Tropospheric Pollution Part II: Sulfate Aerosol and Acid Rain

- Tropospheric sulfate aerosol
- James Lovelock, phytoplankton, dimethyl sulfide (DMS), thermoregulation of the planet
- Sulfate aerosols cool the planet
- A geophysical box model for sulfur
- Sources and trends in sulfur emissions
- Acid rain and mycorrhizae
- Other kinds of tropospheric aerosol

Tropospheric Aerosols

- factory and auto emissions
- agricultural burning
- dust storms
- forest fires
- sea spray
- volcanoes
- pollen
- cat dander
- spritzers

Tropospheric sulfate aerosol

Liquid droplets composed of 3 H_2O x H_2SO_4 ~ 0.1-1.0 microns

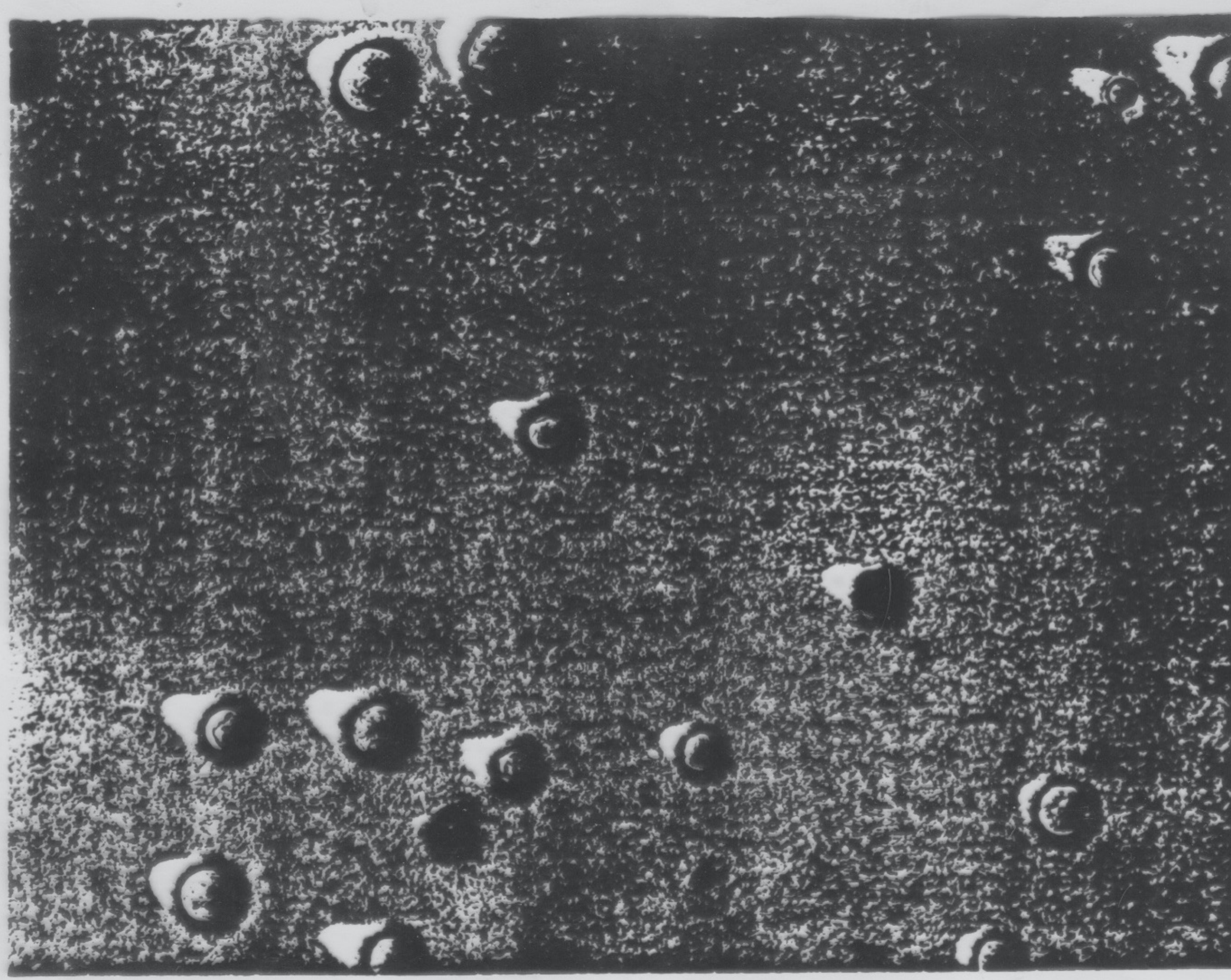
Sources: SO_2 (industry, volcanoes)
DMS $(CH_3)_2S$ (ocean phytoplankton)

+ OH (hydroxyl radical, cleansing agent)

