

# Atmospheric chemistry

## Acidification

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# Acidification

Sulphur- and nitrogen-containing compounds are oxidized in the atmosphere and are transformed from the gas phase to solid or liquid phase in aerosol particles or cloud drops.

Sulphur and nitrogen are then found in the form of sulphates and nitrates.



The acidic aerosol particles and cloud drops are deposited mainly as acid rain (wet deposition).

Levels of SO<sub>2</sub> in Sweden today are so low that they do not constitute a threat to human health.

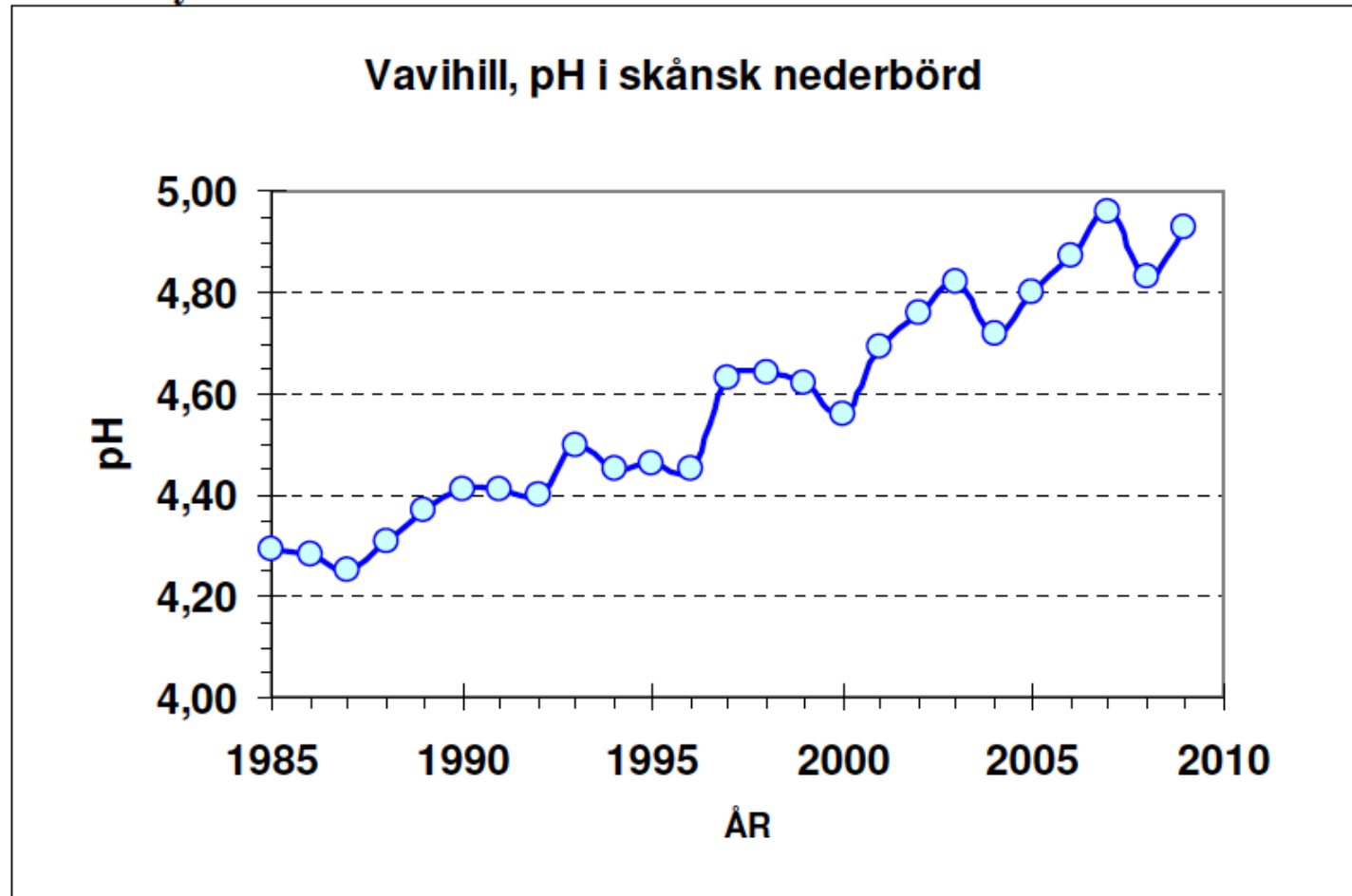
Concentrations of aerosol particles (with sulphates and nitrates as main constituents) can sometimes exceed current air quality limit values.

Acid deposition still exceeds what ecosystems can manage in the long-term (critical load).

