Measuring and modelling gaseous NH3 and aerosol NH4 at the regional scale –

how does ambient concentration respond to emission controls?

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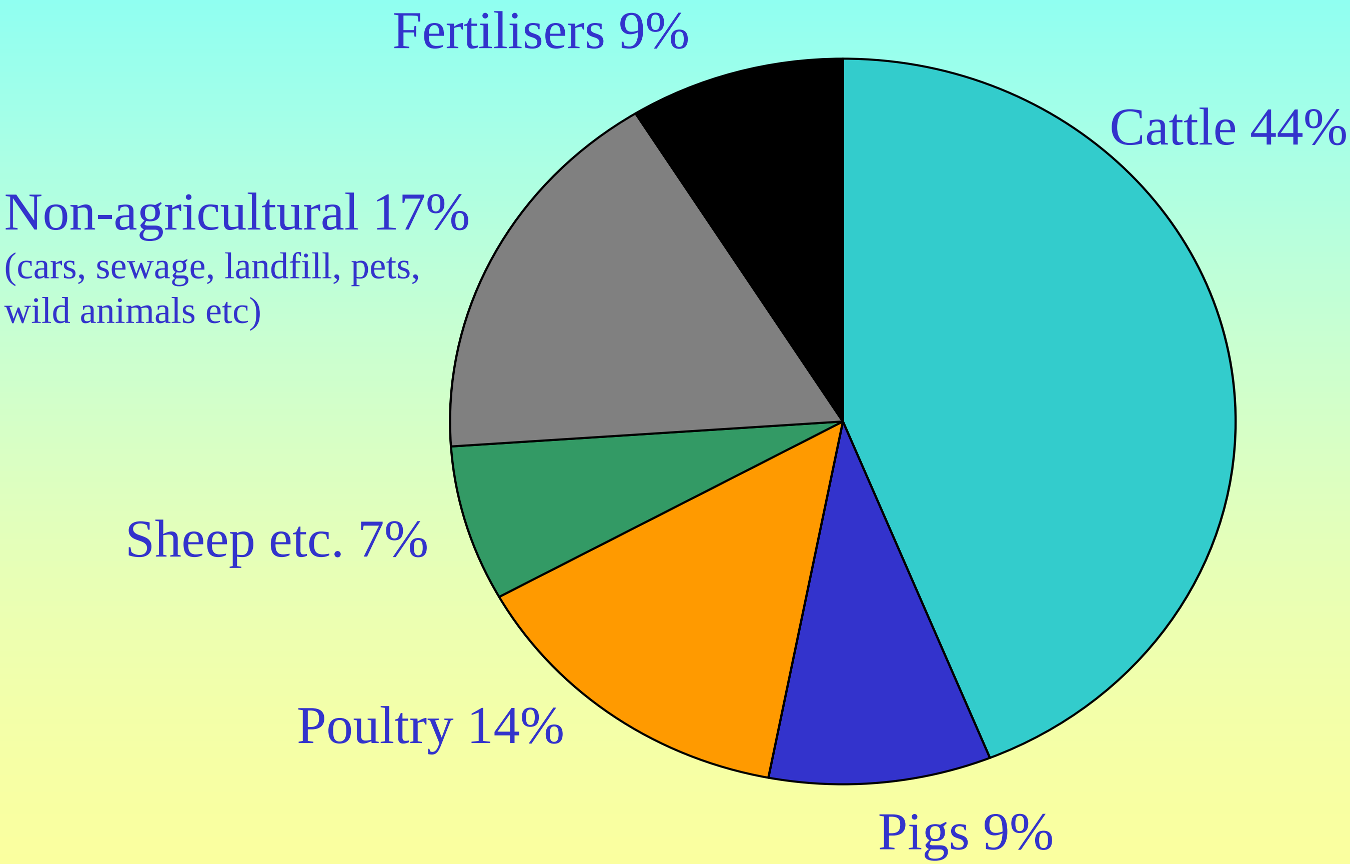
Outline

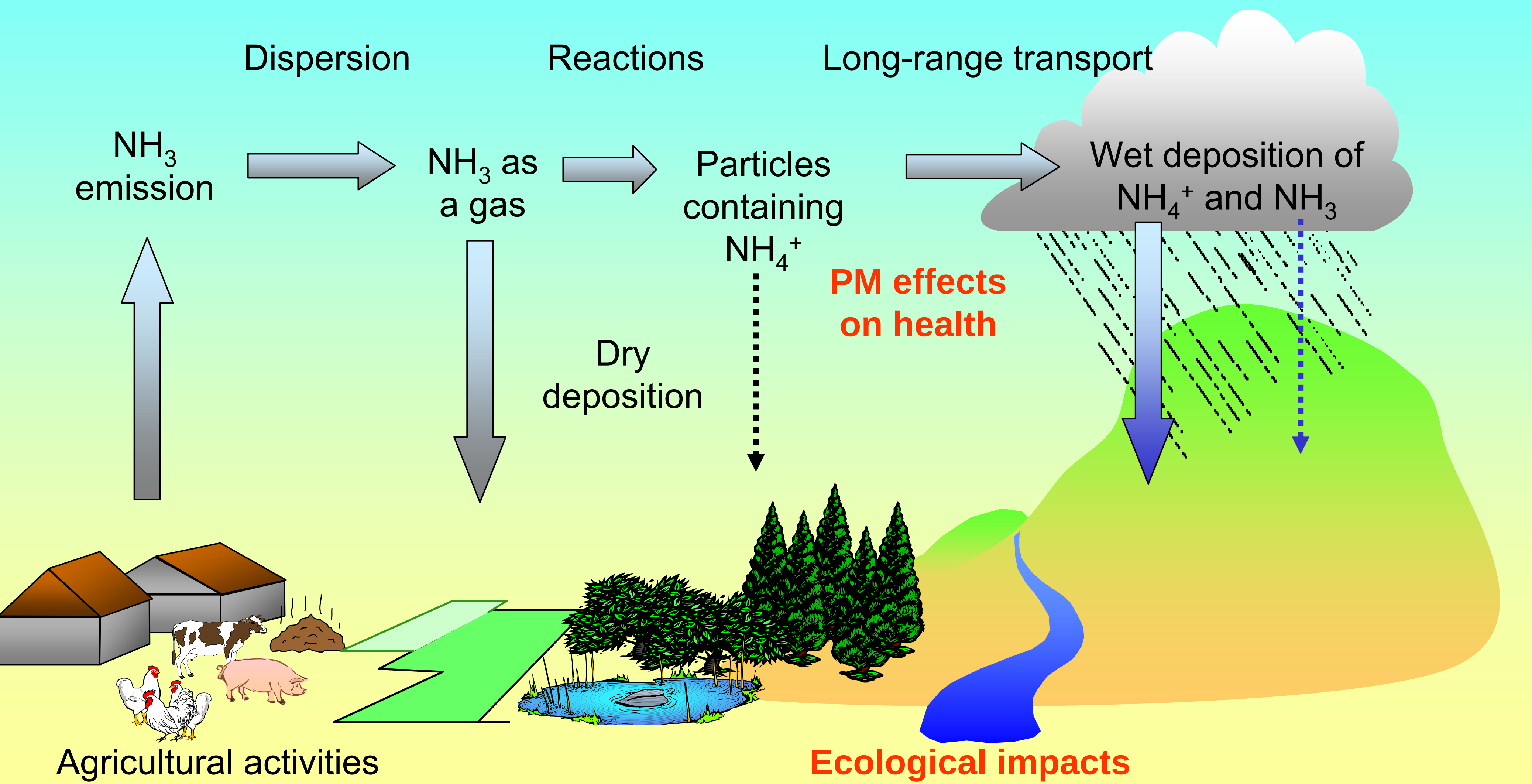
- Background
- Reduced Nitrogen, emissions, deposition and their trends in Europe and North America
- Chemistry and deposition of NH_3
- Observed changes in concentrations and deposition following reductions in emissions
- Spatial variability in NH_3 and NH_4^+ concentration and deposition
- Conclusions