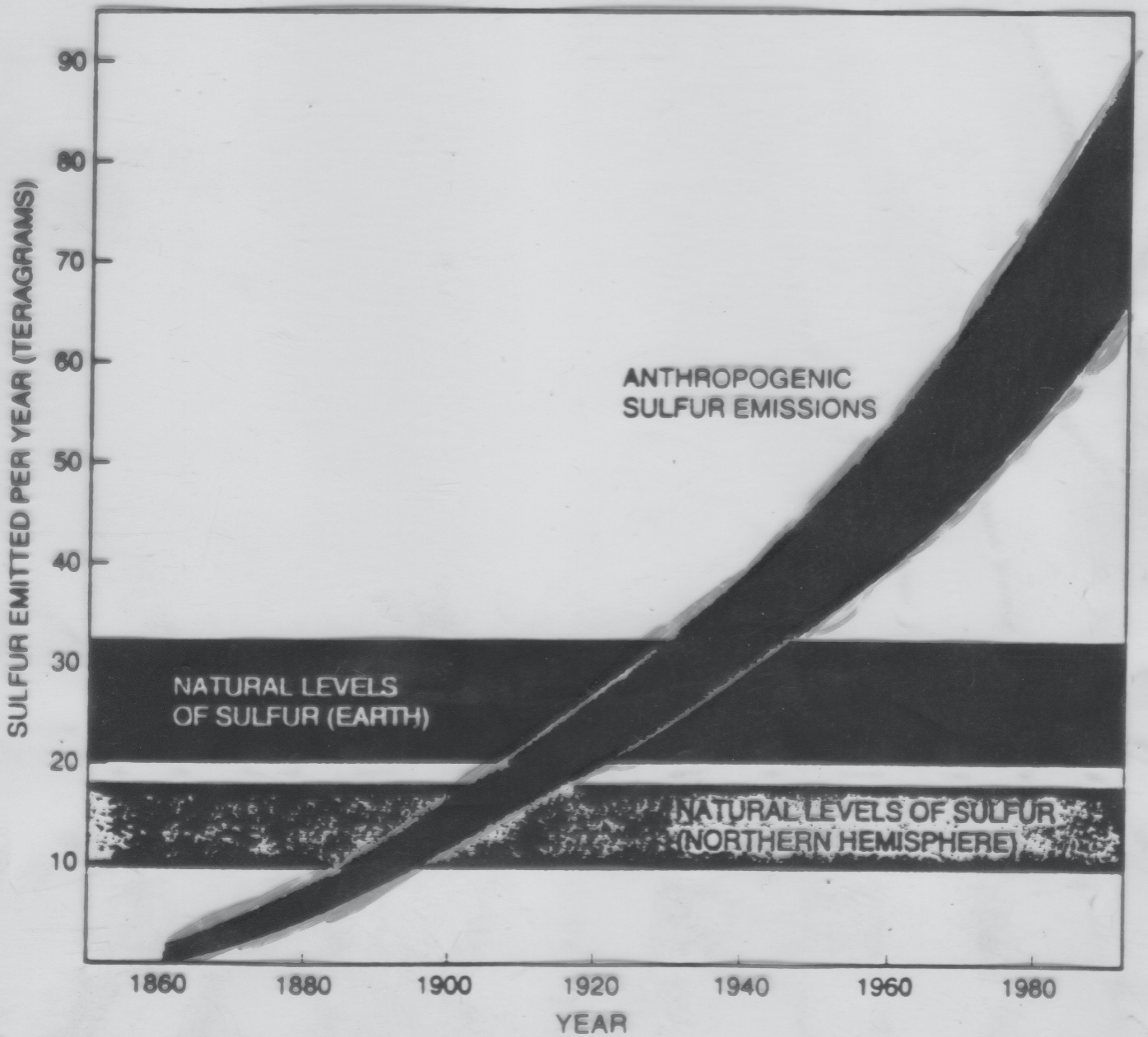
= H_2SO_4 (sulfuric acid, which readily dissolves in raindrops)

- Poor visibility
- Reflects sunlight to space
- Absorbs and emits IR
- Diurnal cycle smaller (warmer nights, daytime not as hot)
- Acid rain/snow deposition harms the biosphere and human structures

If sulfate aerosol are removed, the daytime will be hotter and the average temperature of the planet will be hotter.



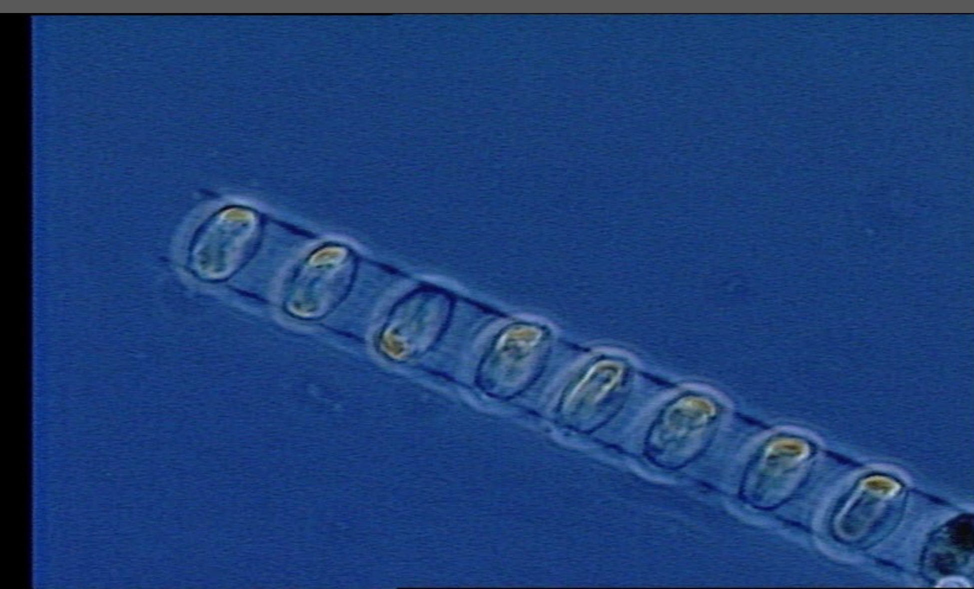
SULFATE AEROSOL sampled from the atmosphere was photographed through an electron microscope. The particles are about 0.1 micron in diameter.

