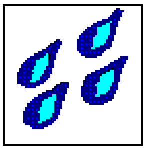
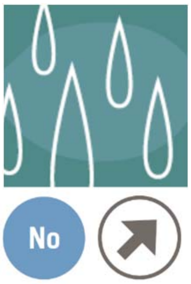


Atmospheric chemistry
Acidification

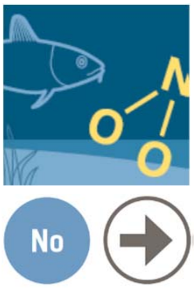
Erik Swietlicki
Avd. för Kärnfysik
Fysiska institutionen
Lunds universitet



NATURAL ACIDIFICATION ONLY

The acidifying effects of deposition and land use must not exceed the limits that can be tolerated by soil and water. In addition, deposition of acidifying substances must not increase the rate of corrosion of technical materials located in the ground, water main systems, archaeological objects and rock carvings.

Miljömål



ZERO EUTROPHICATION

Nutrient levels in soil and water must not be such that they adversely affect human health,
the conditions for biological diversity or the possibility of varied use of land and water.

http://www.miljomal.se/Global/24_las_mer/rapporter/malansvariga_myndigheter/2017/au2017-eng.pdf

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.

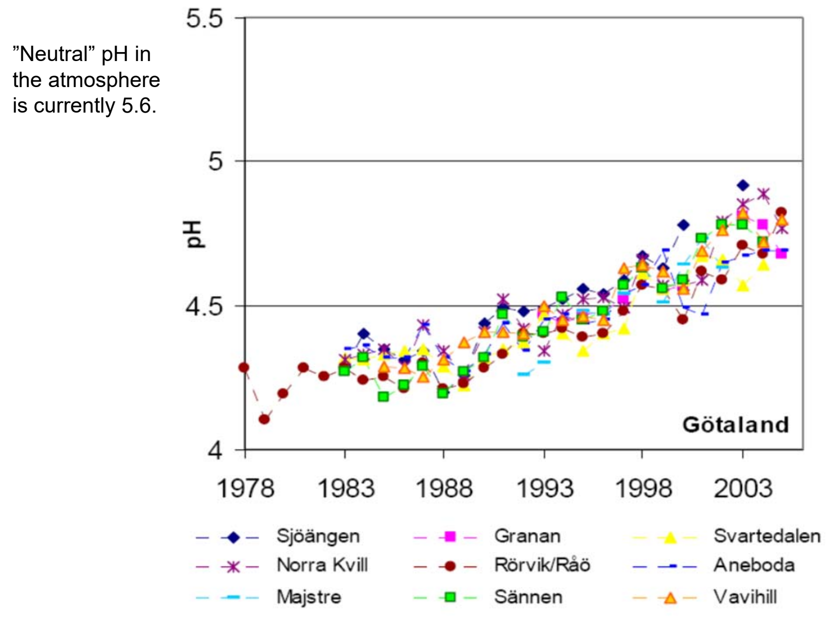
The acidic aerosol particles and cloud drops are deposited mainly as acid rain (wet deposition).

Levels of SO_2 in Sweden today are so low that they do not constitute a threat to human health.

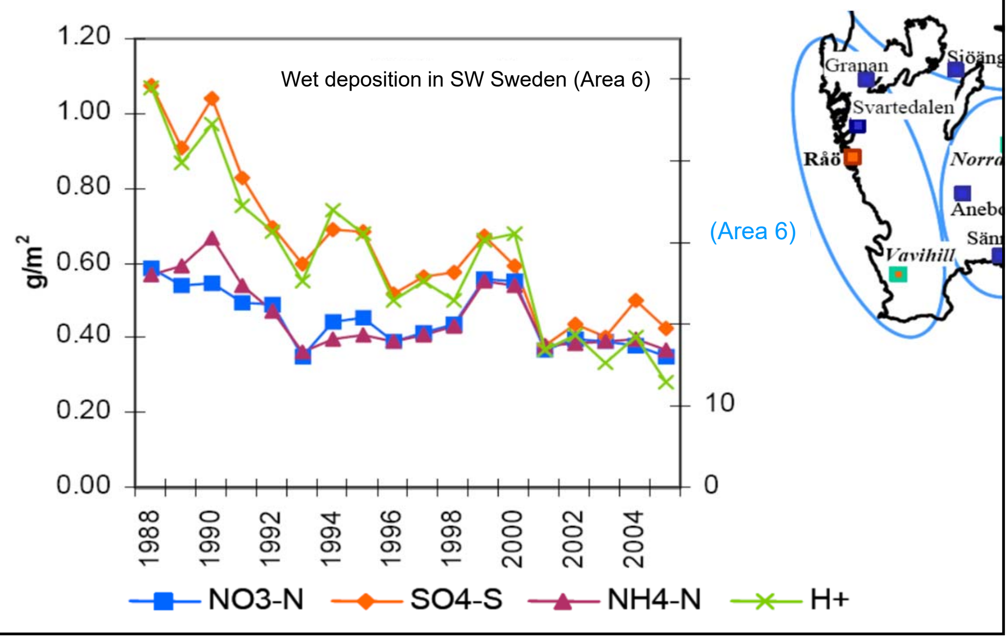
Concentrations of aerosol particles (with sulphates and nitrates as main constituents) can sometimes exceed current air quality limit values.

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

Trend in pH in precipitation - Annual averages



Trend in wet deposition of acidifying compounds



Oxidation of sulphur in the gas phase

Sulphur dioxide 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 OH:

(10) $SO_2 + OH + M \rightarrow HSO_3 + M$

(11) $HSO_3 + O_2 \rightarrow SO_3 + HO_2$ (fast)

(12) $SO_3 + H_2O + M \rightarrow H_2SO_4 + M$ (fast)

Net: $SO_2 + OH + O_2 + H_2O \rightarrow H_2SO_4 + HO_2$

H_2SO_4 (sulphuric acid) is a **strong acid** and dissociates (splits into ions) in aqueous solution.

$H_2SO_4(aq) \rightarrow 2H^+ + SO_4^{2-}$ as S(VI)

Compare nitrogen (nitric acid):

$HNO_3(aq) \rightarrow H^+ + NO_3^-$ as N(V)

Oxidation of sulphur in the aqueous phase

A considerable fraction of the oxidation of sulphur dioxide SO_2 takes place in the aqueous phase.

$SO_2(g)$ is dissolved in an aqueous solution **without being oxidized**:

(13,14) $SO_2(g) \Leftrightarrow SO_2{\cdot}H_2O \Leftrightarrow HSO_3^- + H^+ \Leftrightarrow SO_3^{2-} + 2H^+$

$SO_2(g)$, HSO_3^- (bisulphite ion) and SO_3^{2-} (sulphite ion) are all S(IV).

As $SO_2(g)$ dissolves in water, H^+ ions are released and acidify the solution, but the process is completely reversible and will not permanently acidify the aqueous solution (no oxidation).