The Polluters: Sources of ammonia

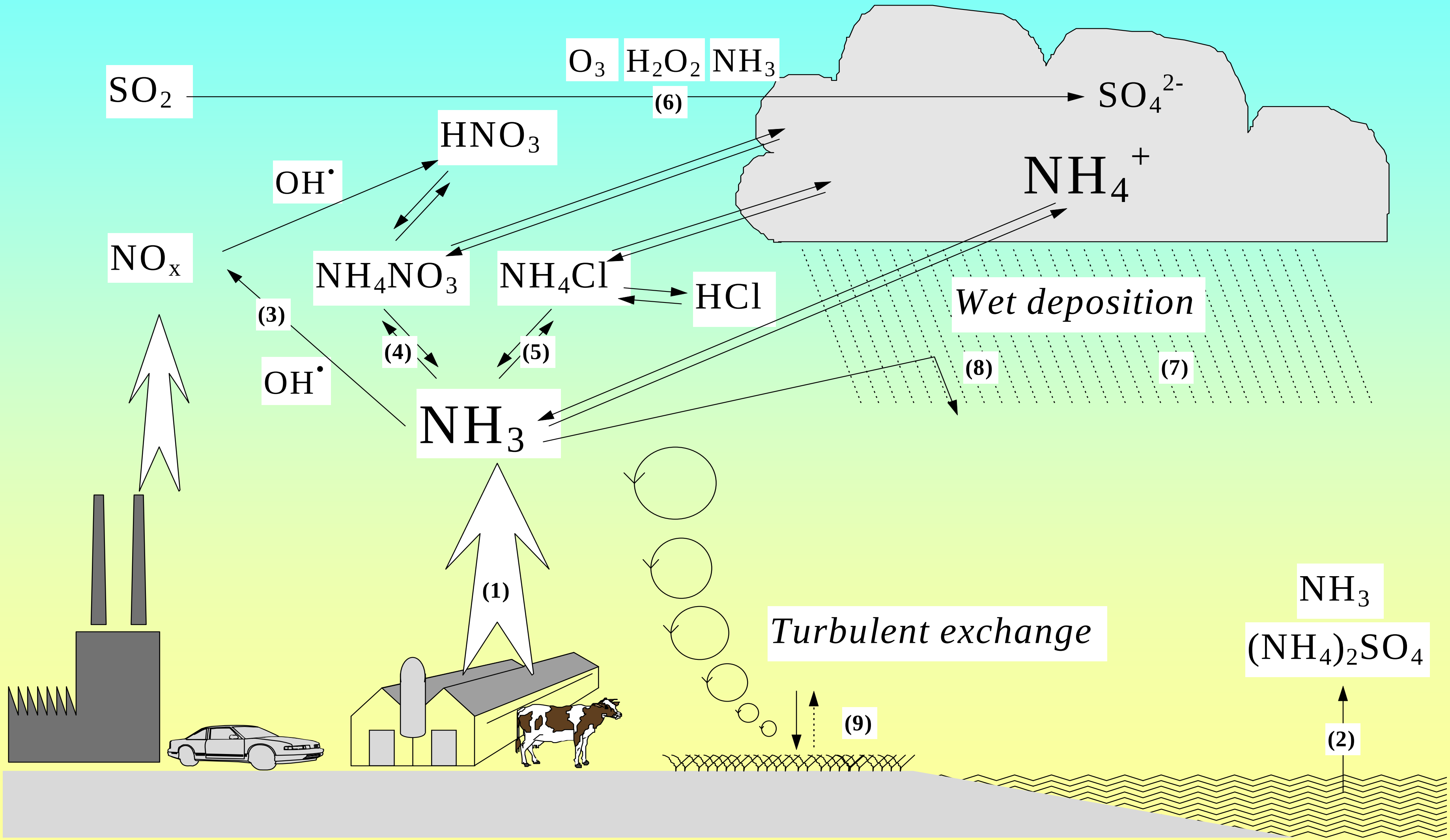


Values for the UK; proportions vary across Europe

Ammonia in the atmosphere



The fate of NH_3 in the atmosphere



Nitrogen reduces the abundance of woodland flowers

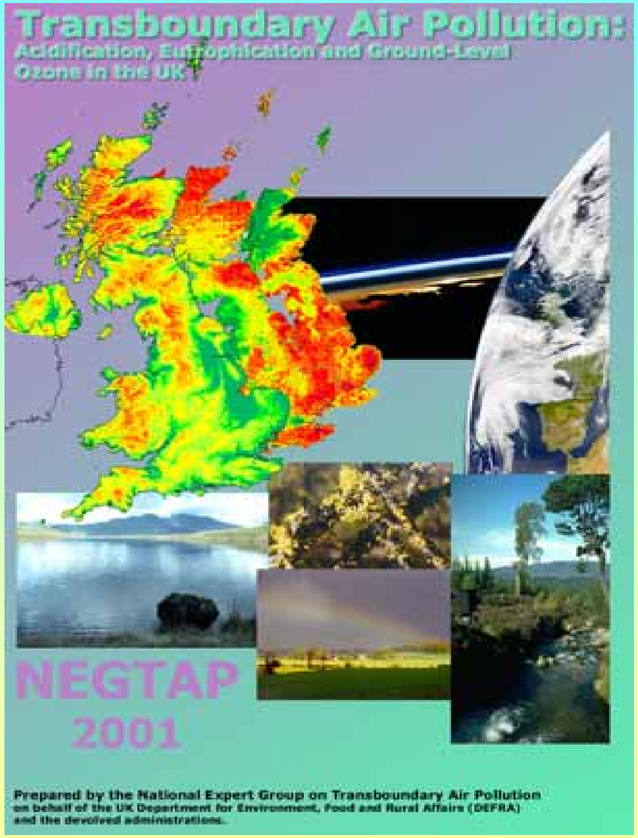
Wood sorrel (*Oxalis acetosella*)

Lost at the expense of:

Velvet grass (*Holcus lanatus*)

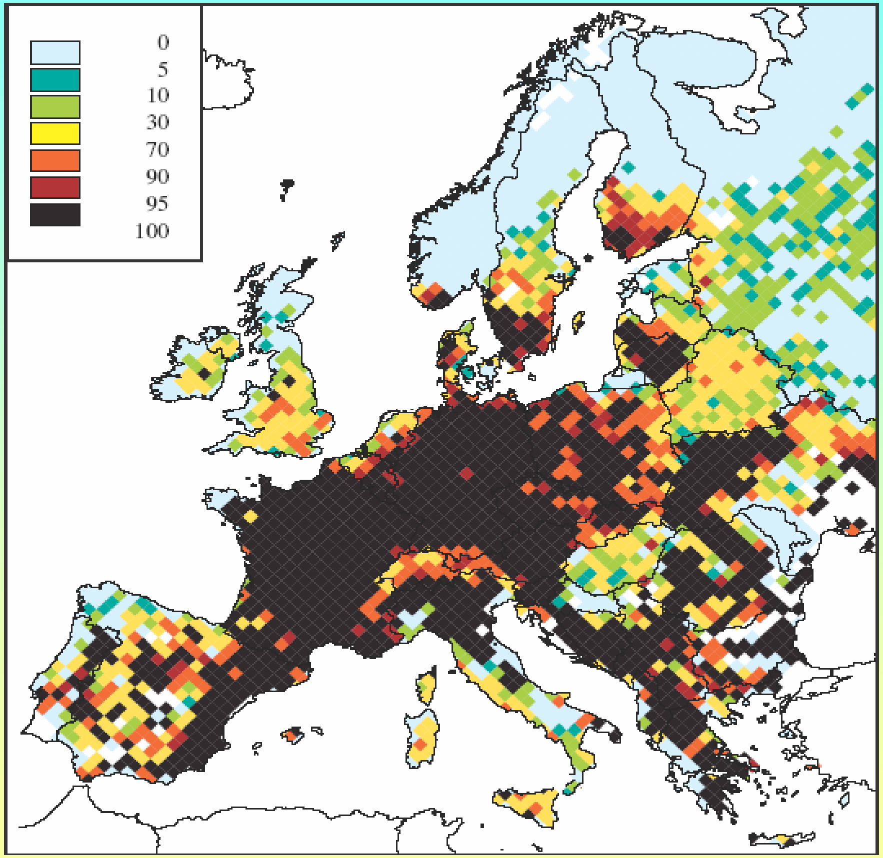
Country scale effects

- Species composition changes are observed at the country scale in semi-natural vegetation
- The only component of the chemical climate of the country associated with these changes is NH_x deposition