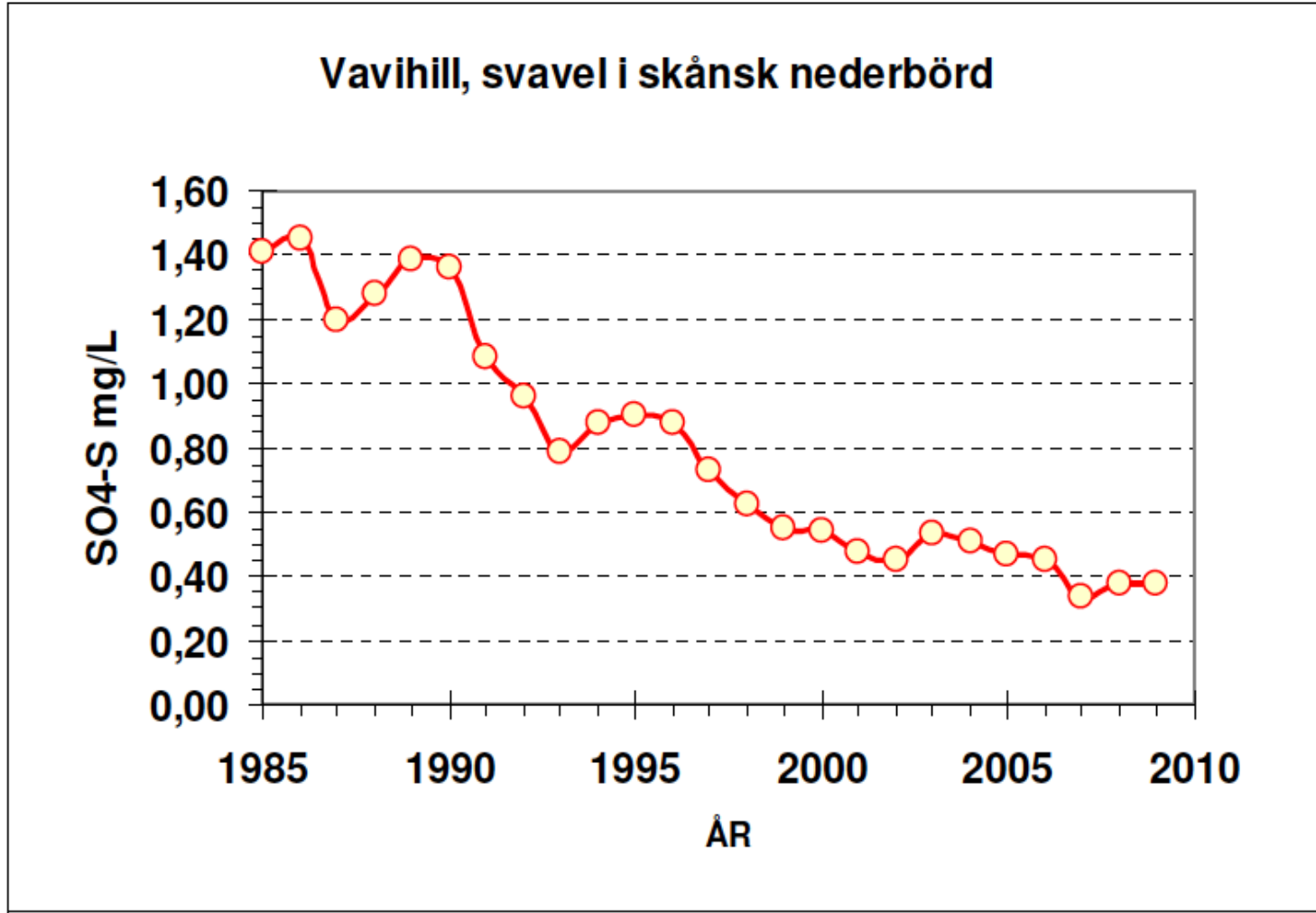


# Trend in pH in precipitation - Annual averages

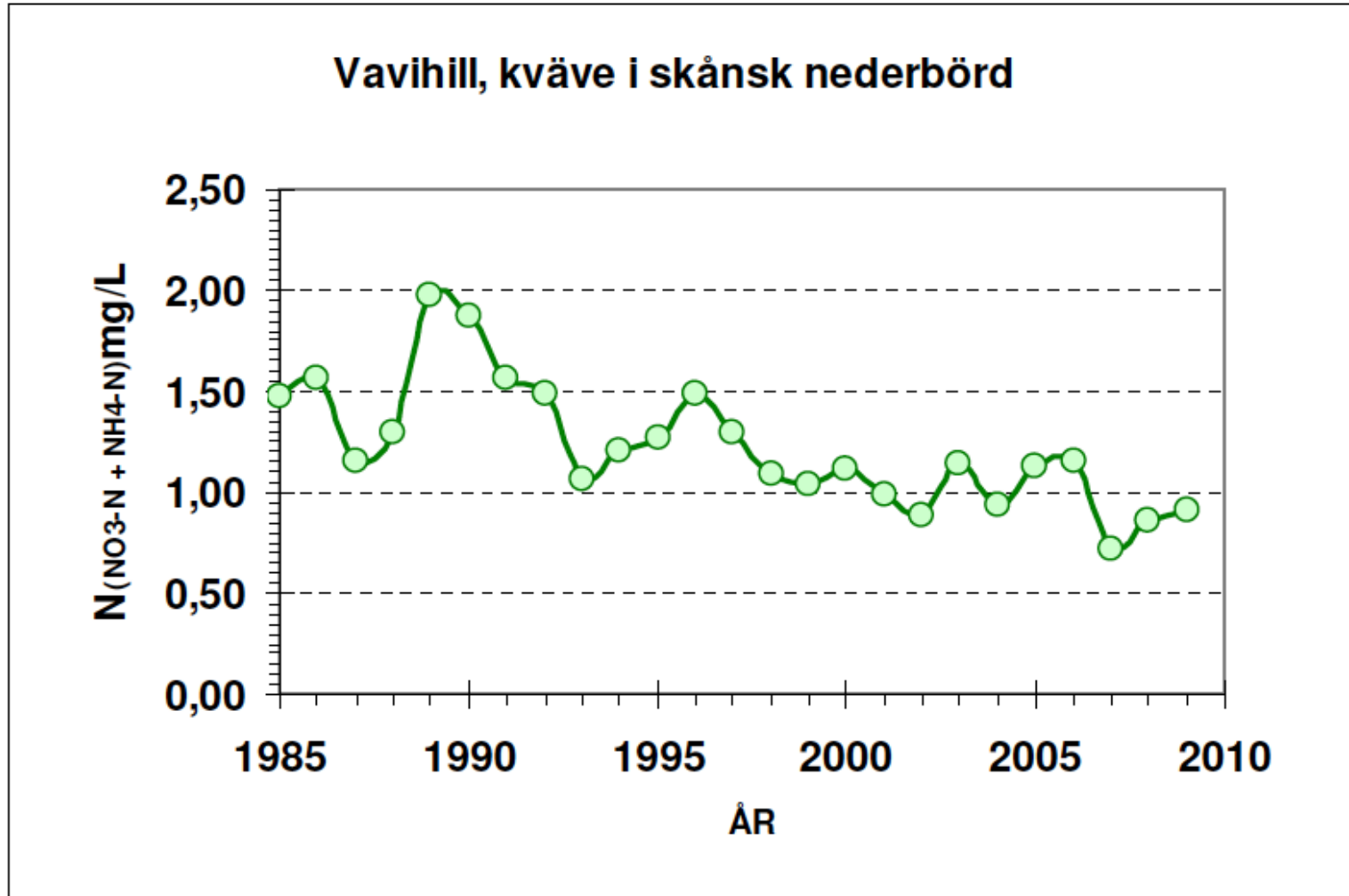
"Neutral" pH in the atmosphere is currently 5.6.



# Trend in wet deposition of acidifying compounds



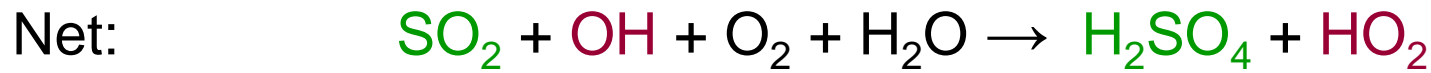
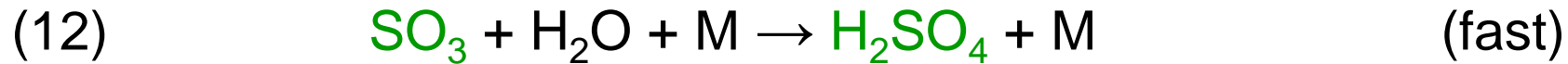
# Trend in wet deposition of acidifying compounds



# Oxidation of sulphur in the gas phase

Sulphur dioxide  $\text{SO}_2$  is emitted by combustion of fossil sulphur-containing fuels, and is oxidized to sulphuric acid.

Gas-phase oxidation proceeds via the hydroxyl radical  $\text{OH}$ :



$\text{H}_2\text{SO}_4$  is low volatile and water soluble and is removed from the gas phase by condensation onto aerosol particles and cloud droplets.

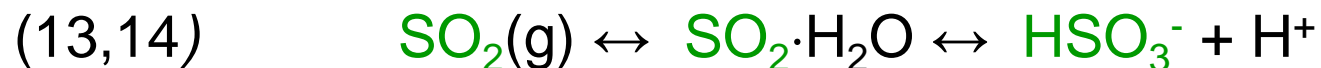
$\text{H}_2\text{SO}_4$  (sulphuric acid) is a **strong acid** and dissociates (splits into ions) in aqueous solution.



# Oxidation of sulphur in the aqueous phase

A considerable fraction of the oxidation of sulphur dioxide  $\text{SO}_2$  takes place in the aqueous phase.

$\text{SO}_2(\text{g})$  is dissolved in an aqueous solution **without being oxidized**:



$\text{SO}_2(\text{g})$ ,  $\text{HSO}_3^-$  (bisulphite ion) and  $\text{SO}_3^{2-}$  (sulphite ion) are all S(IV).

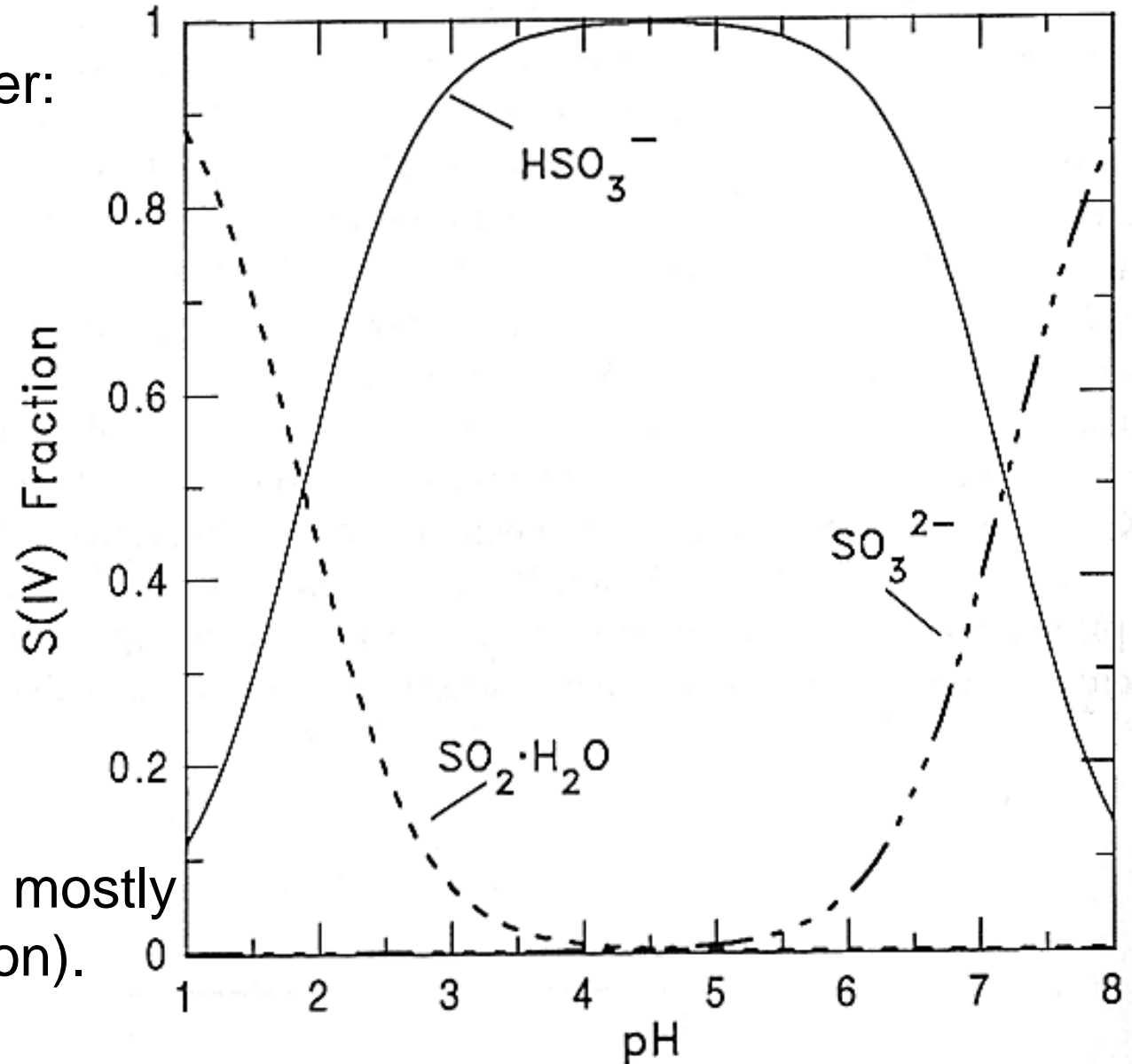
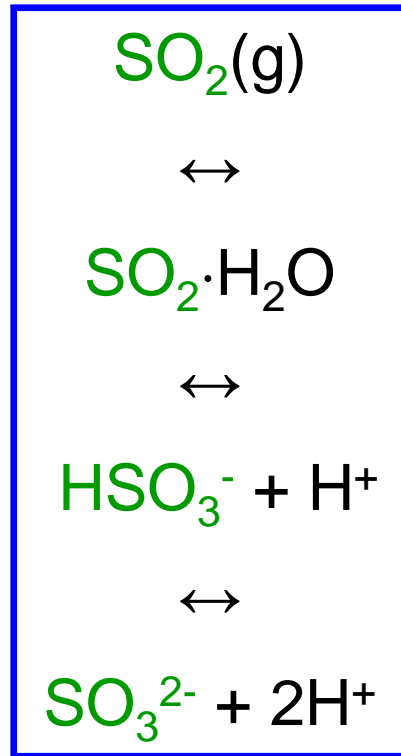
As  $\text{SO}_2(\text{g})$  dissolves in water,  $\text{H}^+$  ions are released and acidify the solution, but the process is completely reversible and will not permanently acidify the aqueous solution (no oxidation).