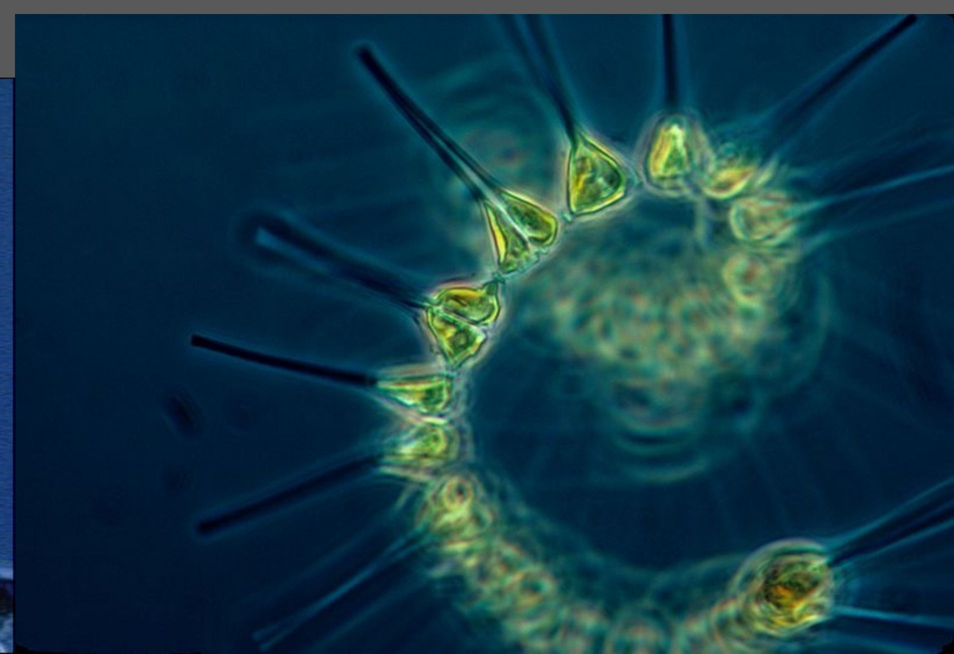


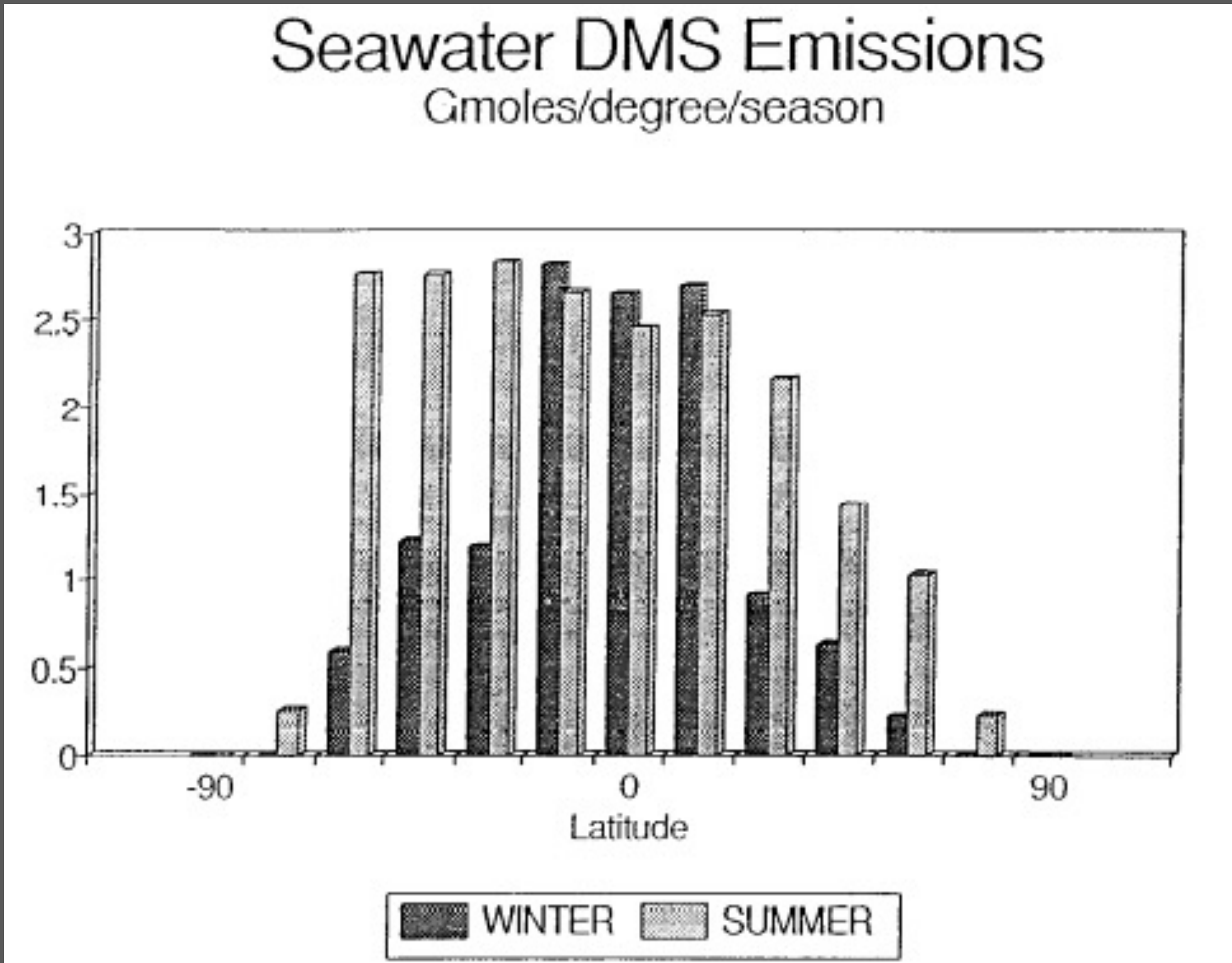
ANTHROPOGENIC SULFUR EMISSIONS now far outstrip those from natural sources, such as marine phytoplankton. It is estimated that humans currently release between 65 billion to 90 trillion grams, or teragrams, of sulfur every year.

Oceanic Source

- The oceans are a major source of sulfate aerosols
- Phytoplankton produce dimethyl sulphide gas (DMS) when they die
- DMS slowly diffuses into the atmosphere where it oxidizes to form sulfur dioxide, then converts to sulfate aerosols