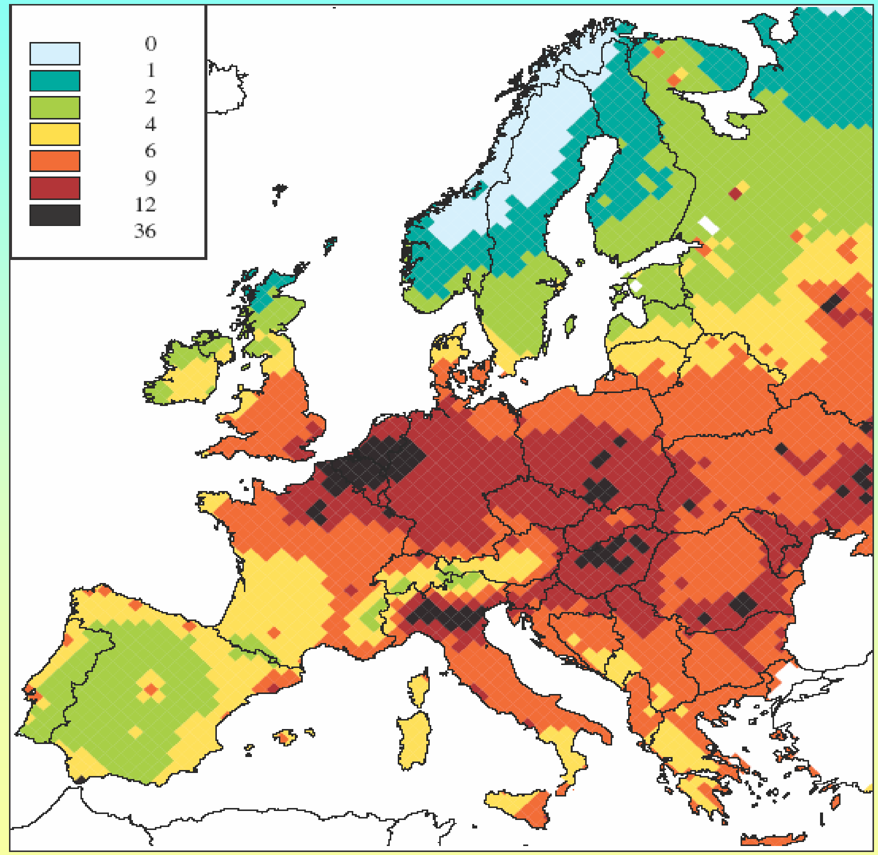
Predicted effects across Europe

Critical load exceedance
for N effects on ecosystems



% of ecosystems area with grid average N deposition > eutrophication critical loads (for 2000)

Loss in life expectancy
attributable to $PM_{2.5}$

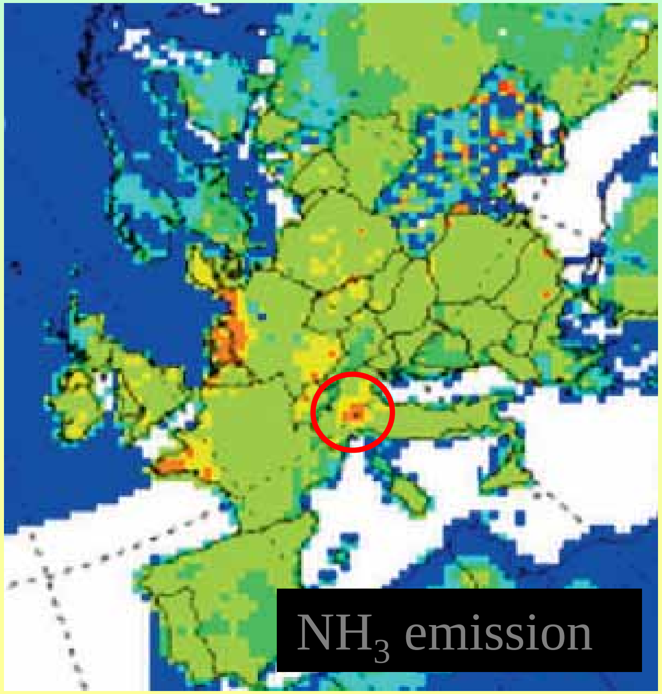


Loss in average life expectancy in months due to identified anthropogenic $PM_{2.5}$ (for 2000)

IIASA

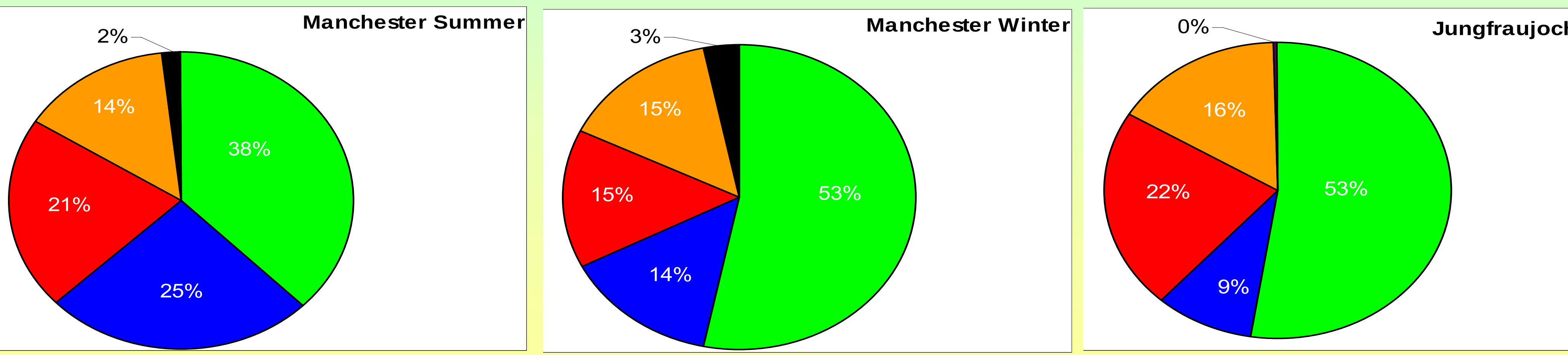
Ammonia contributes substantially to particulate matter (PM) concentrations

- Reduced visibility
- Human heath impacts



Ammonium as a fraction of PM1.0

- Example data from Aerosol Mass Spectroscopy (AMS)
- Ammonium ~15% of total PM1.0
- Ammonium ~ 20-35% of the ionic fraction



Ammonium Sulphate Nitrate Chloride Organic (SOA)

Conclusion: Ammonia is an important problem

- In 2020 ammonia will be the largest contributor to acidification, eutrophication and a major contributor to particulate matter in Europe
- Current ammonia abatement is small compared with other sectors: more effort is required.
- Few countries have adopted substantial emission reduction strategies for NH_3

Nitrogen Emissions (2002) in the USA and Europe

	Population (10^6)	OxN (kt N)	RedN (kt N)	per capita (kg N/person)
EU25	459	3319	3190	7
USA	296	5826	5230	18

Peak emissions and %change

[kt]	NH_3	NOx	SOx	VOC
Europe				
Peak (year)	4945(85)	16433(80)	35763(80)	16915(85)
2002	3874	10905	8040	9179
% change	- 22%	-34%	-76%	-43%
USA				
Peak (year)	5230(02)	25080(77)	28320(70)	31442(70)
2002	5230	19143	13928	15008
% change	+ve	- 24%	- 51%	- 52%

NH_3 Emission Controls

There is a perception that controlling NH_3 is difficult relative to S.

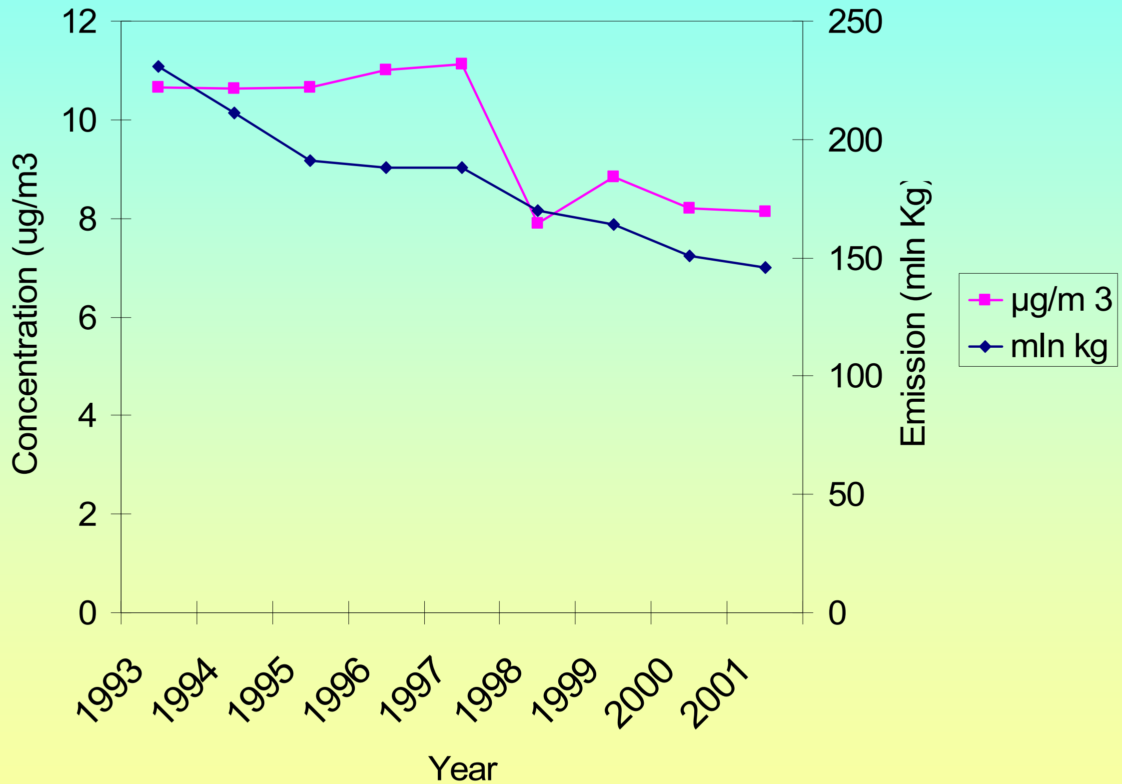
- Sources are complex and effects of control are difficult to quantify
- The politics of controls on agriculture are more difficult for our Governments