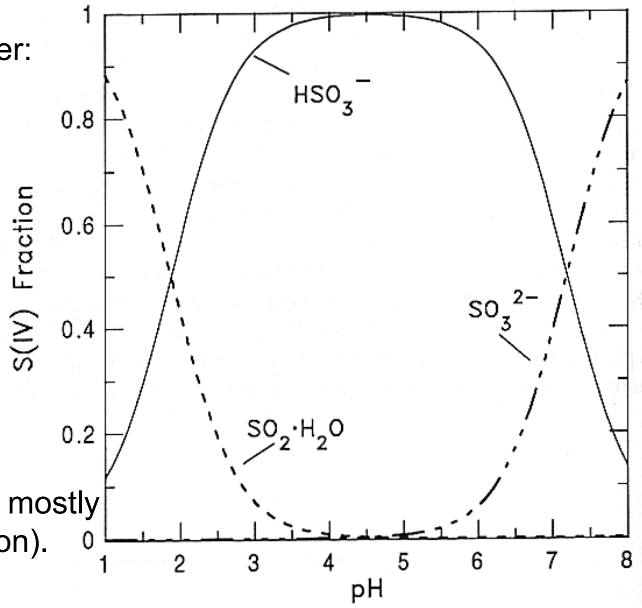
SO_2 returns to the gas phase as the cloud droplet or the aerosol particle dries out.

At normal pH (3-6), nearly all S(IV) in aqueous solution exists as HSO_3^- (bisulphite ion).

Oxidation of sulphur in the aqueous phase

S(IV) dissolves in water:

$SO_2(g)$
$\Leftrightarrow$
$SO_2 \cdot H_2O$
$\Leftrightarrow$
$HSO_3^- + H^+$
$\Leftrightarrow$
$SO_3^{2-} + 2H^+$



S(IV) in aqueous solution mostly as HSO_3^- (bisulphite ion).

Oxidation of sulphur in the aqueous phase

S(IV) is **oxidized** in aqueous solution mainly via $\boldsymbol{H_2O_2}$.
(H_2O_2 = hydrogen peroxide, very water-soluble)

(15) $H_2O_2(g) \Leftrightarrow H_2O_2(aq)$

(16) $HSO_3^- + H_2O_2(aq) + H^+ \Leftrightarrow 2H^+ + SO_4^{2-} + H_2O$

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

The reaction is very fast. Either all S(IV) or all H_2O_2 is titrated out in the aqueous solution.

Lack of hydrogen peroxide $H_2O_2(g)$ is often the limiting factor.

Hydrogen peroxide H_2O_2 is formed via $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ in the gas phase (termination of HO_x radicals).

Oxidation of sulphur in the aqueous phase

S(IV) is **oxidized** in aqueous solution

- Via hydrogen peroxide H_2O_2

  $HSO_3^- + H_2O_2(aq) + H^+ \Leftrightarrow$
  $2H^+ + SO_4^{2-} + H_2O$

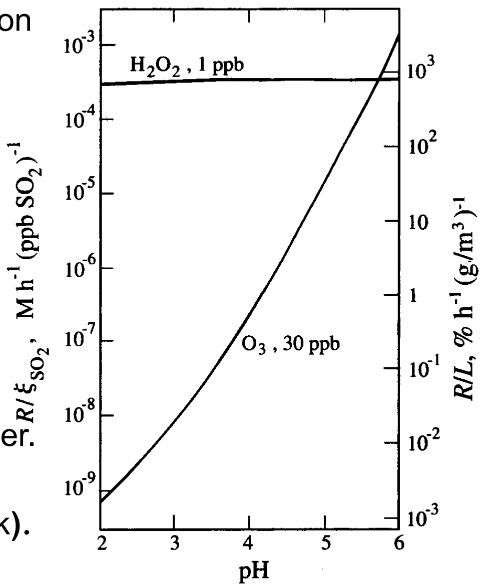
- Via ozone O_3

  $S(IV) + O_3(aq) \rightarrow$
  $S(VI) + 2H^+ + O_2$

- Catalyzed by transition metals

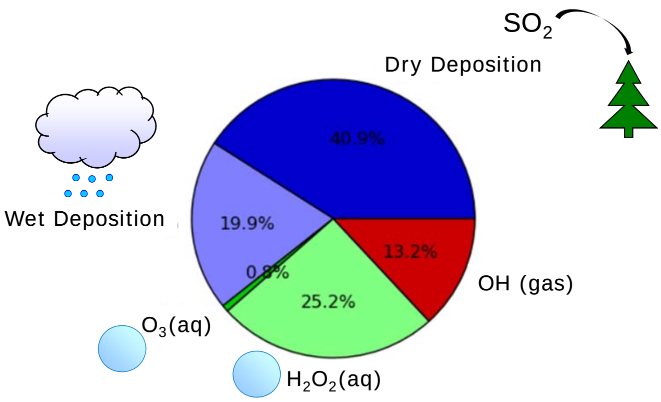
(e.g. Mn, Fe) nighttime, during winter.

$$-\frac{d}{dt}[SO_2] = \%/\mathrm{h} \qquad (\tau_{SO2} = \sim 1 \text{ week}).$$



Pathways of loss of SO_2 = S(IV)

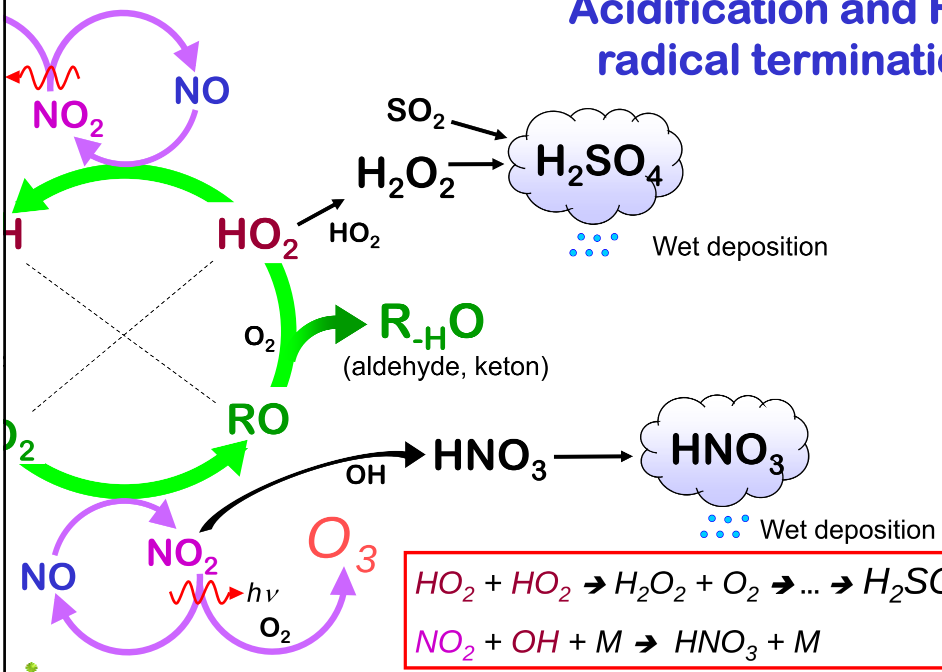
According to the GEOSS-CHEM Global chemistry model



Fractional contributions of SO_2-loss pathways predicted by the global atmospheric chemistry model GEOS-Chem.