$\text{SO}_2$  returns to the gas phase as the cloud droplet or the aerosol particle dries out.



# Oxidation of sulphur in the aqueous phase

S(IV) dissolves in water:

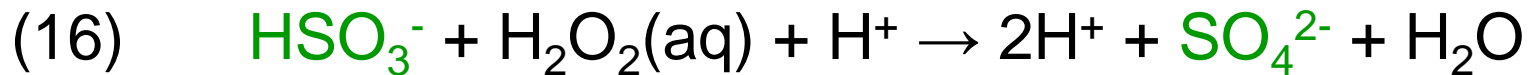
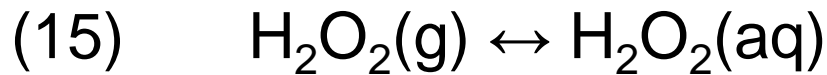


S(IV) in aqueous solution mostly as  $\text{HSO}_3^-$  (bisulphite ion).



# Oxidation of sulphur in the aqueous phase

**S(IV)** is **oxidized** in aqueous solution mainly by  $\text{H}_2\text{O}_2$ .  
( $\text{H}_2\text{O}_2$  = hydrogen peroxide, very water-soluble)



The oxidation is acid-catalyzed (requires  $\text{H}^+$ ) which makes this **S(IV)** oxidation pathway efficient also at low pH.

The reaction is very fast. Either all **S(IV)** or all  $\text{H}_2\text{O}_2$  is titrated out in the aqueous solution.

Hydrogen peroxide  $\text{H}_2\text{O}_2$  is formed via  $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$  in the gas phase (termination of  $\text{HO}_x$  radicals).



# Nitrate N(V) formation

Nitric acid form in the gas-phase via oxidation of  $\text{NO}_2$  with OH:



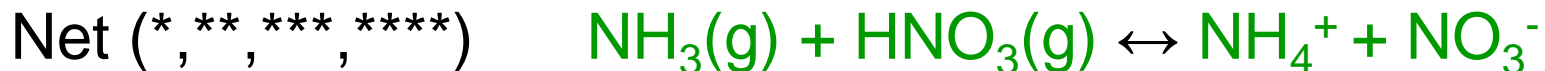
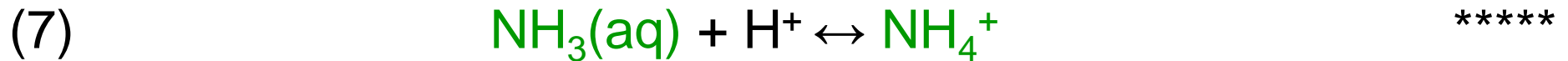
$\text{HNO}_3(\text{g})$  is dissolve in aquesous solutions:



In cloud and rain droplets the dissociation of  $\text{HNO}_3(\text{aq})$  is complete and  $\text{HNO}_3(\text{g})$  is taken up efficiently.

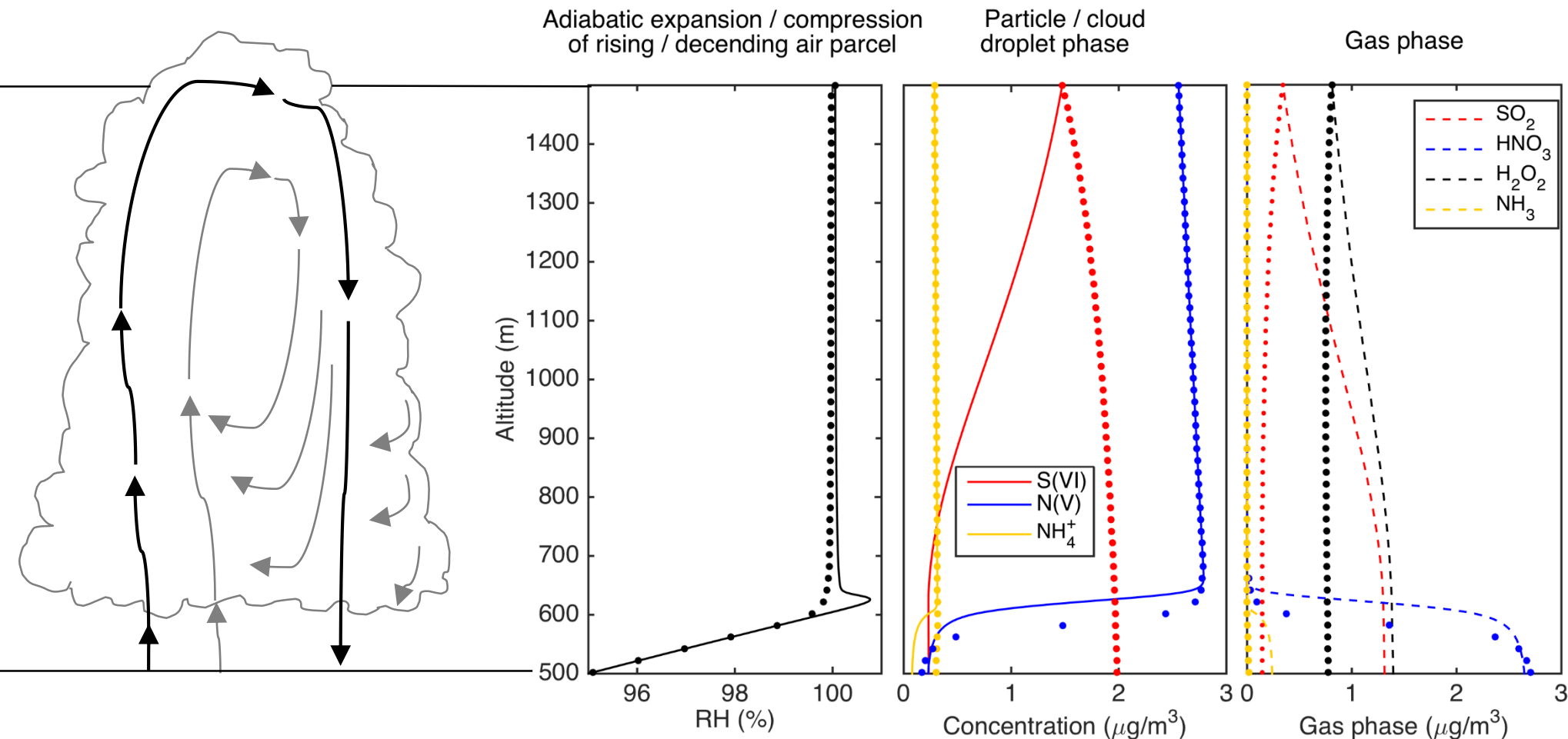
In aerosol particle nitrate formation requires bases which can neutralize the concentrated acidic aqueous solution.