Effects of control measures

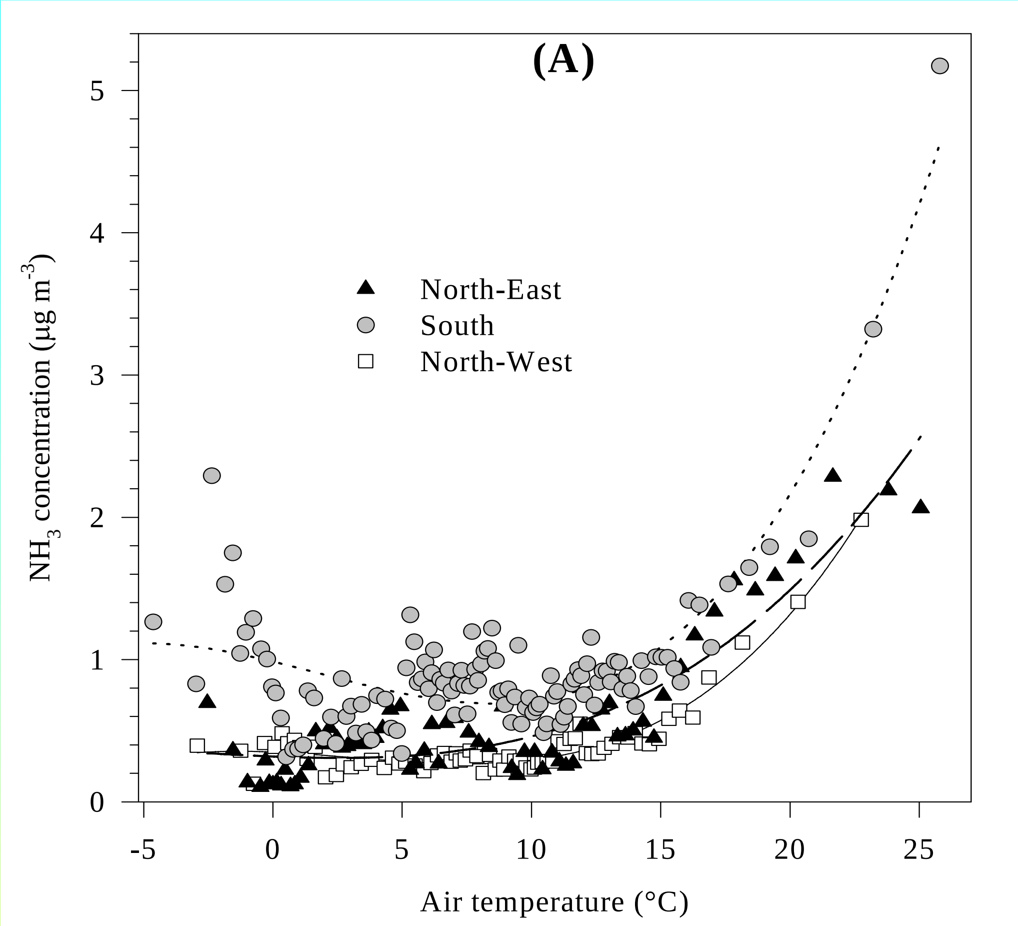
- The Netherlands introduced NH_3 controls in the early 1990s
- The objective of the control measures was a ~30% reduction in NH_3 emission
- A wide range of changes in agricultural practices were introduced

Emission and concentration in the Netherlands

- **Emission decreased by 40%**
- **Decreases is in concentration were initially hard to detect**
- **Concentrations represent only 8 sampling stations**
- **One year passive sampler measurements were made to characterize sampling stations**



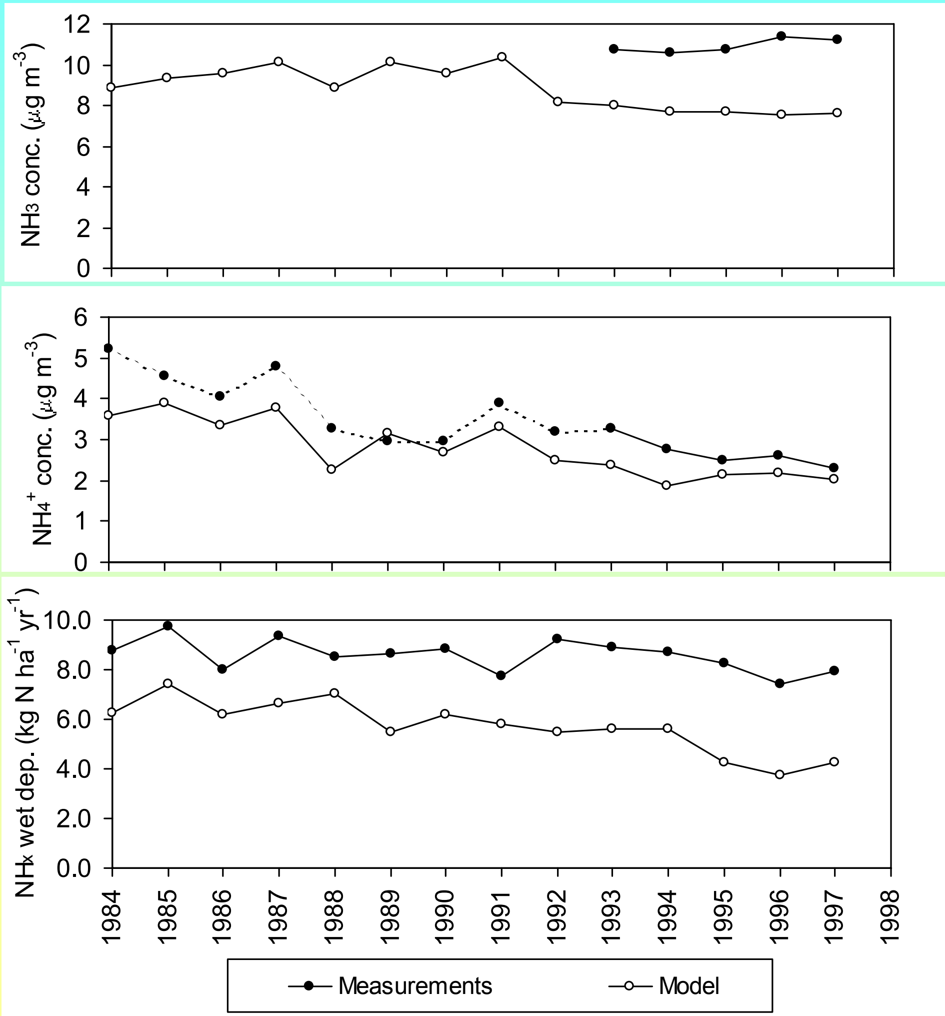
Data: RIVM



Ammonia concentrations (μg m^{-3}) in relation to air temperature (° C)

$$p_{NH_3} = 10^{4.1218 - 4507.05/T}\left(\left[NH_4^+\right]/\left[H^+\right]\right)$$