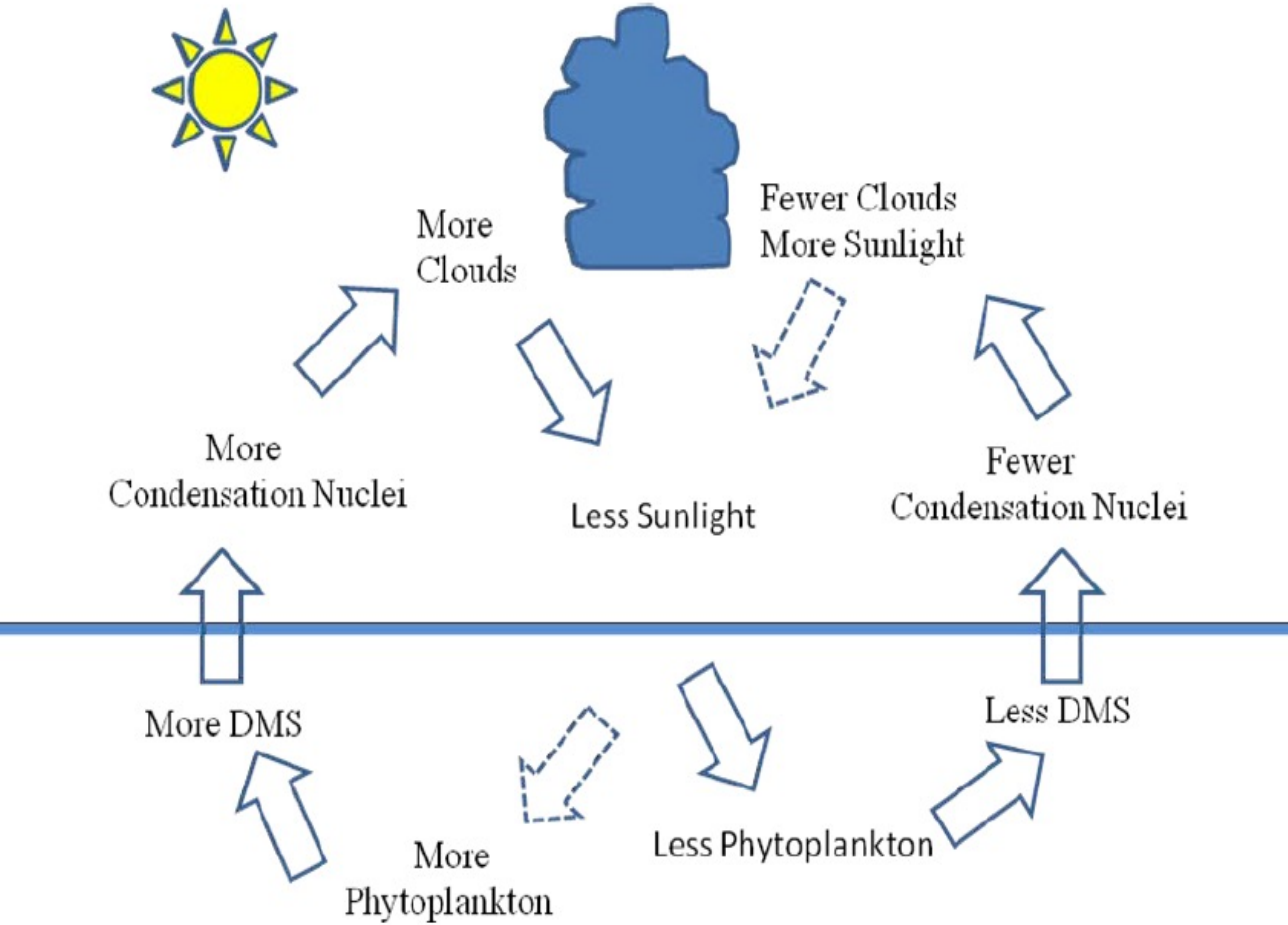





Seawater DMS Emissions
Gmoles/degree/season
3
2.5
2
1.5
1
0.5
0
-90
0
90
Latitude
WINTER
SUMMER

Thermoregulation of the planet through DMS – James Lovelock

- DMS emitted by phytoplankton in sunlight can create effective cloud condensation nuclei (CCN) and form clouds
- If there is too much sunlight and CCN, clouds will shut off the sunlight and DMS formation so that the clouds will go away and the sun will come out again


More Clouds
Fewer Clouds
More Sunlight
More Condensation Nuclei
Less Sunlight
Fewer Condensation Nuclei
More DMS
Less DMS
More Phytoplankton
Less Phytoplankton

How do sulfate aerosols affect the temperature of the planet?

- By absorbing and emitting infrared, sulfate aerosol keep the nighttime warmer than it would be without them
- By reflecting sunlight during the day, sulfate aerosol keep the daytime cooler than it would be without them
- The diurnal range has decreased by more than 1 K in the last century
- In major fossil fuel burning regions, radiative observations show that anthropogenic aerosol reflect 2 – 10 W m^{-2} of solar energy back to space across N. America and Eurasia