Ammonia ( $\text{NH}_3$ ) scavenges  $\text{H}^+$  in aqueous solutions:



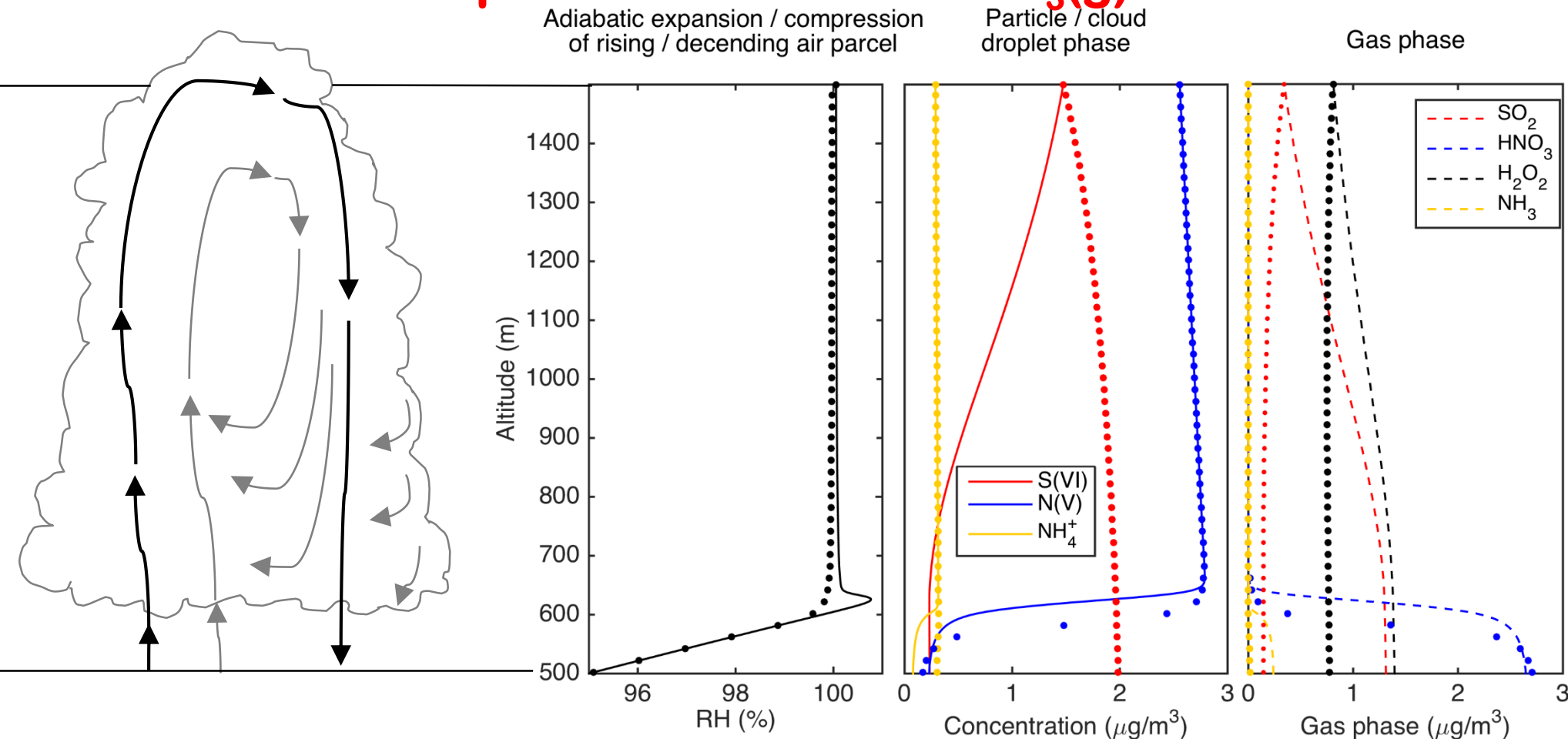
# Oxidation of sulphur in the cloud aqueous phase

**Net effect: More S(VI) in the aerosol particles and less SO<sub>2</sub>(g)**



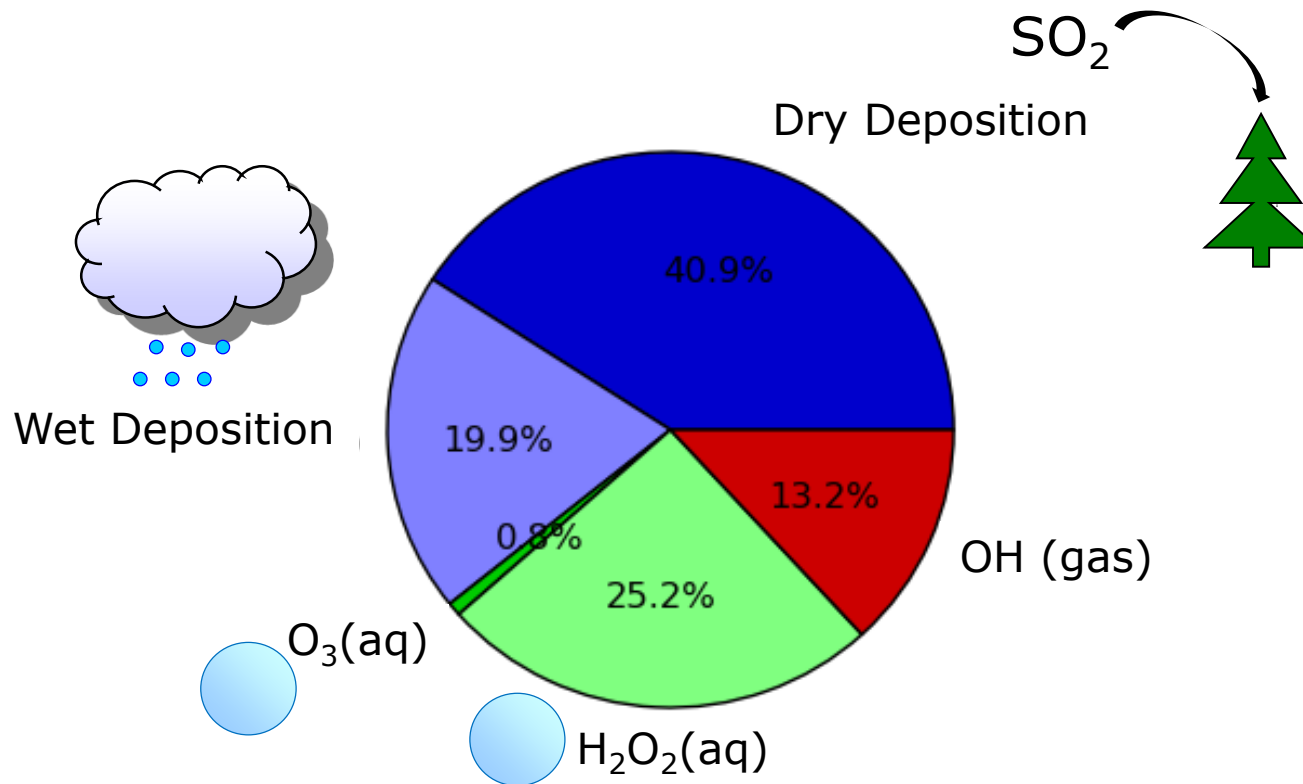
# Dissolution of $\text{HNO}_3$ and formation of $\text{N(V)}$ in the cloud aqueous phase

**Non-precipitating clouds have no net effect on the  $\text{N(V)}$  aerosol particle content or  $\text{HNO}_3(\text{g})$**



**But if the cloud forms precipitation  $\text{N(V)}$ ,  $\text{HNO}_3(\text{g})$ ,  $\text{S(VI)}$ ,  $\text{SO}_2(\text{g})$ ,  $\text{N(III)}$  ( $\text{NH}_4^+$ ) and  $\text{NH}_3(\text{g})$  and are lost by wet deposition**