Netherlands



- 35% emission reduction
- 10% reduction NH_4 wd
- 29% reduction NH_4 aerosol

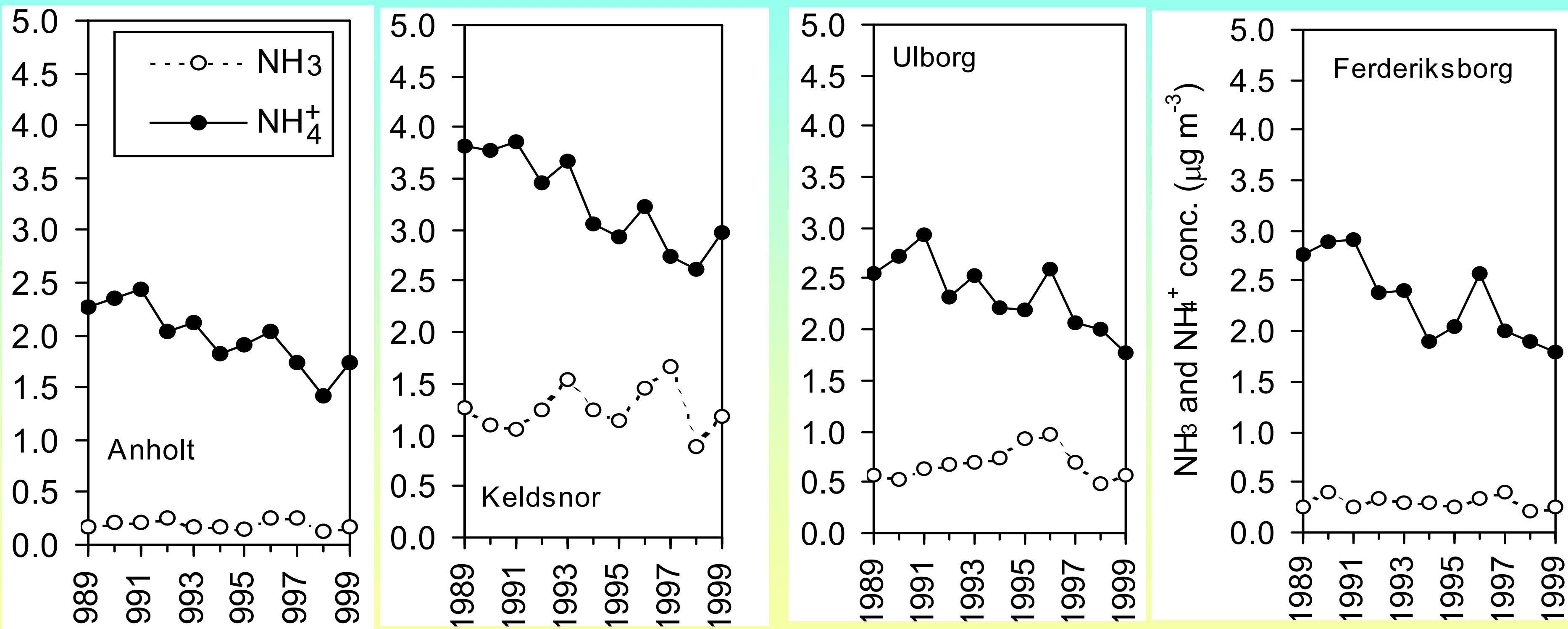
- Again: part of the explanation - parallel changes in SO_2 and NO_x emission
- But also: overestimation of effectiveness of measures

Denmark

- Emission controls introduced through the 1990s

- Monitoring networks provided gas and aerosol phase measurements at a small number of stations, and wet deposition

Changes in NH_3 and NH_4^+ in Denmark



Relative trends in NH_x concentrations and deposition in Denmark (% change of the values for 1999 compared with 1989).

Component	NH_3 in air	NH_4^+ in air	NH_x wet deposition[a)]
Ulborg	*14*	**-32**	*-22*
Tange/Sepstrup Sande[b)]	**-26**	**-33**	*-12*
Lindet	[c)]	**-35**	*-21*
Anholt	*-10*	**-35**	*-19*
Frederiksborg	*-13*	**-38**	**-27**
Keldsnor	*5*	**-32**	*-17*[d)]

Bold values are significant at a level > 99%; *Italic* values are not significant to this level. Negative values indicate reductions.
a) The amount of precipitation has also increased during this period, but not significantly.
b) NH_3 and NH_4^+ in air taken from Tange. NH_x wet deposition taken from Sepstrup Sande. The distance between these stations is about 30 km.
c) Not taken into account because height is changed.
d) Less certain precipitation data at this site makes this value doubtful.

Detecting the trends in emission

- NH_3 concentrations are very spatially variable,
- The footprint of most sites is very small

- NH_4^+ aerosol and wet deposition integrates the effects over a much larger region

EUROPEAN REGIONS

Based on Year 2000	Red N	Ox N	Ox S
1 – Source Region → export	20%	50%	20%
2 – Source Region → export	10%	60%	30%
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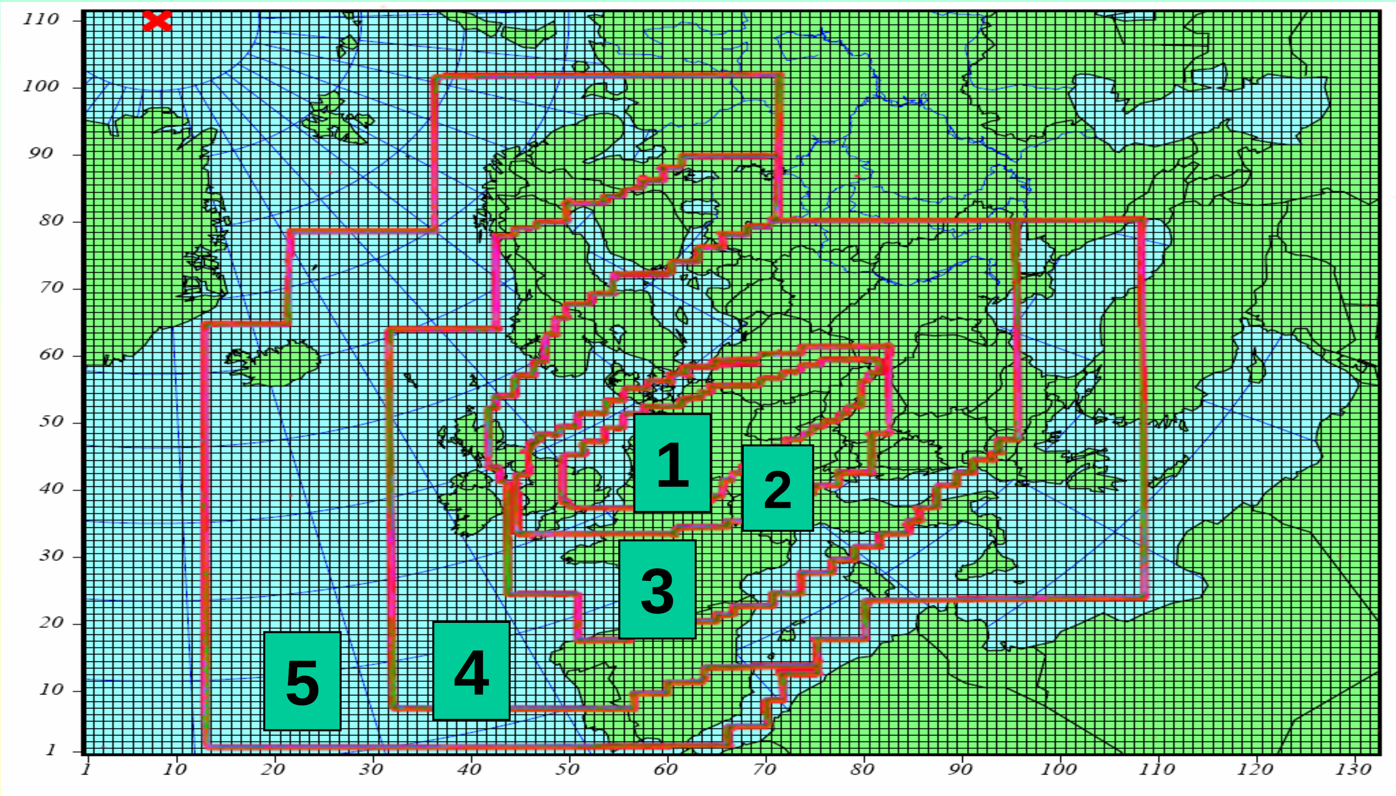
3 – Sink Region →import	10%	10%	20%
4 – Sink Region → import	60%	10%	20%
5 – Sink Region → import	70%	50%	80%



REDUCED NITROGEN

Δ European Emissions -23%

AMMONIA – NH_3

There is no network of NH_3 concentration measurements for Europe as a whole (UK, Denmark, The Netherlands)