Pierce et al, ACP(2012)

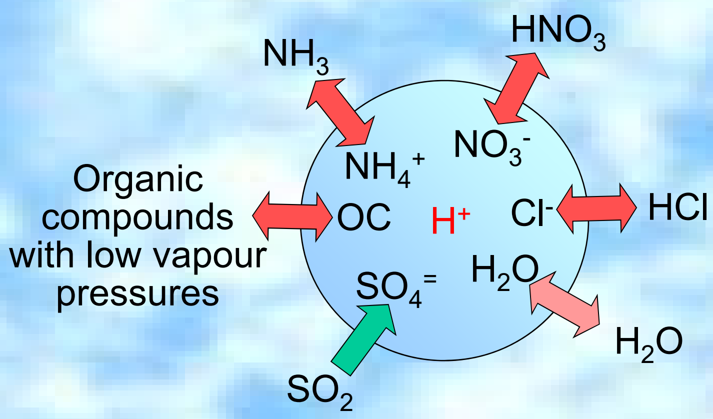
Acidification and HOx radical termination



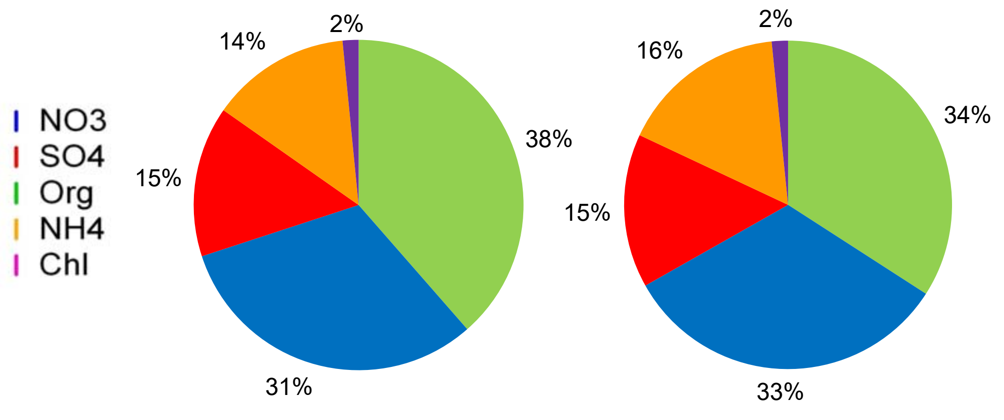
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \rightarrow \ldots \rightarrow H_2SO_4$

$NO_2 + OH + M \rightarrow HNO_3 + M$

Exchange between different phases



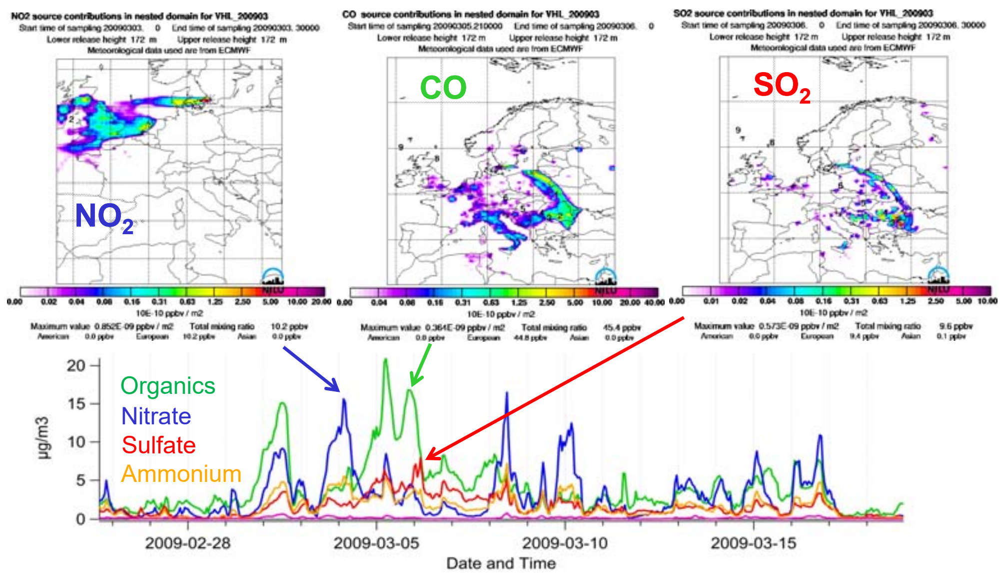
Aerosol Mass Spectrometer Measurements at Vavihill (S Sweden)



Sept-Oct 2008 March 2009

Crippa et al, ACP(2014)

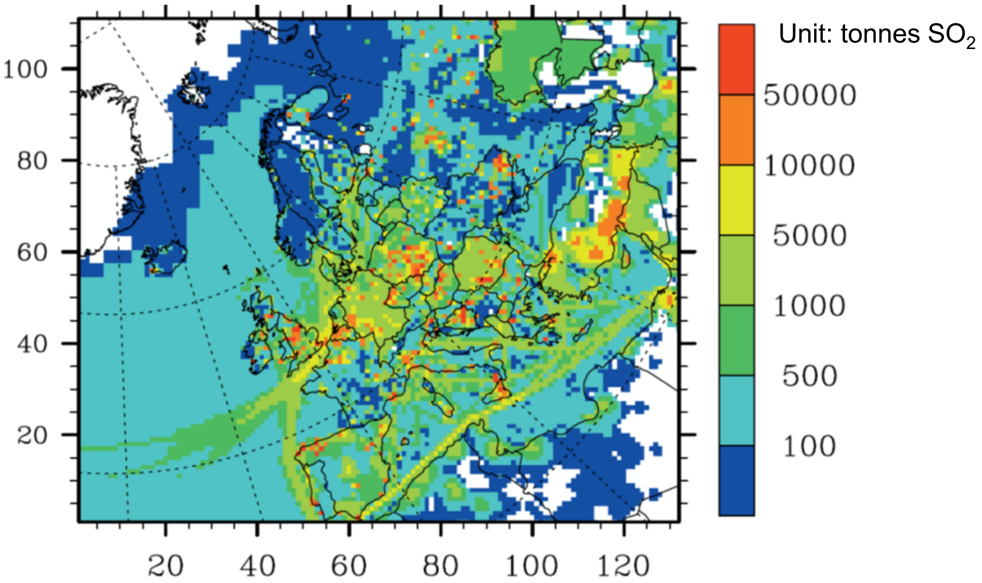
Aerosol measurements at Vavihill – Source regions



Measured with an Aerosol Mass Spectrometer

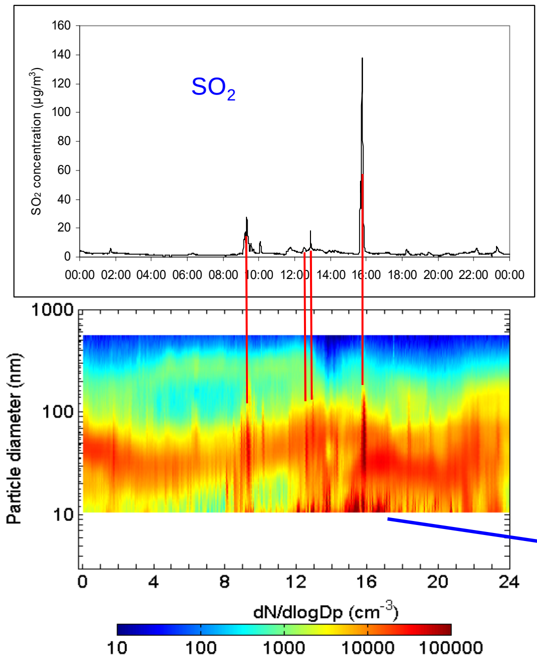
FLEXPART source region calculations: http://transport.nilu.no/flexpart-projects?stn=VHL