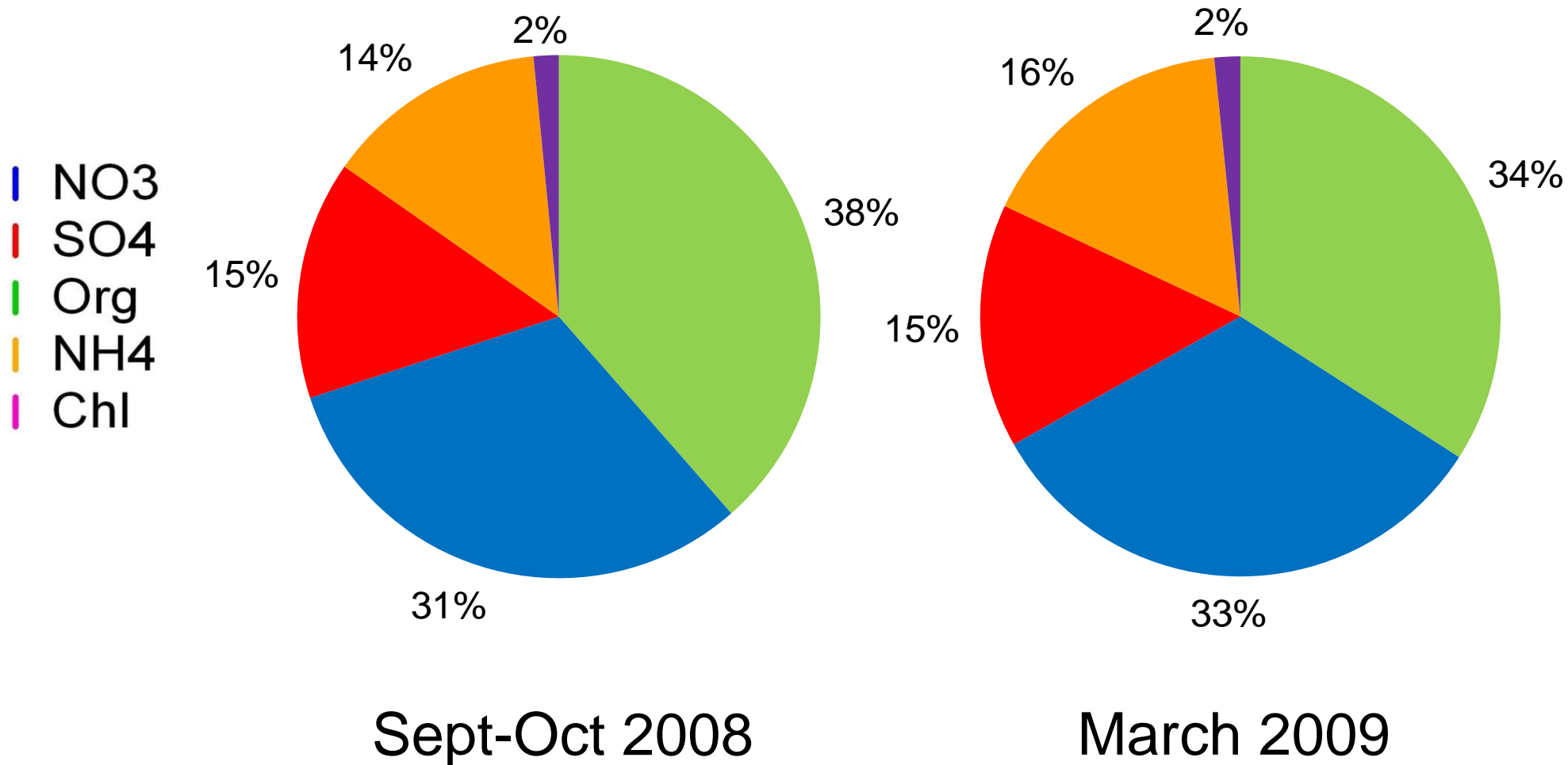
# Pathways of SO<sub>2</sub> loss (GEOSS-CHEM Global chemistry model)



Fractional contributions of SO<sub>2</sub>-loss pathways predicted by the global atmospheric chemistry model GEOS-Chem.

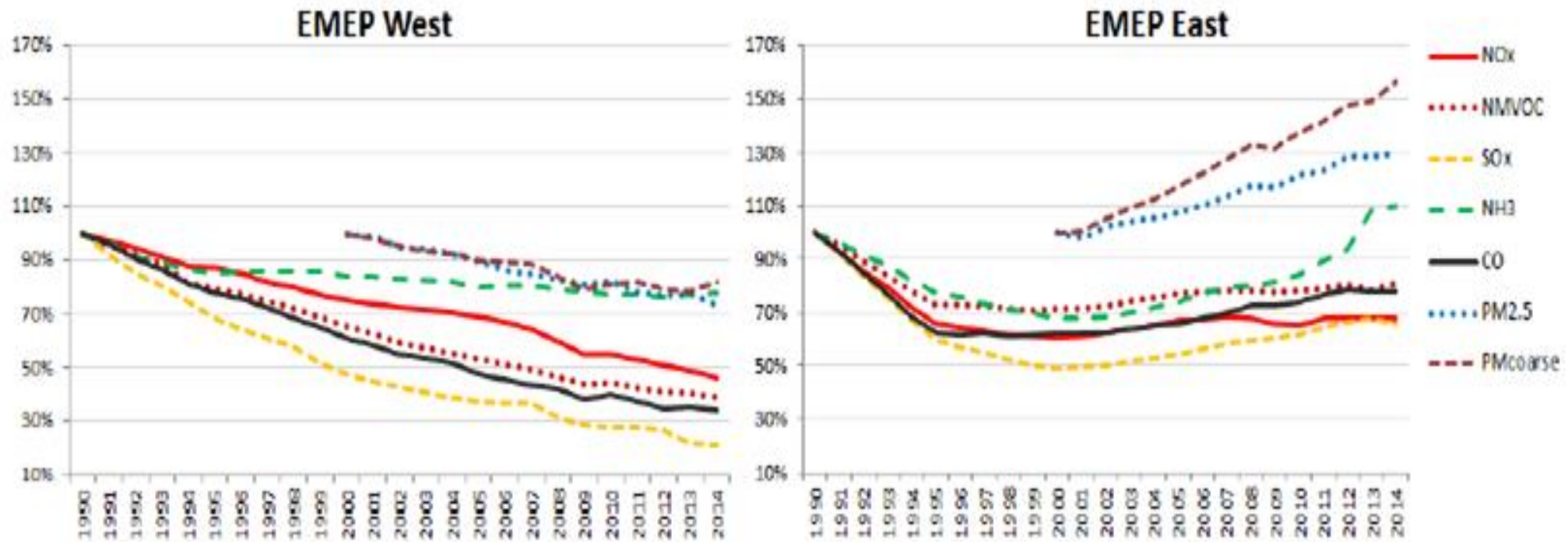
Pierce et al, ACP(2012)

# Aerosol Mass Spectrometer Measurements at Vavihill (S Sweden)



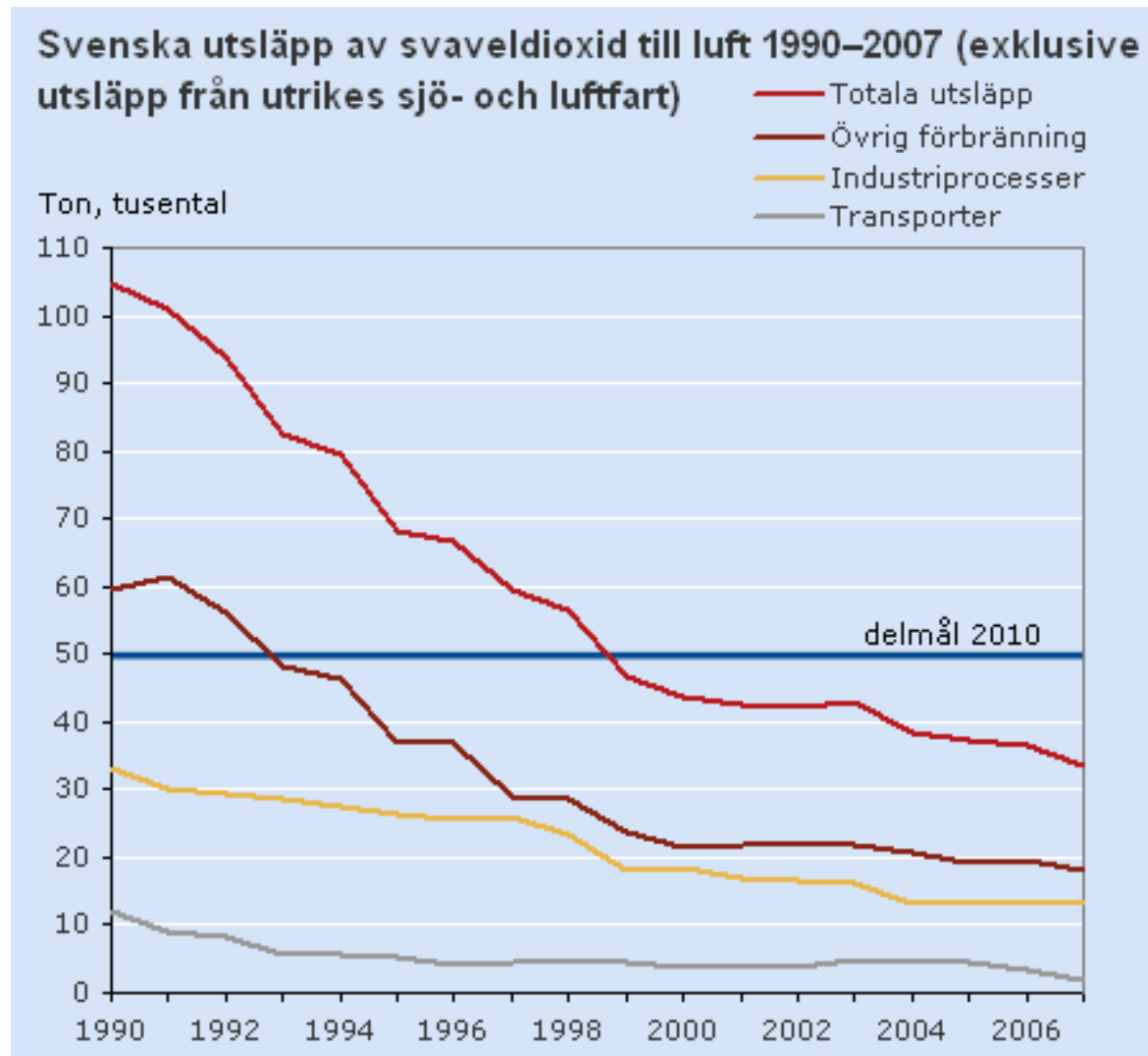
Crippa et al, ACP(2014)