AMMONIUM – NH_4^+ concentration in precipitation

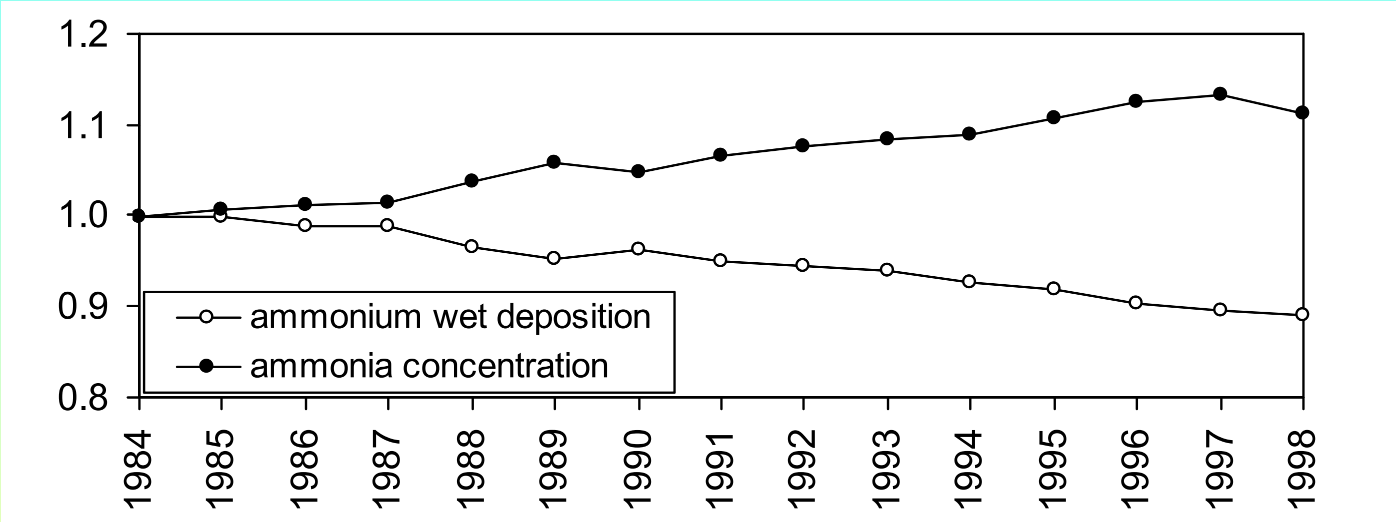
Changes in NH_4^+ in precipitation 1980-2000

	R1	R2	R3	R4	R5
ΔNH_4^+ in ppt	-28%	-41%	-26%	+7%	+43%
ΔEmission	-29%	-22%	-28%	-6%	+10%

European changes in NH_x emission and deposition

	Emission	Deposition	NH_4 in precipitation
1980	5499.37	5791.05	0.65
1985	5653.30	5738.82	0.52
1990	5328.06	5129.04	0.50
1995	4807.04	4844.52	0.46
2000	4186.47	4599.84	0.42

Netherlands – effect of changing SO_2 and NO_x



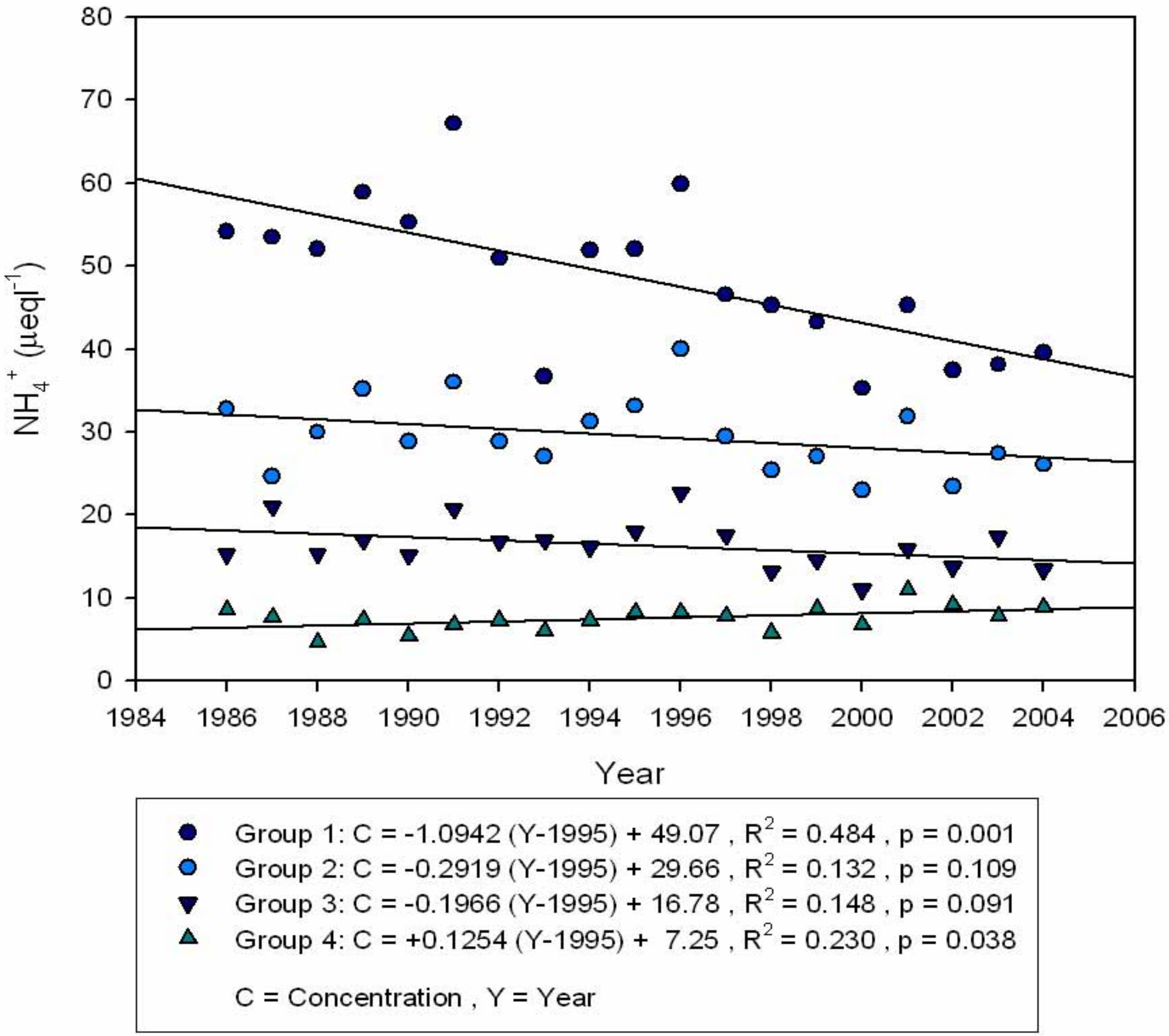
- 1984 SO_2 and NO_x emissions and actual emissions
- increase in NH_3 conc. and decrease in NH_4 wd

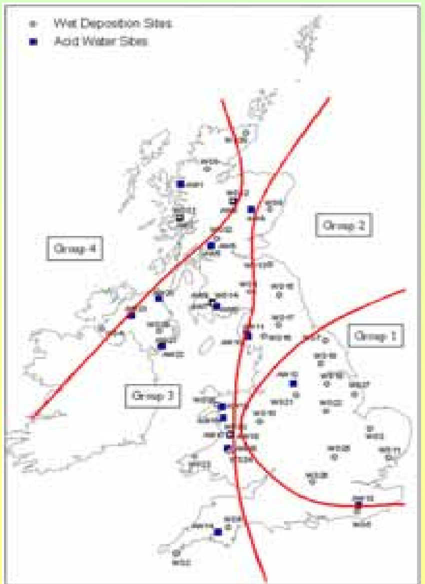
Ammonium in precipitation 1986-2004

Trend in Group 1 (negative) and 4 (positive) are significant at α = 0.05 level

Trend in Group 4 was negative (& not significant) for 1986-2001, now for 1986-2004 it is positive and significant at α = 0.05 level

Trend in Group 3 was positive for 1986-2001, now for 1986-2004, it is negative (both not significant)