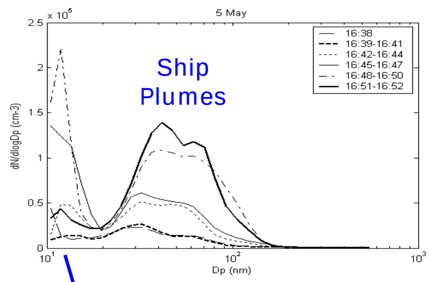
Emissions of SO_2 in 2000 (EMEP)



Ship Traffic Contribution - Malmö

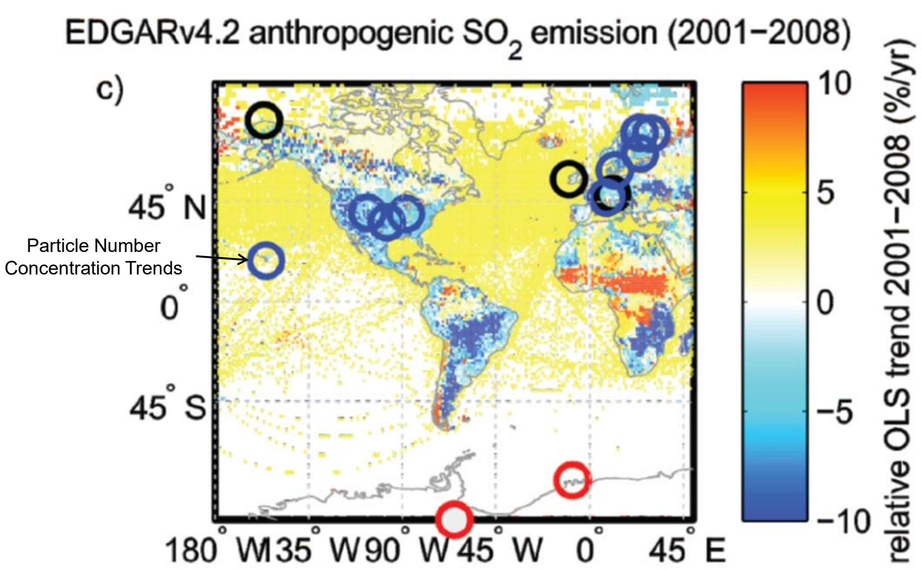
Ship plumes from Malmö City Harbour





Nucleation mode particles from homogeneous nucleation of H_2SO_4 + H_20 ?

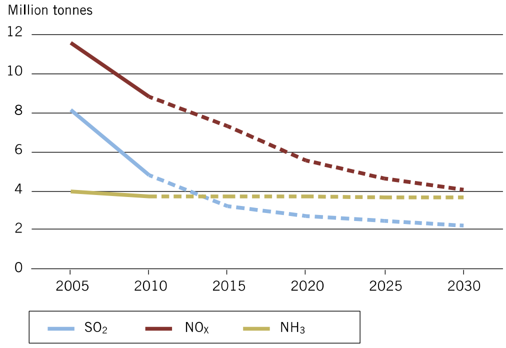
Trends in SO_2, emissions world-wide according to the EDGAR emission inventory



Asmi et al, ACP (2012)

Miljömål

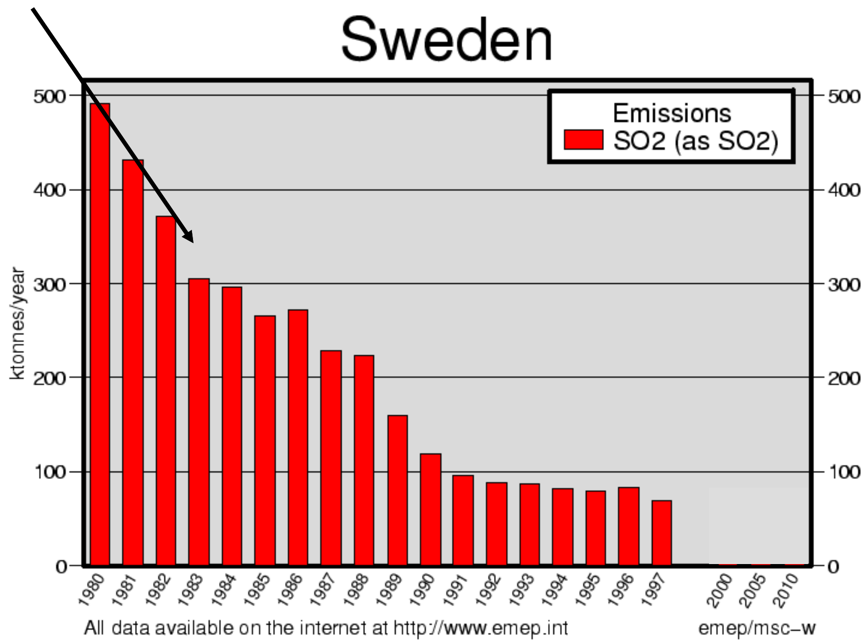
Emissions of acidifying pollutants in the EU 2005–2010, with projections to 2030



