.

(4) So the relative ratio of ammonia to sulphate has changed (less acidic)

(5) So the chemical regime changes, to one allowing more particle nitrate to form.

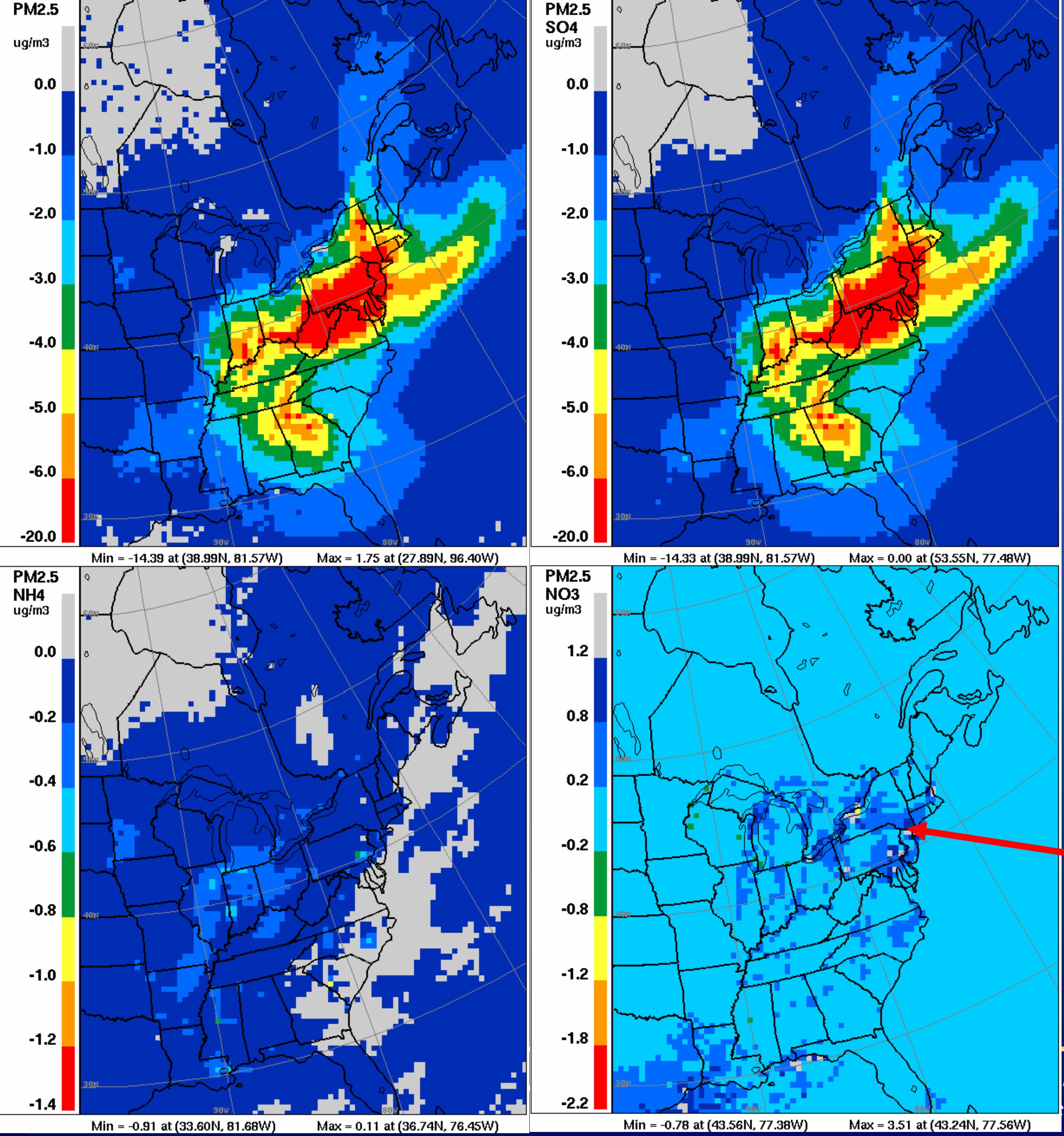
(6) And the decrease in particle sulphate is sometimes more than offset by an increase in particle nitrate.



Interesting note: this *doesn't* happen in the summer.

Average PM$_{2.5}$ 8-18 July exceeds CWS limits of 30 ug/m^3.

Very little nitrate; mostly sulphate and ammonia.



"Control"-"Base"; negatives mean PM decreased; positive means PM increased.

In the summer, the large decrease in $PM_{2.5}$ sulphate is *NOT* counteracted by a large increase in $PM_{2.5}$ nitrate and ammonium.

Though the nitrate *does* go up a *little*.

(3) Air-Quality Models and Government Policy

c. Some examples from recent Air-Quality Model Applications.

Why does this happen in winter and not in summer?

→Temperature effect of nitrate equilibrium; 20x more efficient for nitrate ion formation, and 1000x more efficient for ammonium nitrate formation, at 273K (0 C) than at 298K (25C).

Conclusion (from the above): if you want the control scenarios to be effective in the winter, you need to reduce NOx (hence nitrate) even more than is being considered for future legislation, and/or you need to reduce ammonia.

➔ **Which is one of the reasons why we're currently working on NH_3 (NAESI)**

… any questions?