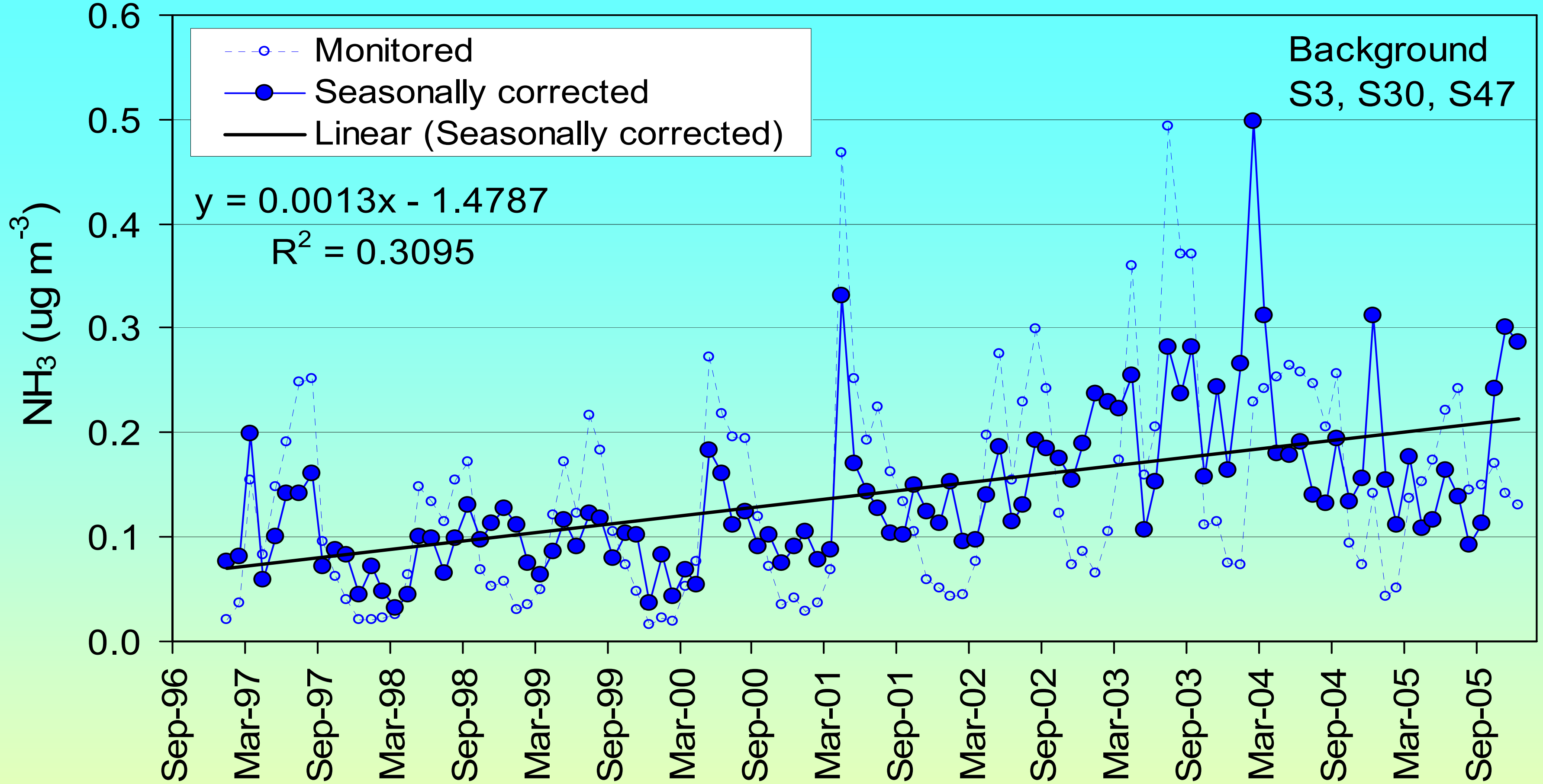
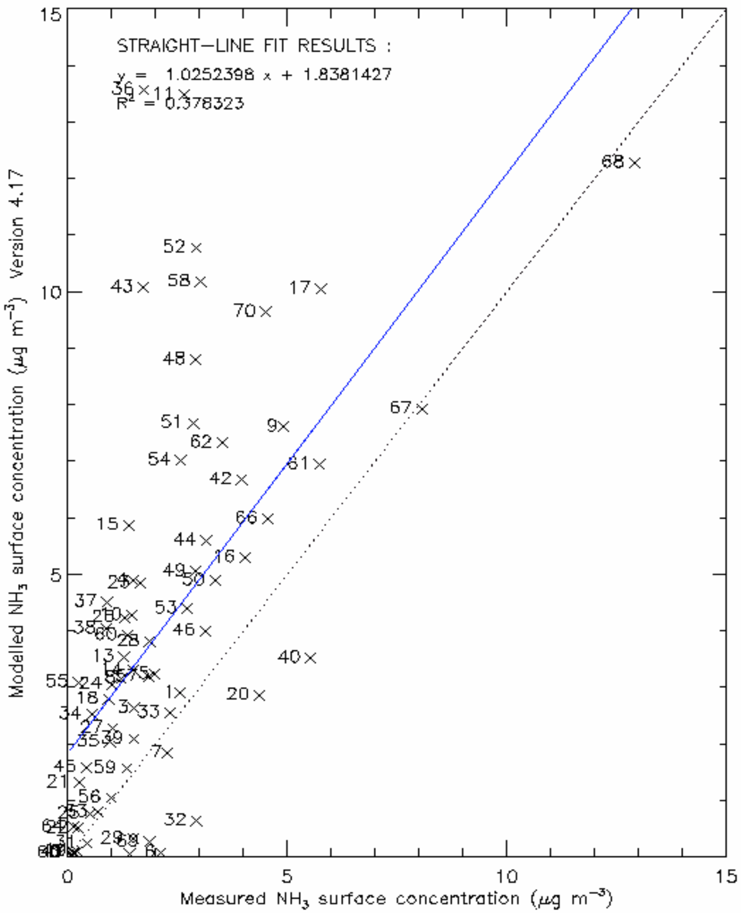


Figure 65: Long term trend in mean monitored (--o--) and seasonally-detrended mean NH_3 concentration (--•--) from three remote sites in the NAMN, S3 Inverpolly, S30 Strathvaich Dam and S47 Rum. All measurements are made using the DELTA system throughout. The seasonal detrending was derived from the mean seasonal cycle for the whole period normalized to 1, and then multiplying each monthly value by the appropriate value.

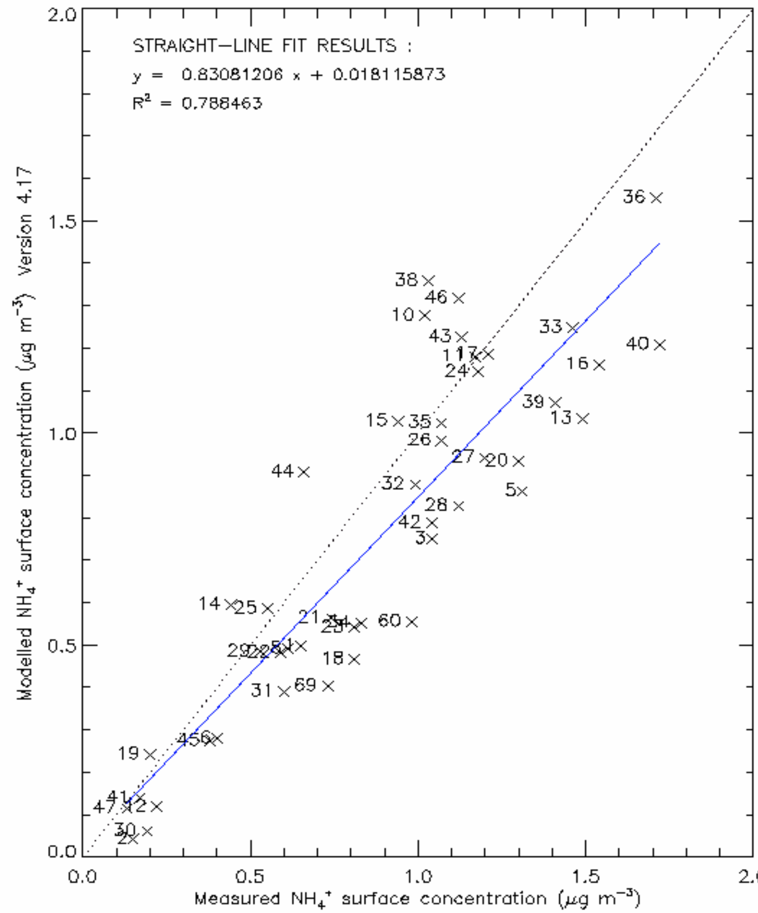
How well do the models perform?