SOURCE: IIASA, ANALYSIS IN SUPPORT OF NEGOTIATIONS

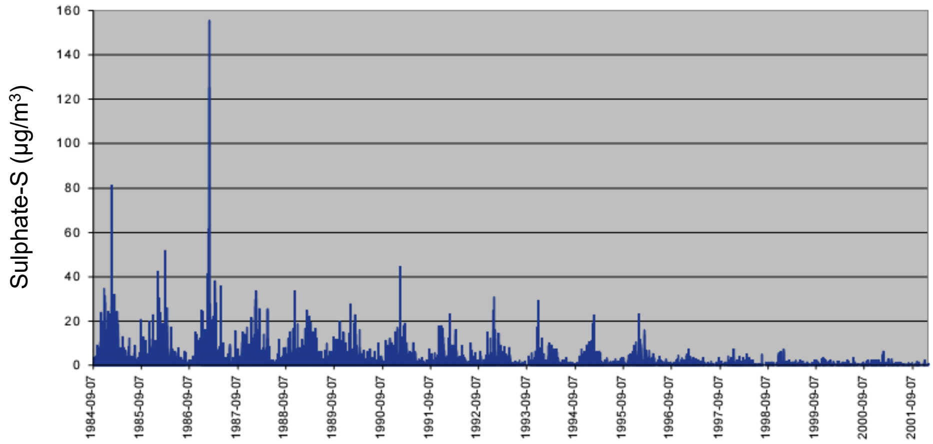
NATUR VÅRDS VERKET

SWEDISH ENVIRONMENTAL PROTECTION AGENCY

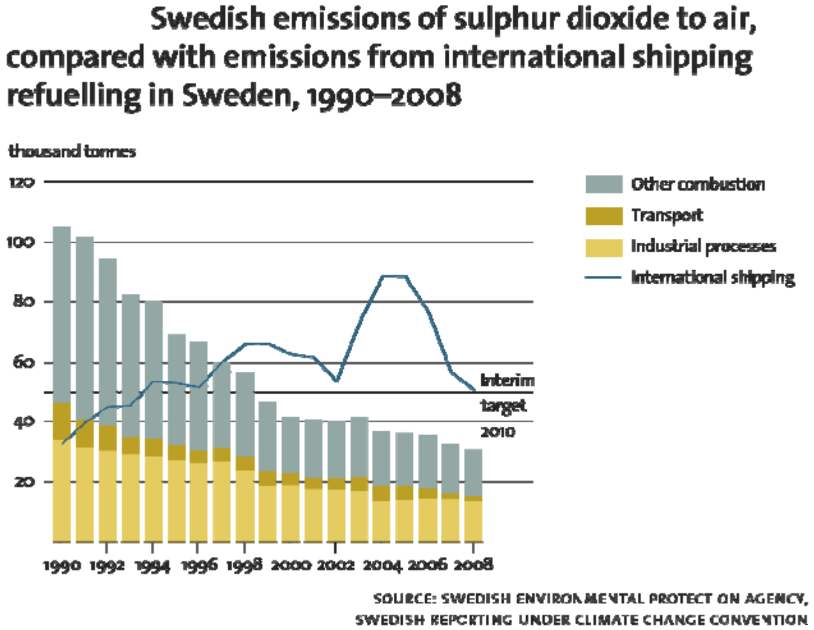


Daily averages of particulate sulphate SO_4^{2-} at Vavihill 1984-2001

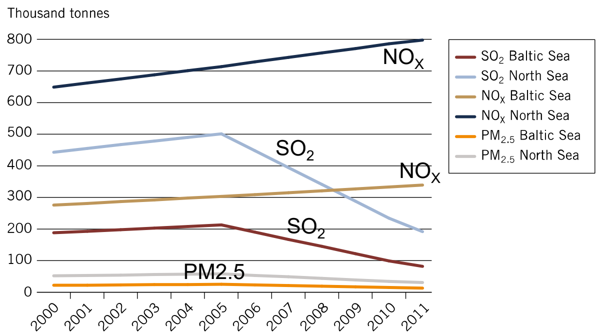
http://www.emep.int/assessment/Part2/219-228_Part2.pdf



Trends in SO_2 emissions in Sweden



Emissions of sulphur dioxide, nitrogen oxides and particulate matter (PM2.5) from international shipping on the Baltic and North Seas, 2000–2011

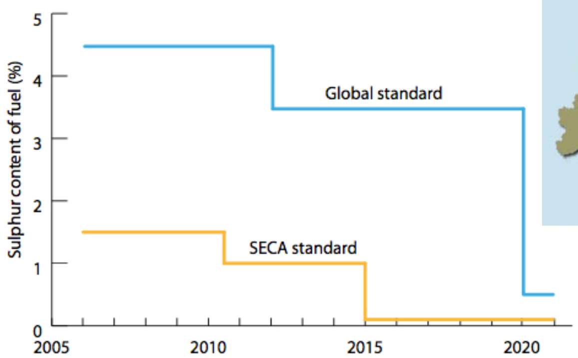


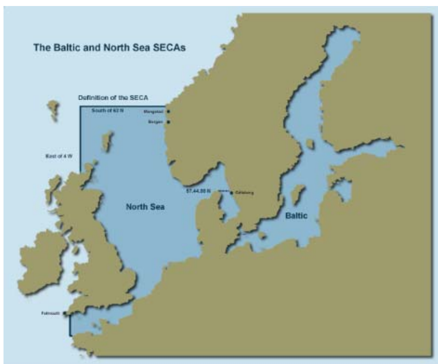
SOURCE: EUROPEAN MONITORING AND EVALUATION PROGRAMME (EMEP)

NATURVÅRDSVERKET
SWEDISH ENVIRONMENTAL PROTECTION AGENCY

Sulphur Emission Control Areas (SECAs) or Emission Control Areas (ECAs)

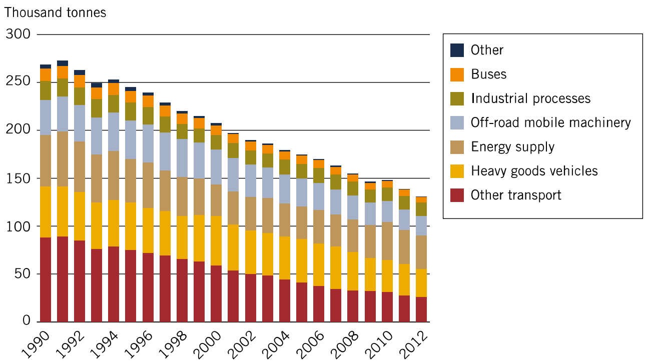
Sea areas in which stricter controls were established to minimize airborne emissions (SOx, NOx, VOC) from ships





Miljömål

Swedish emissions of nitrogen oxides to air, 1990–2012



SOURCE: SWEDISH ENVIRONMENTAL PROTECTION AGENCY, INTERNATIONAL REPORTING BY SWEDEN

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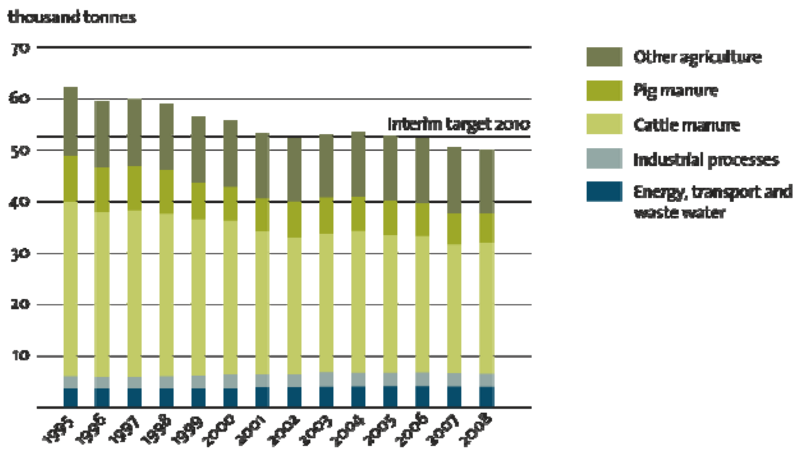
SWEDISH ENVIRONMENTAL PROTECTION AGENCY

FIGURE 7.4 Emissions of ammonia to air, 1995–2008



SOURCE: SWEDISH ENVIRONMENTAL PROTECTION AGENCY

Environmental Quality Objective 3: Natural Acidification Only

Nitrogen oxides ⇨ Emissions 148 000 ton

Sulphur dioxide ⇨ Emissions 50 000 ton

Forest soils ⇨ Acidification trend broken

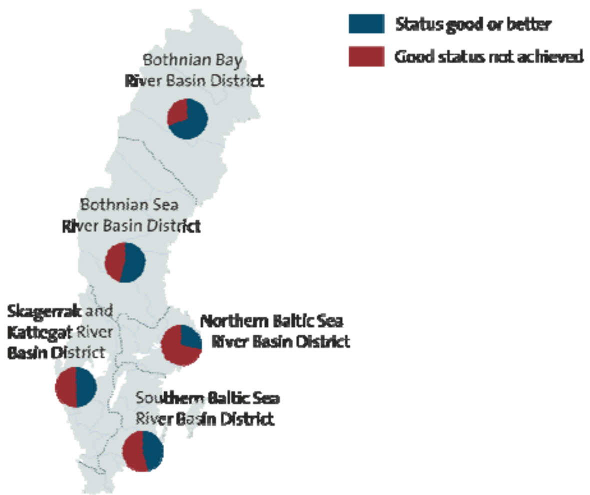
Lakes
Streams ⇨ max 5% acidified
max 15% acidified

Year

2000 2005 2010 2015 2020

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.

FIGURE 8.1 Ecological status of Sweden's lakes and watercourses under EU Water Framework Directive



SOURCE: RIVER BASIN DISTRICT AUTHORITIES, WISS (WATER INFORMATION SYSTEM SWEDEN) DATABASE

The Convention on Long-Range Transboundary Air Pollution CLRTAP

http://www.unece.org/env/lrtap/welcome.html

Now 51 Parties (countries)

Under UN-ECE

Since 1979 the CLRTAP has addressed some of the major environmental problems of the UNECE region through scientific collaboration and policy negotiation.