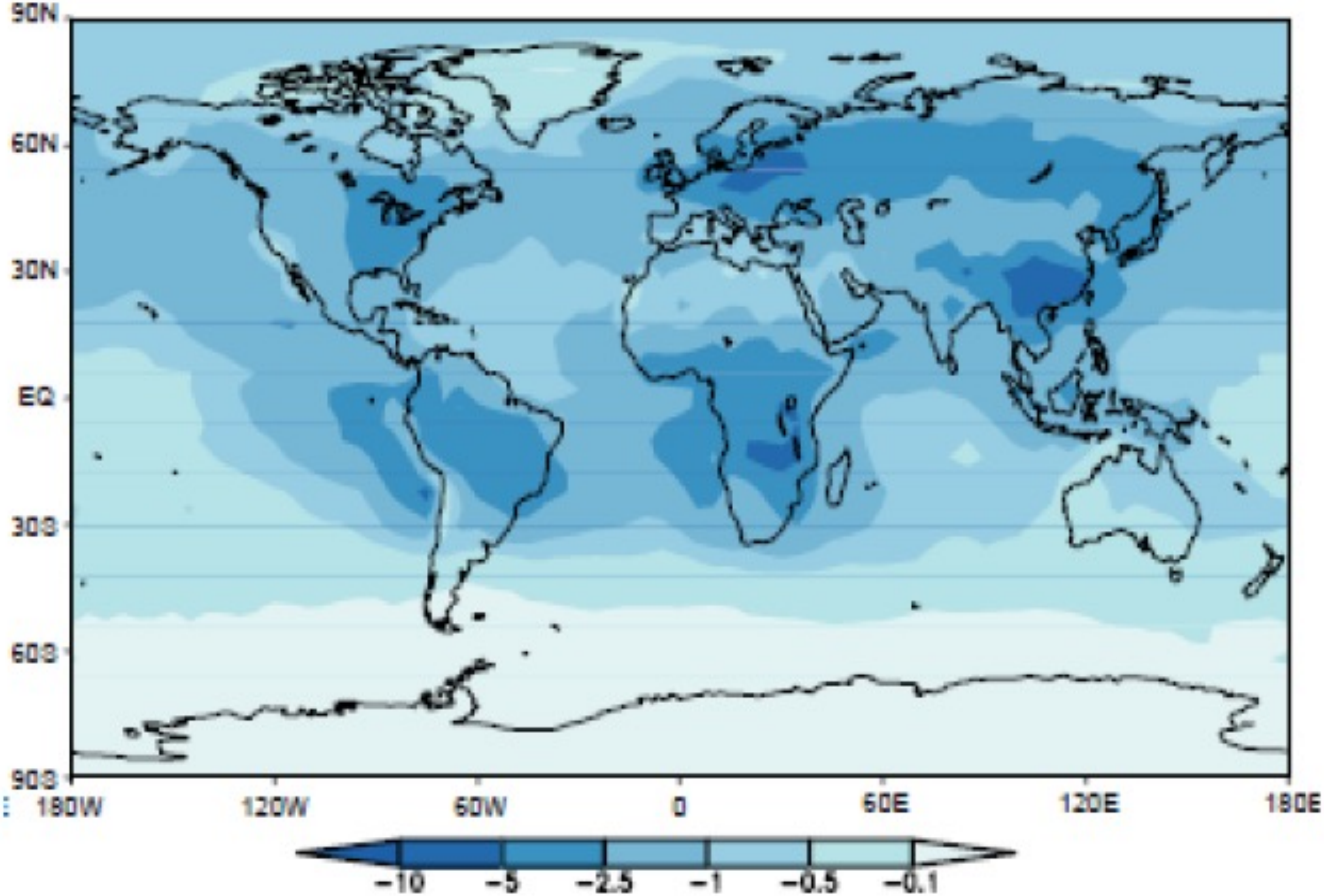
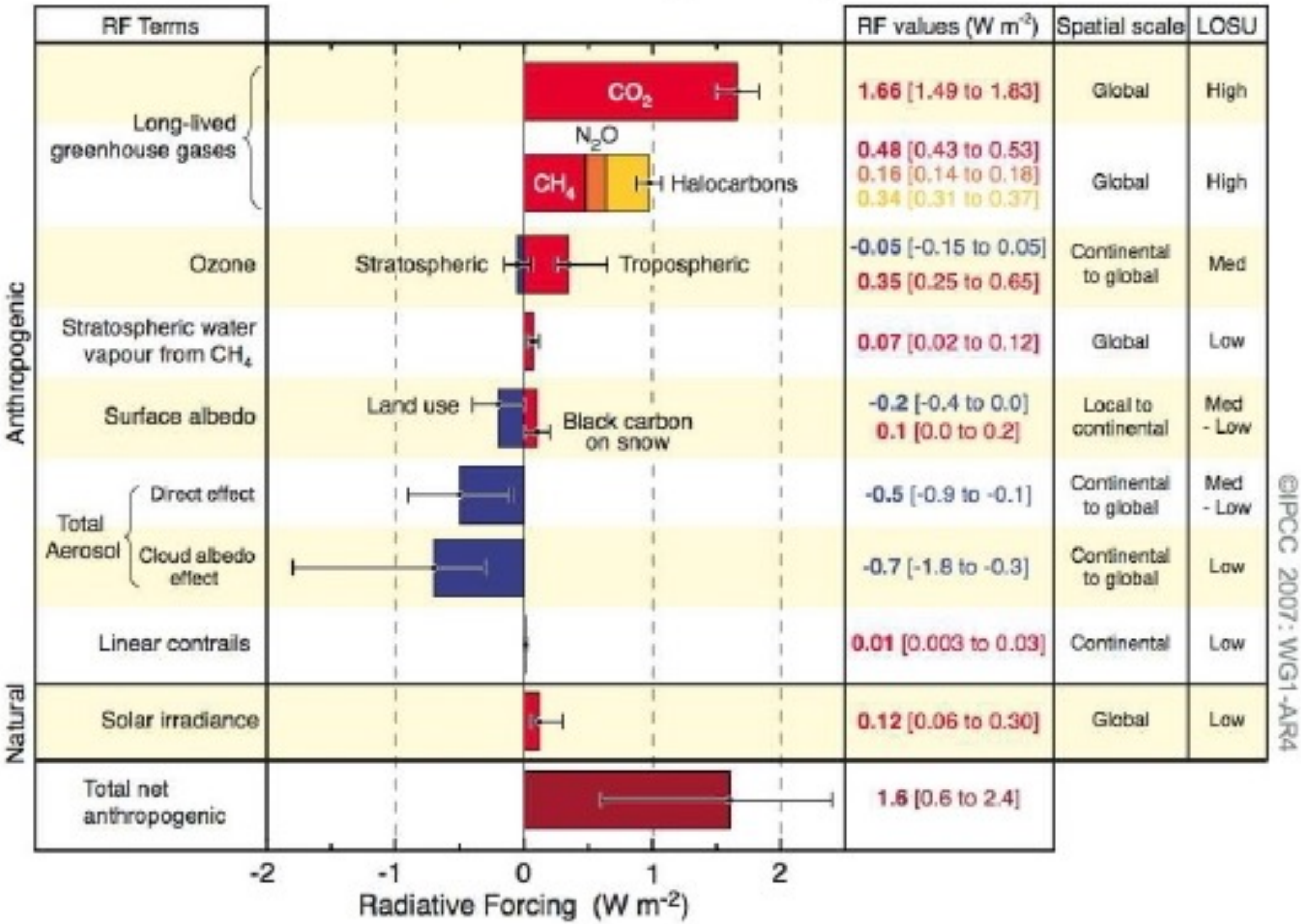


Figure 6.8. Annual mean anthropogenic aerosol forcing in W m^{-2} (Chen and Penner 2005). Larger negative values (darker blue) correspond to more solar radiation scattered back to space.


RF Terms
RF values (W m-2)
Spatial scale
LOSU
Long-lived greenhouse gases
CO2
1.66 [1.49 to 1.83]
Global
High
N2O
CH4
Halocarbons
0.48 [0.43 to 0.53]
0.16 [0.14 to 0.18]
0.34 [0.31 to 0.37]
Global
High
Ozone
Stratospheric
Tropospheric
-0.05 [-0.15 to 0.05]
0.35 [0.25 to 0.65]
Continental to global
Med
Stratospheric water vapour from CH4
0.07 [0.02 to 0.12]
Global
Low
Surface albedo
Land use
Black carbon on snow
-0.2 [-0.4 to 0.0]
0.1 [0.0 to 0.2]
Local to continental
Med - Low
Total Aerosol
Direct effect
-0.5 [-0.9 to -0.1]
Continental to global
Med - Low
Cloud albedo effect
-0.7 [-1.8 to -0.3]
Continental to global
Low
Linear contrails
0.01 [0.003 to 0.03]
Continental
Low
Solar irradiance
0.12 [0.06 to 0.30]
Global
Low
Total net anthropogenic
1.6 [0.6 to 2.4]
Anthropogenic
Natural
-2
-1
0
1
2
Radiative Forcing (W m-2)
©IPCC 2007: WG1-AR4

Box model - Sulfur over the eastern U.S.