# Trends in SO<sub>2</sub>, NO<sub>2</sub> and NH<sub>3</sub> emissions in Europe EMEP emission inventory



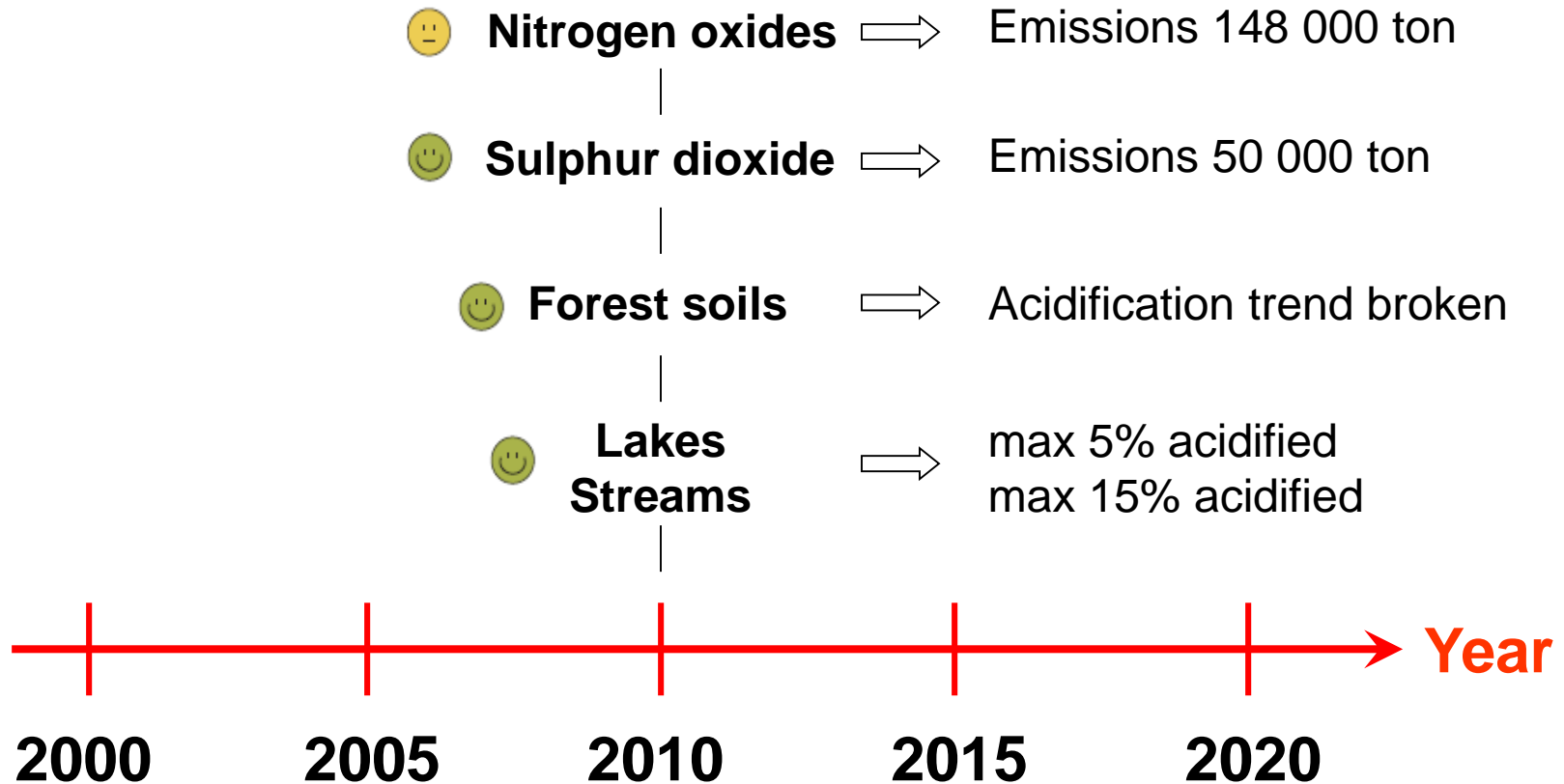
Estimated total emissions of SO<sub>x</sub>(SO<sub>2</sub>), NO<sub>x</sub>, NH<sub>3</sub>, NMVOC, CO, PM2.5, PMcoarse for West Europe and East Europe for the period 1990-2014.