The Convention has been extended by **eight protocols** that identify specific measures to be taken by Parties to cut their emissions of air pollutants.

8th protocol (Gothenburg):
The **1999** Protocol to Abate Acidification, Eutrophication and Ground-level Ozone; 25 Parties.
Entered into force on 17 May 2005.

The aim of the Convention is that Parties shall endeavour to **limit** and, as far as possible, gradually reduce and **prevent air pollution including long-range transboundary air pollution**.

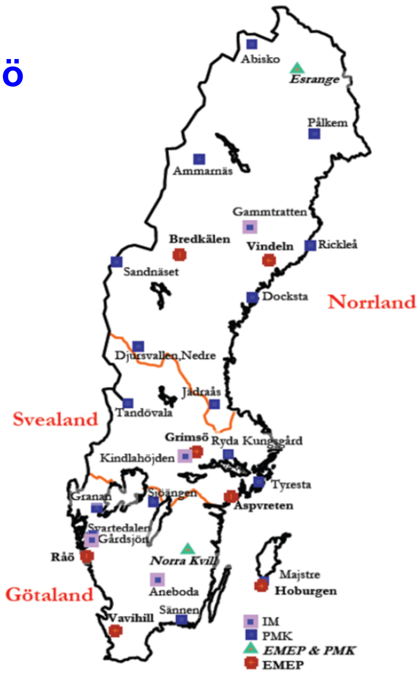
Currently, the Convention's priority activities include review and possible **revision of its most recent protocols**, **implementation** of the Convention and its protocols across the entire UNECE region.

Summary 31

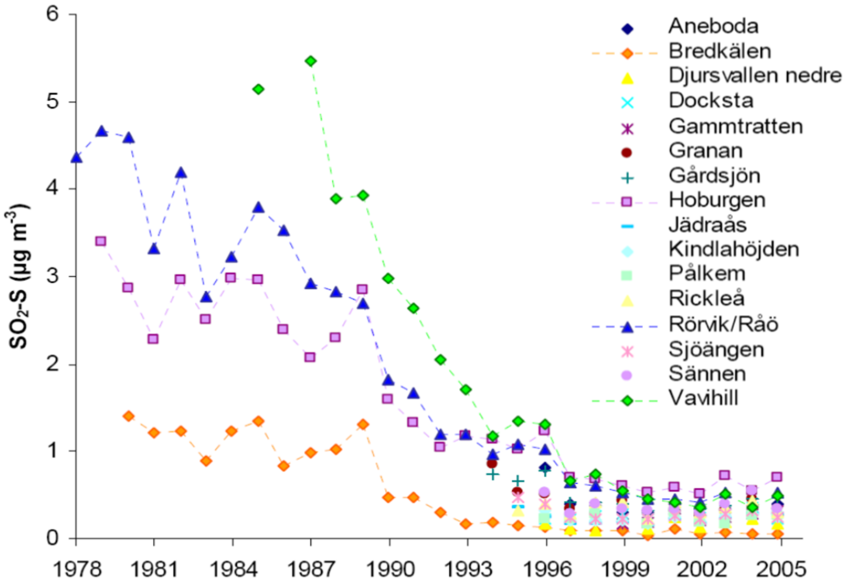
Miljöövervakning
Luft - Bakgrundsmiljö

Mätstationernas läge inom

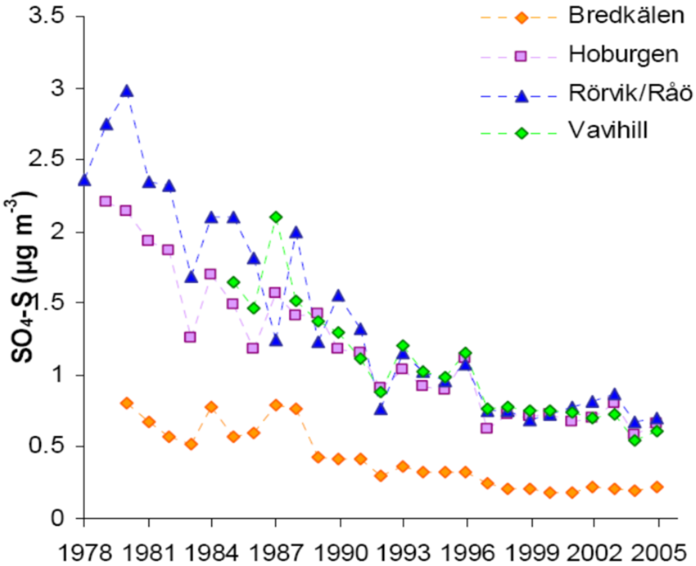
- EMEP
- IM (Integrated Monitoring)
- Luft- och nederbördskemiska nätet