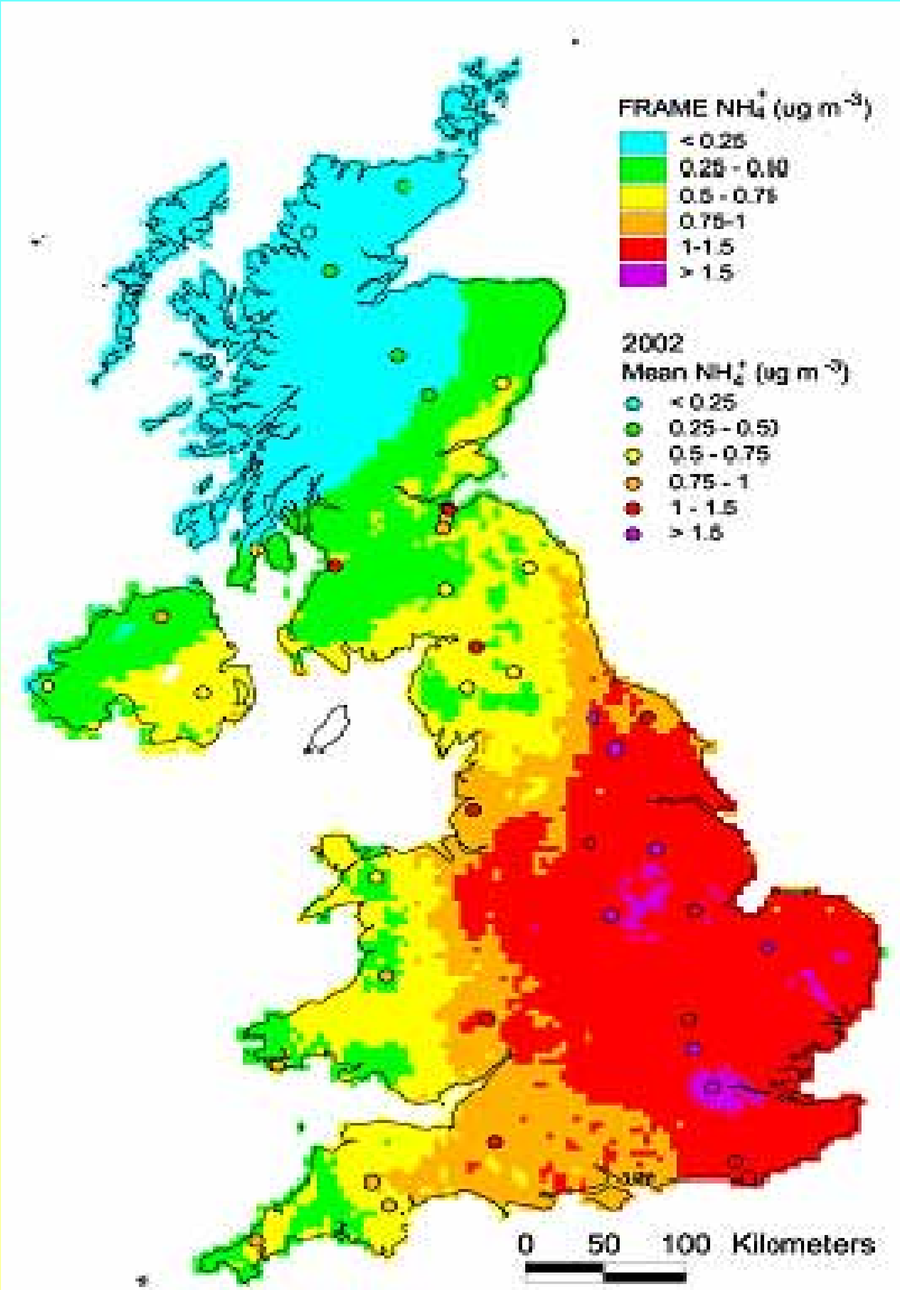
- How important are models in describing the concentration and deposition fields?

NH_3

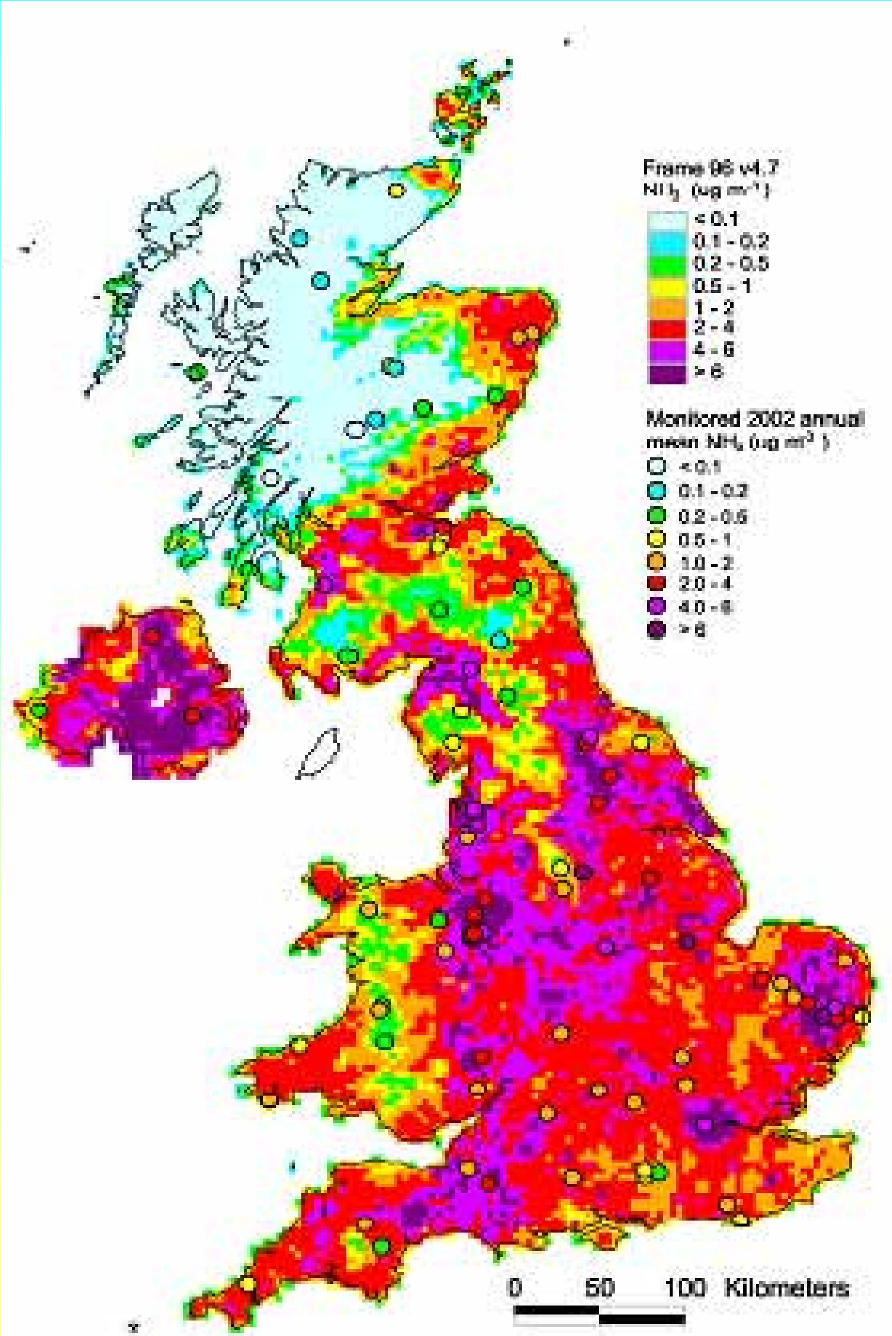

STRAIGHT–LINE FIT RESULTS :
y = 1.0252398 x + 1.8381427
R² = 0.378323
Modelled NH₃ surface concentration (μg m⁻³) Version 4.17
Measured NH₃ surface concentration (μg m⁻³)

NH_4^+


STRAIGHT–LINE FIT RESULTS :
y = 0.83081206 x + 0.018115873
R² = 0.788463
Modelled NH₄⁺ surface concentration (μg m⁻³) Version 4.17
Measured NH₄⁺ surface concentration (μg m⁻³)



Modelled and measured NH_4 aerosol concentrations



Modelled and measured NH_3 concentrations


Frame 96 v4.7
NH_3 (ug m^{-3})
≤ 0.1
0.1 - 0.2
0.2 - 0.5
0.5 - 1
1 - 2
2 - 4
4 - 6
> 6
Monitored 2002 annual mean NH_3 (ug m^{-3})
< 0.1
0.1 - 0.2
0.2 - 0.5
0.5 - 1
1.0 - 2
2.0 - 4
4.0 - 6
> 6
0 50 100 Kilometers

Conclusions

- Models are the only practical tool available to define the concentration and dry deposition field for NH_3.
- Models are able to capture the regional changes in concentration and deposition….the regional models do not capture the fine scale structure in NH_3concentration
- Validation with extensive field measurements is vital
- Country specific parameterization of the surface – atmosphere transfer scheme is necessary

Conclusions

- Effective controls for NH_3 emissions have been introduced in the Netherlands and Denmark
- The scale of emission reduction achieved has been largely consistent with the initial goal
- Demonstrating compliance through monitoring of NH_3 is challenging and requires a long time series of data and/or large numbers of sites

Conclusions

- Monitoring NH_4^+ in aerosol and rain provides effective integration at the regional scale and reveals the trends in emissions
- Concentrations in most of Europe are declining while in remote regions concentrations and deposition are increasing
- There has been a change in the chemistry of ammonia as a consequence of sulphur emission reductions