- Reservoir = Amount of a constituent **(Tg)**
- F**lux** = Rate of transport of a constituent from one reservoir to another (Tg/yr)
- 1 Tg = 10^6 tons (the mass of a million cars)
- Smokestacks and vehicles in the eastern U.S. emit 12 Tg S/yr (flux into the atmospheric reservoir)
- ~8 Tg S/yr fall back to the ground as acid rain (flux out of the atmospheric reservoir)

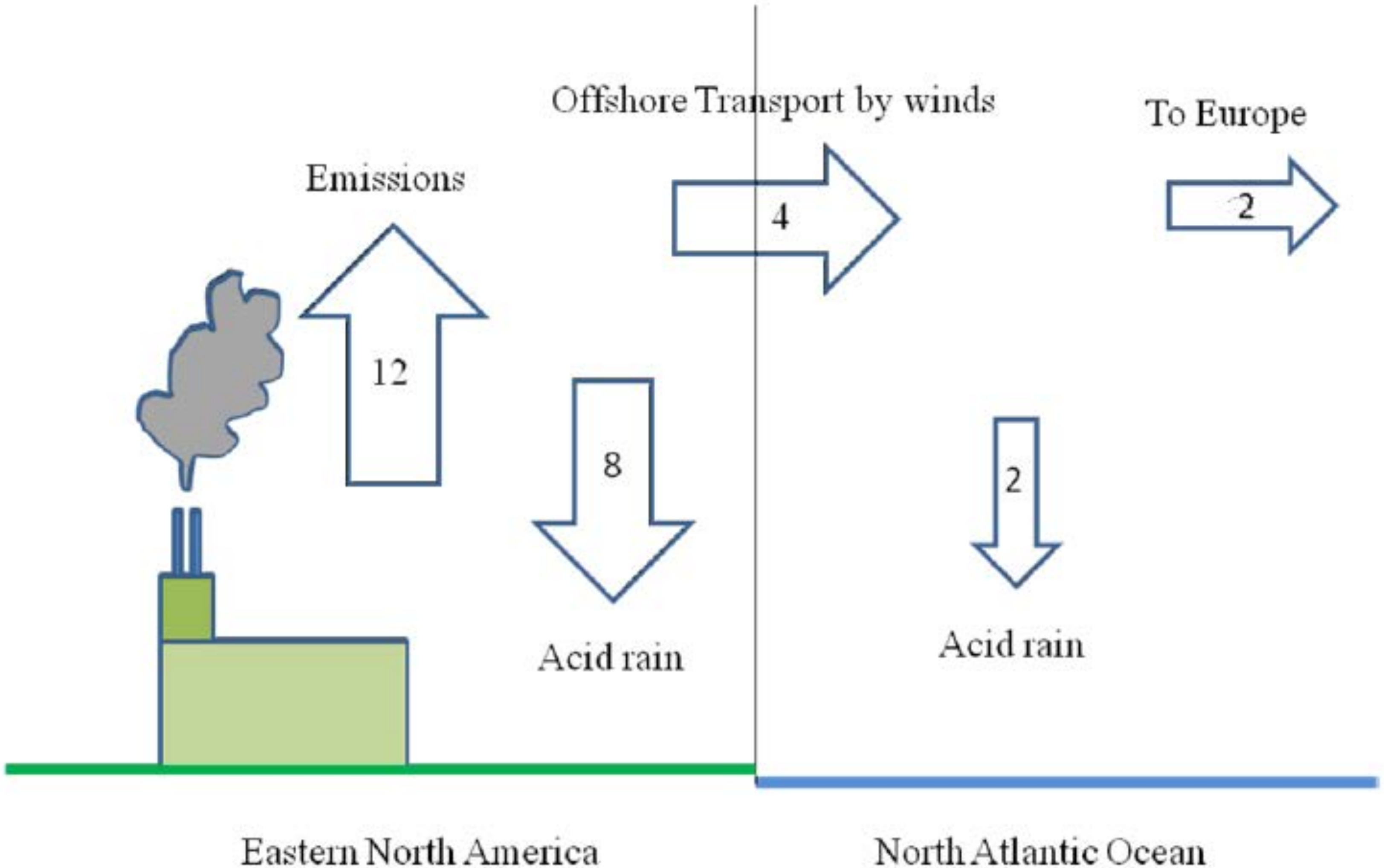


Figure 6.14. Geophysical budget model for sulfur showing fluxes into and out of the atmospheric reservoirs over the Eastern U. S. and the North Atlantic.