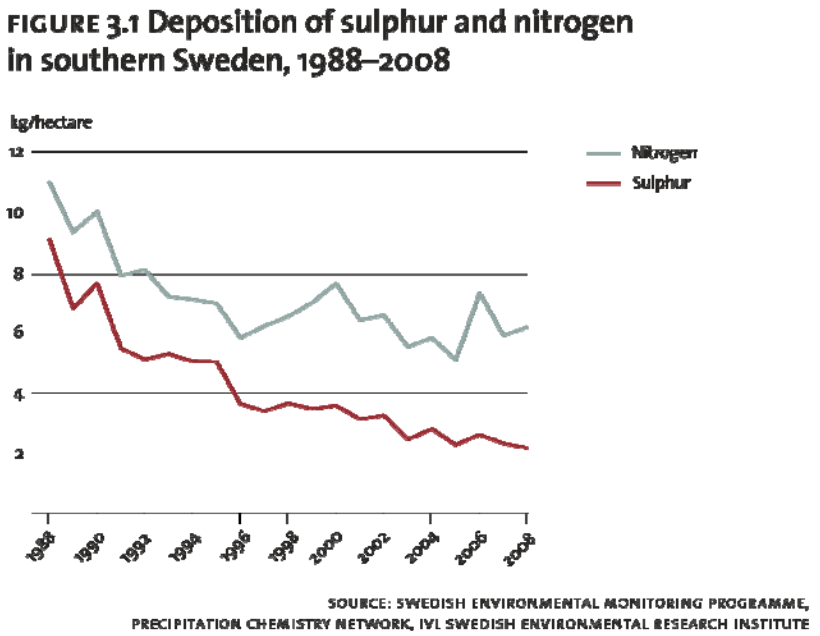


Annual averages of SO_2–S in air in Sweden

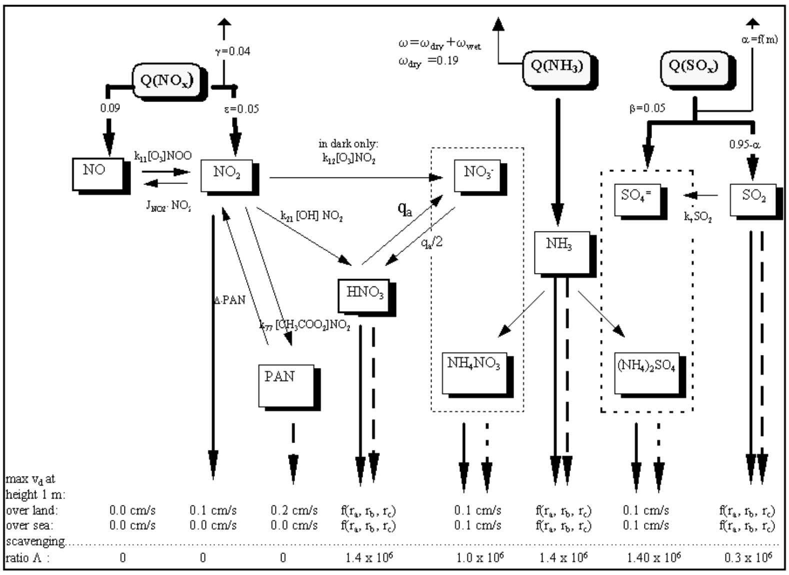


Annual averages of SO_4^{2-} – S in air in Sweden

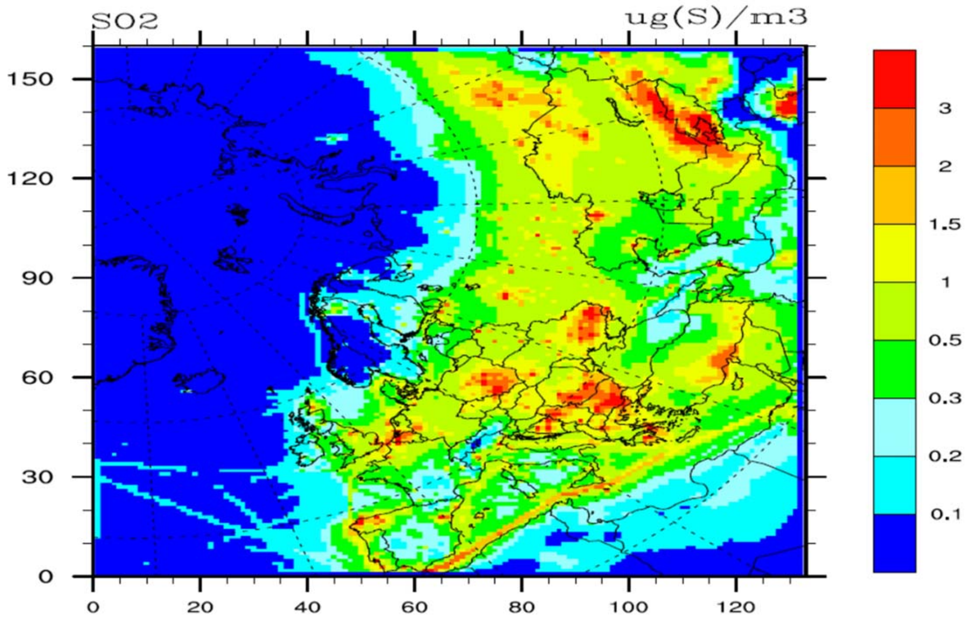




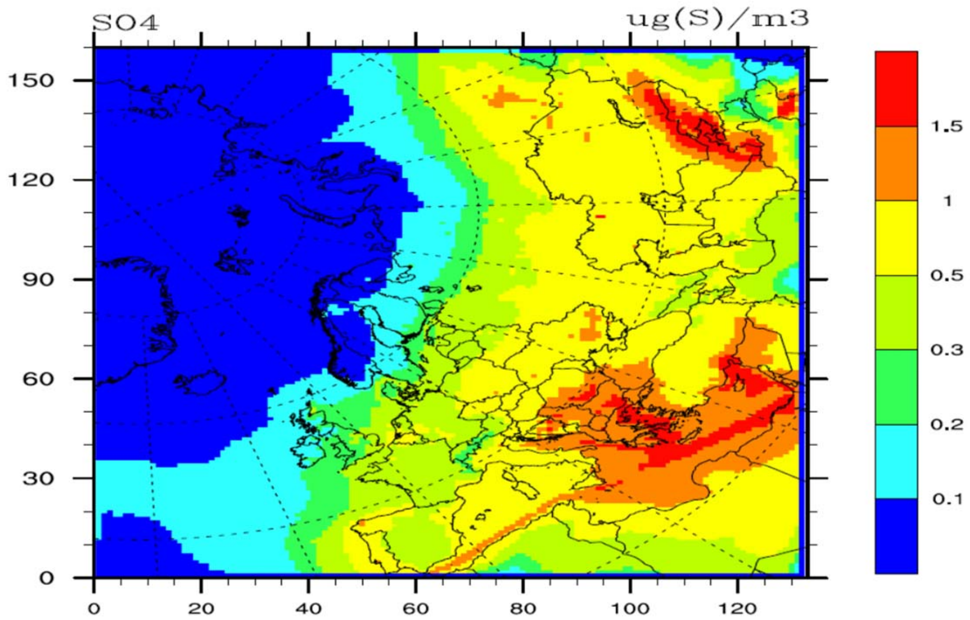
EMEP model – Inorganic chemistry



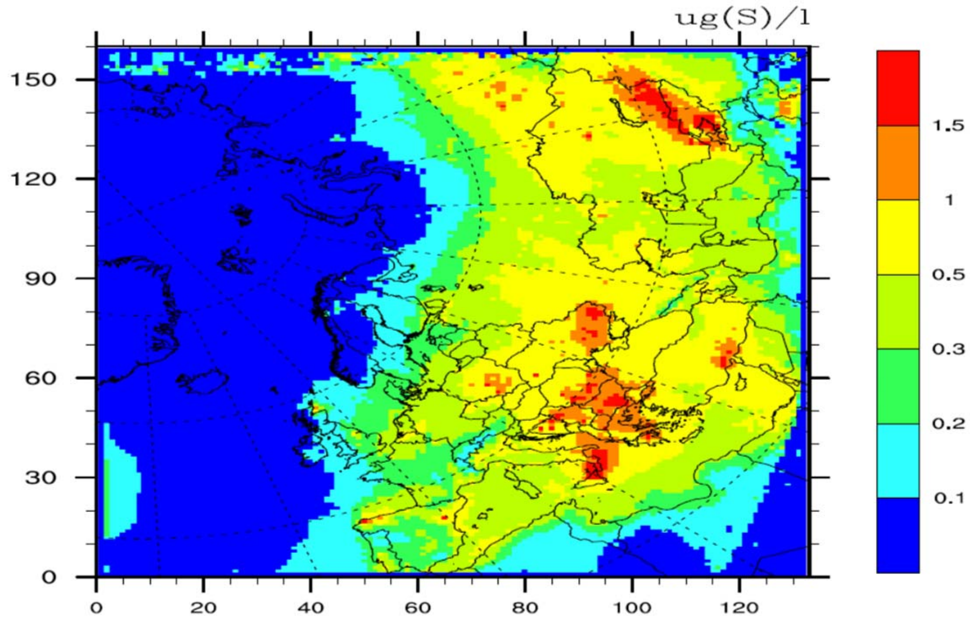
EMEP model – SO_2 in air (2007)



EMEP model – SO_4^{2-} in air (2007)