# Trends in SO<sub>2</sub> emissions in Sweden





## Environmental Quality Objective 3: Natural Acidification Only

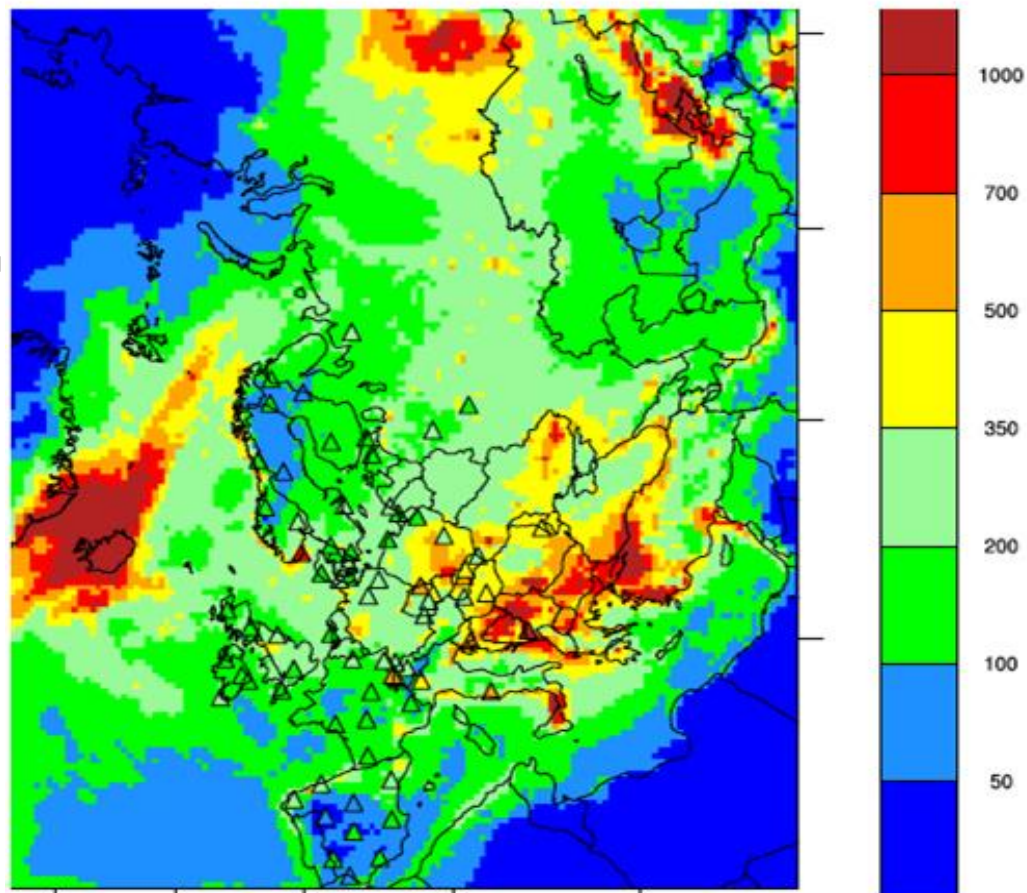
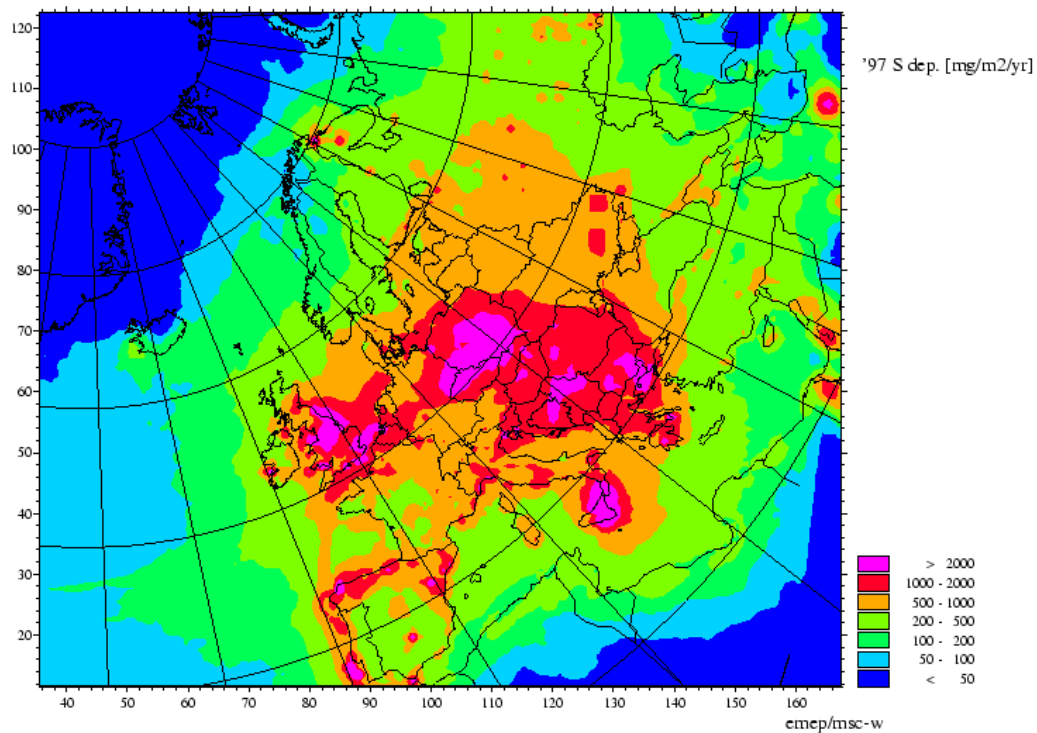


*This objective will be very difficult or not possible to achieve by 2020, even if further action is taken. The trend in the state of the environment is positive.*

# EMEP Eulerian Acid Deposition model - Sulphur

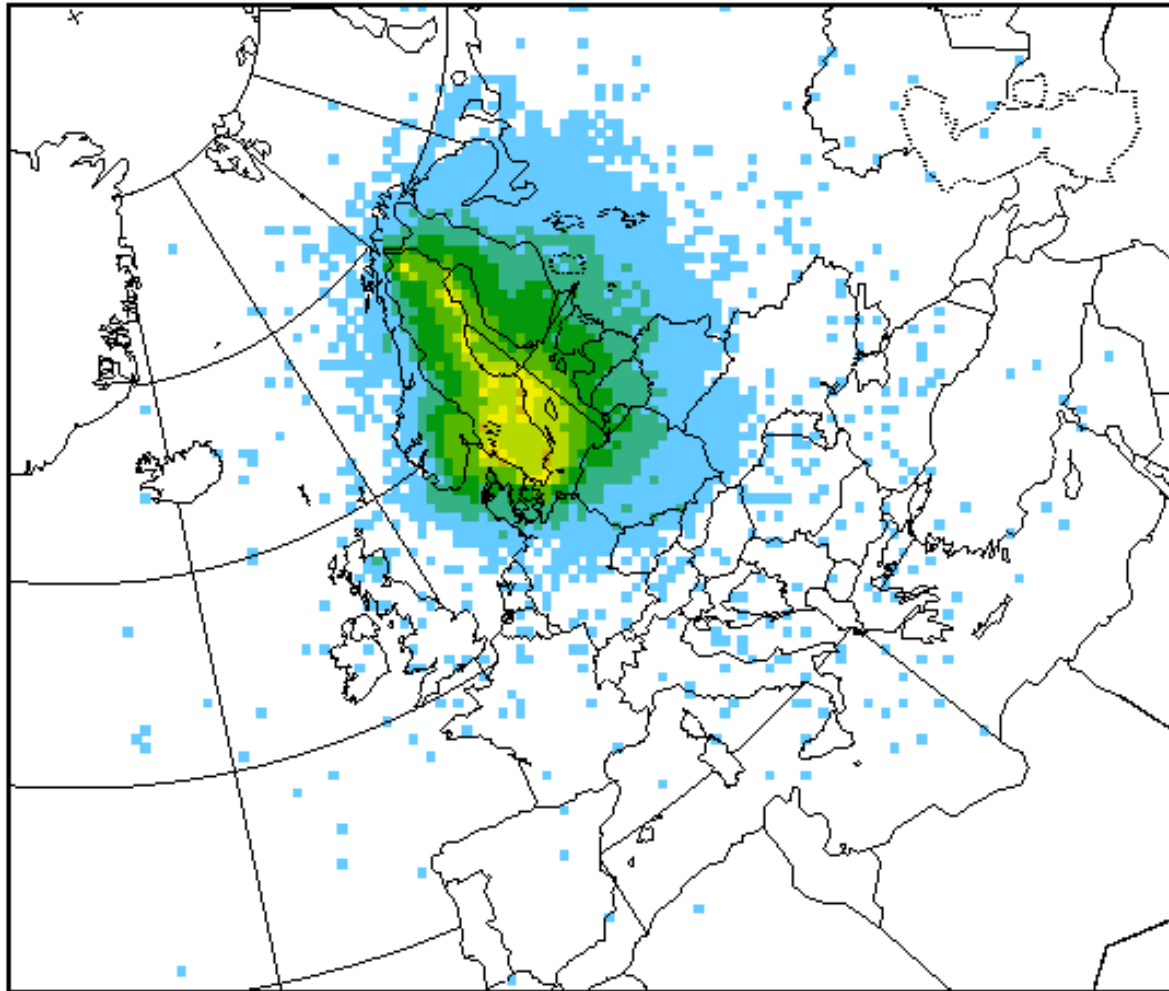
2014

1997



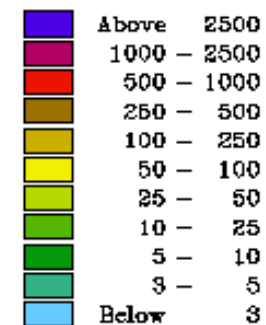
# EMEP Eulerian Acid Deposition model - Sulphur