1 Teragram = 1 x 10^9 kilograms

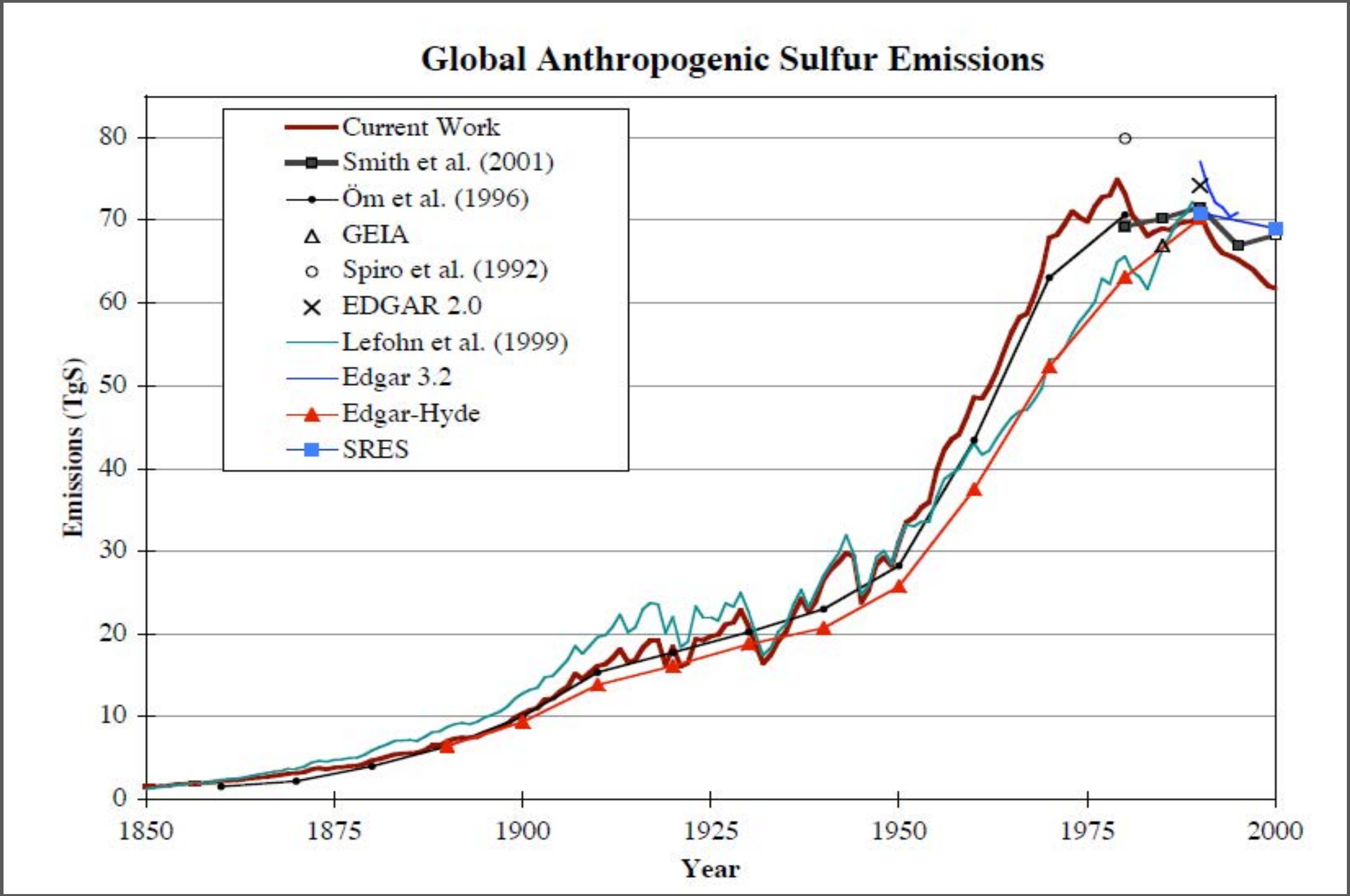
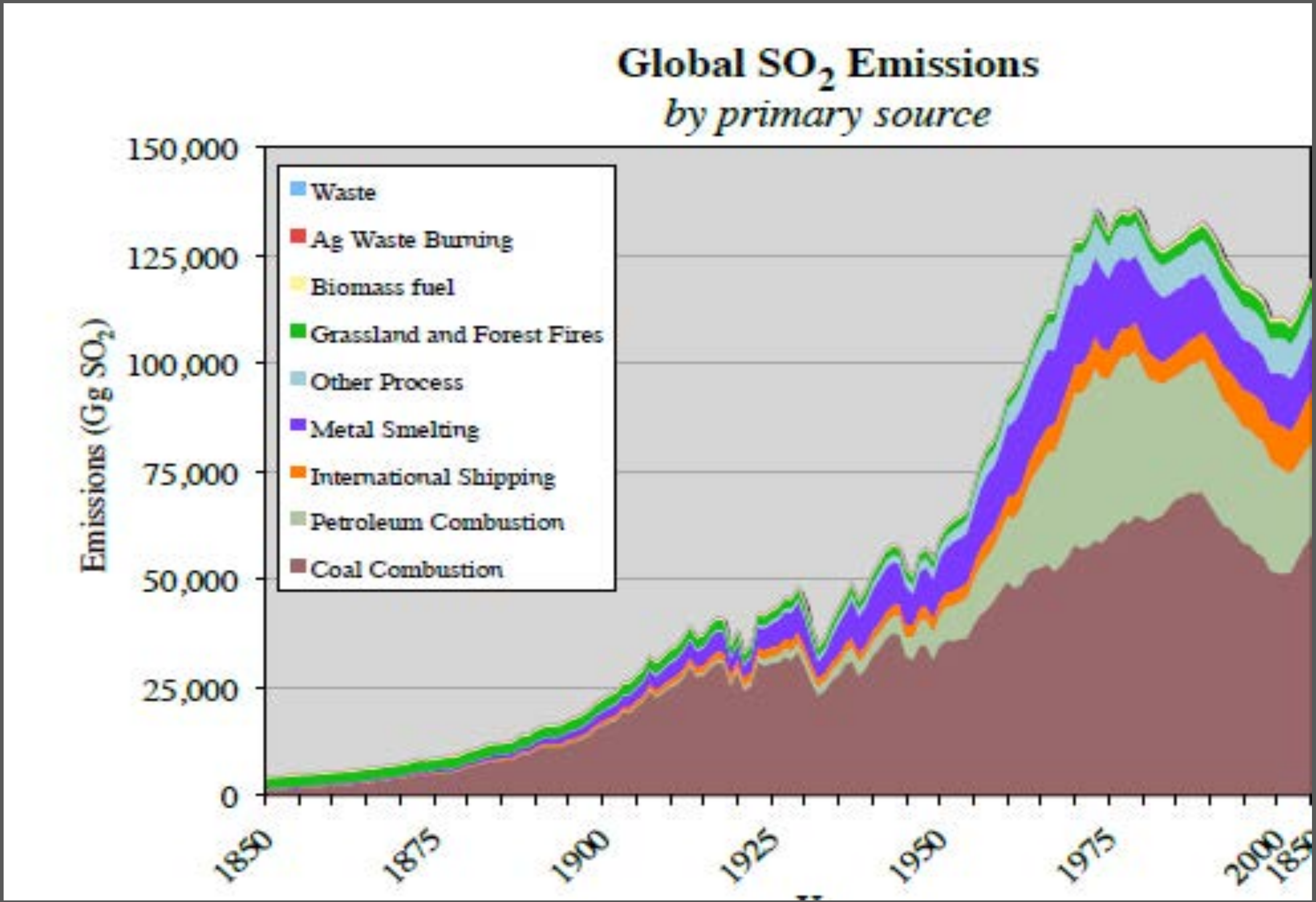


Figure 1–Global sulfur dioxide emissions from this study (thick line) and several other recent estimates (see text). Note that the Lefohn *et al*. estimate does not include all anthropogenic emissions sources. References not shown on the cart are: GEIA (Benkovitz *et al*.1996); EDGAR 2.0 (Olivier *et al* 1996); EDGAR 3.2 (Olivier and Berdowski, 2001); EDGAR-HYDE (Van Aardenne *et al*. 2001); and SRES (Nakicenovic and Swart 2000).