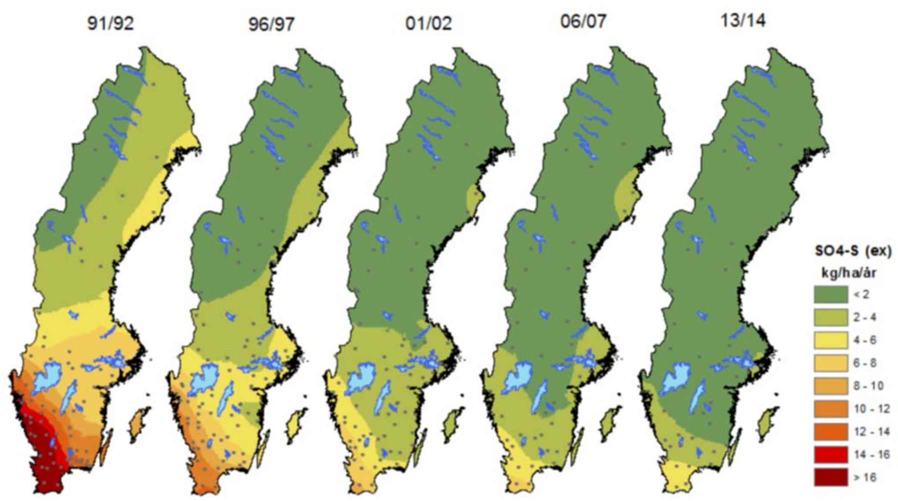


EMEP model – Sulphur deposition in precipitation (2007)



Sulphur deposition – A success story

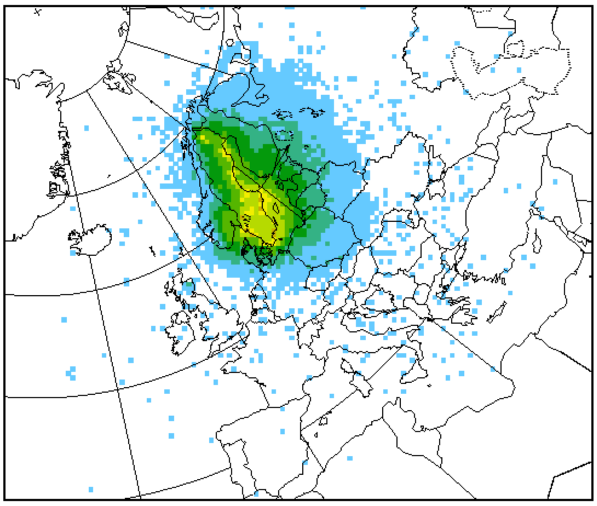
Estimated SO_4^{2-} deposition in Sweden at Vavihill 1991-2014



Det beräknade svavelnedfallet (exklusive havssaltsbidraget) till granskog i Sverige vid olika tillfällen sedan början av 1990-talet. Nedfallet är beräknat med hjälp av geografisk interpolation (Kriging) baserat på alla befintliga mätplatser vid respektive tidpunkt. Ovanför varje karta anges det hydrologiska år (okt-sep) som beräkningarna gäller för.

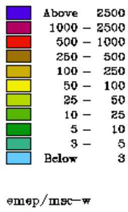
EMEP Eulerian Acid Deposition model - Sulphur

1997 deposition of oxidized sulphur from Sweden



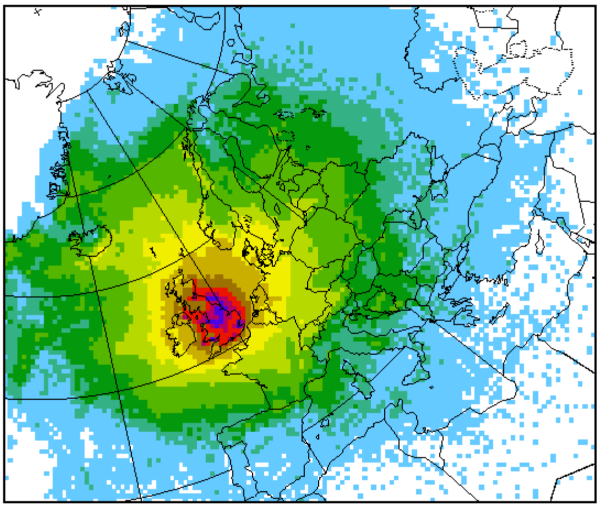
Deposition of oxidized sulphur from Swedish sources 1997

Unit: (μg-S / m^2)



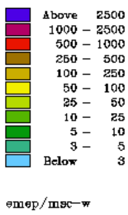
EMEP Eulerian Acid Deposition model - Sulphur

1997 deposition of oxidized sulphur from United Kingdom



Deposition of oxidized sulphur from British sources 1997

Unit: (μg-S / m^2)



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.

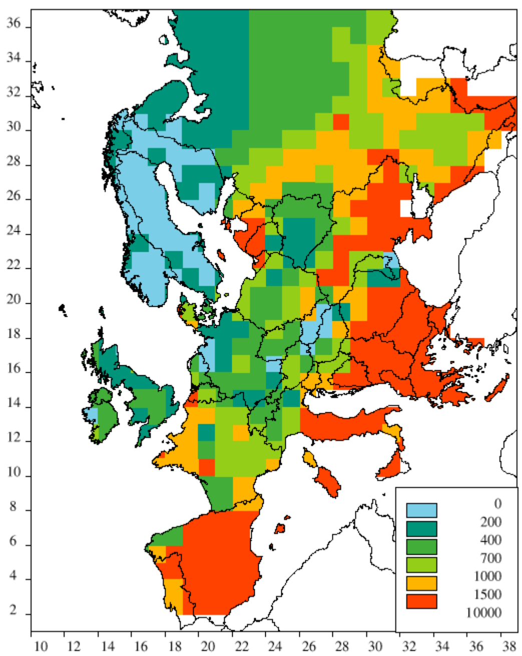
Can be expressed in many ways.

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.

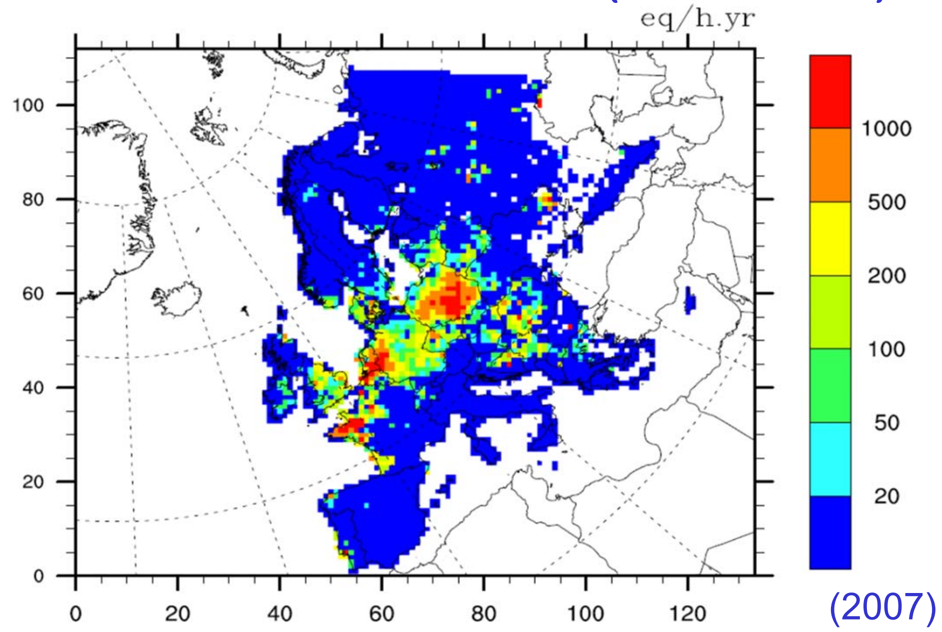
Critical load

The critical load for **acidification** given as the 2- percentile (protects 98% of all ecosystems)

(equivalents / ha / yr)



Exceedence of critical load (acidification)



Exceedence of critical load (eutrophication)