1997 deposition of oxidized sulphur from Sweden



Deposition of oxidized sulphur from Swedish sources 1997

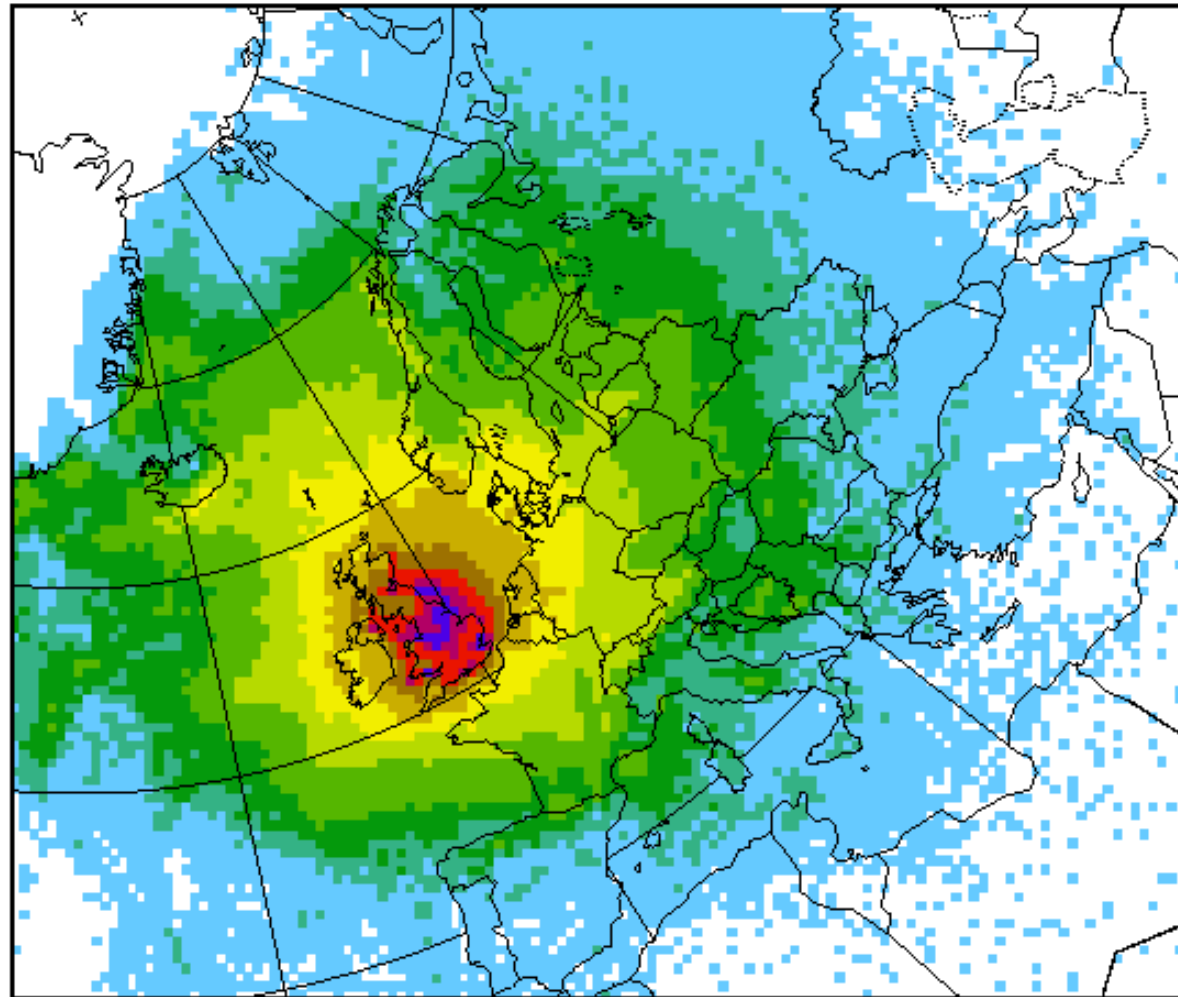
Unit: ( $\mu\text{g-S} / \text{m}^2$ )



emep/msc-w

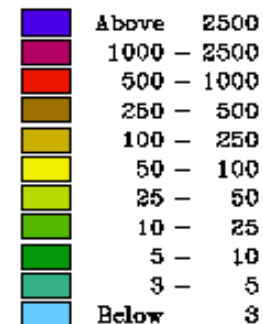
# EMEP Eulerian Acid Deposition model - Sulphur

1997 deposition of oxidized sulphur from United Kingdom



Deposition of oxidized sulphur from British sources 1997

Unit: ( $\mu\text{g-S} / \text{m}^2$ )



emep/msc-w

# Critical load – acidification, eutrofication

**Definition** (Nilsson and Grennfelt, 1988):

”The threshold below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge is called the **critical load.**”

**Critical load** (*kritisk belastning*) for acidification, eutrofication

Defines a total **deposition which is sustainable in the long-term.**

Can be expressed in many ways.

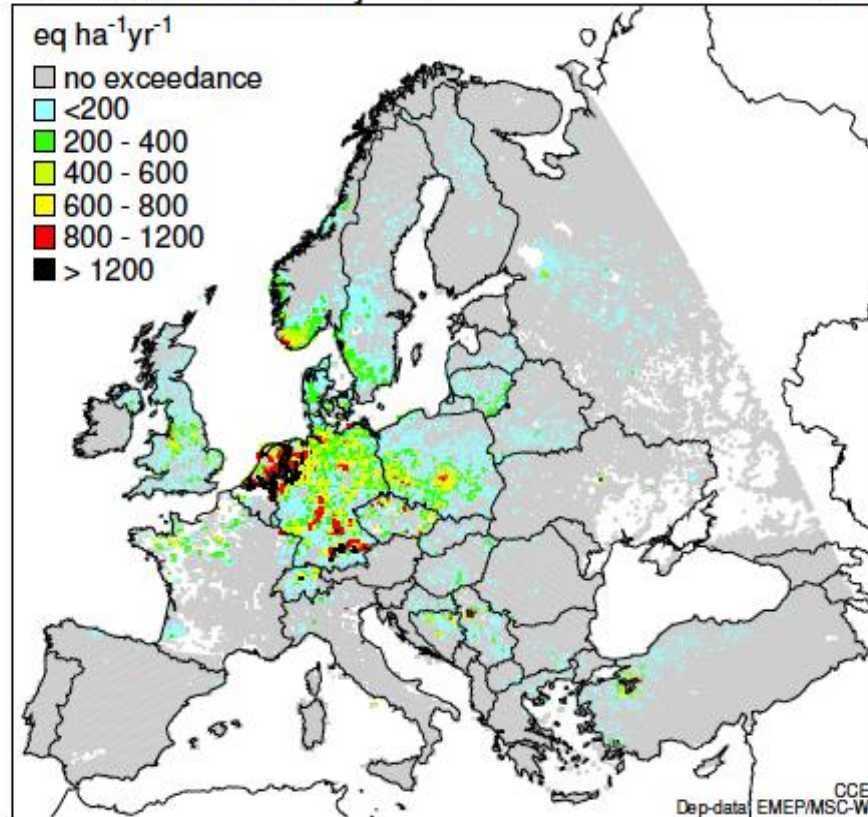
Ex: The 2-percentile for critical load is the deposition of acidifying (or eutrofying) compounds at which 98% of all ecosystems are protected in the long-term.



# Exceedence of critical load

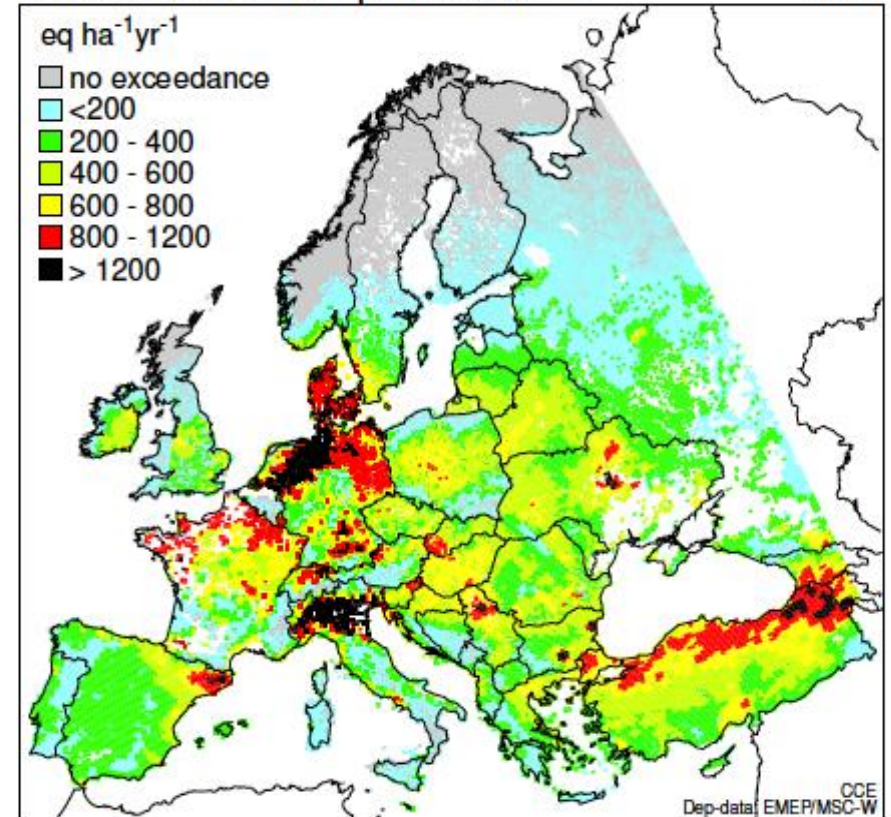
The critical load given as the 2- percentile (protects 98% of all ecosystems) (equivalents / ha / yr)

Exceedance of acidity CLs 2014



(c) Acidification, 0.250° × 0.125° grid

Exceedance of eutrophication CLs 2014



(d) Eutrophication, 0.250° × 0.125° grid