1 Gg (Gigagram) = 1 million kg

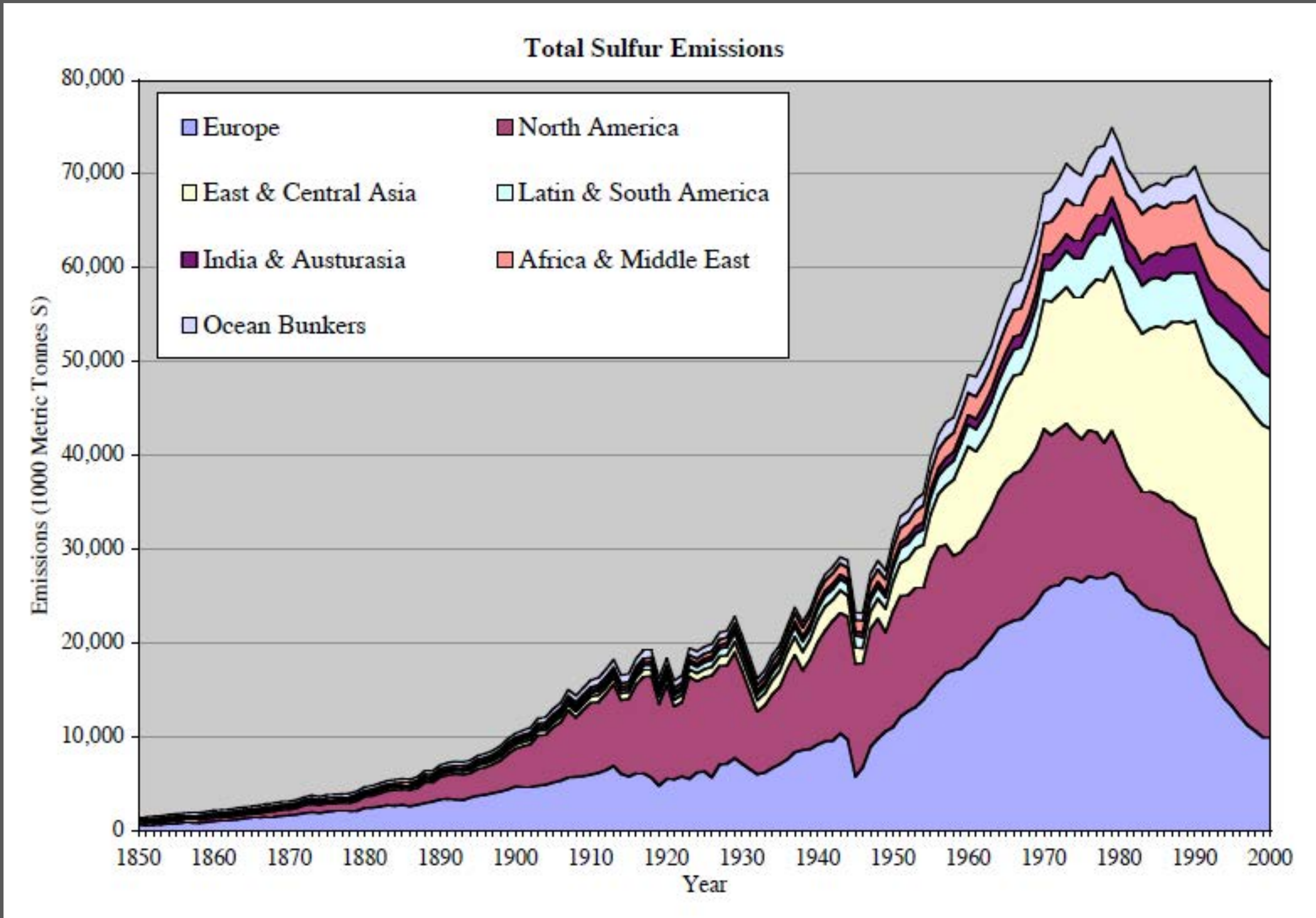
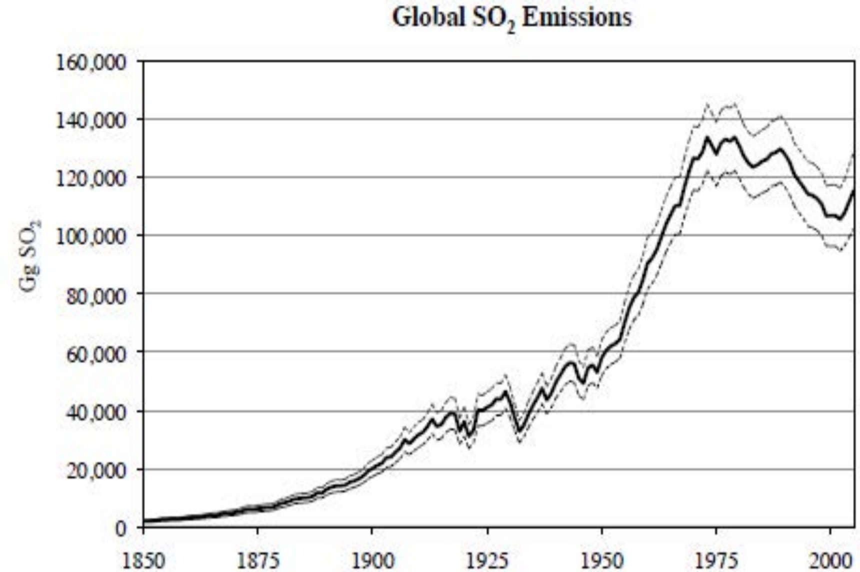
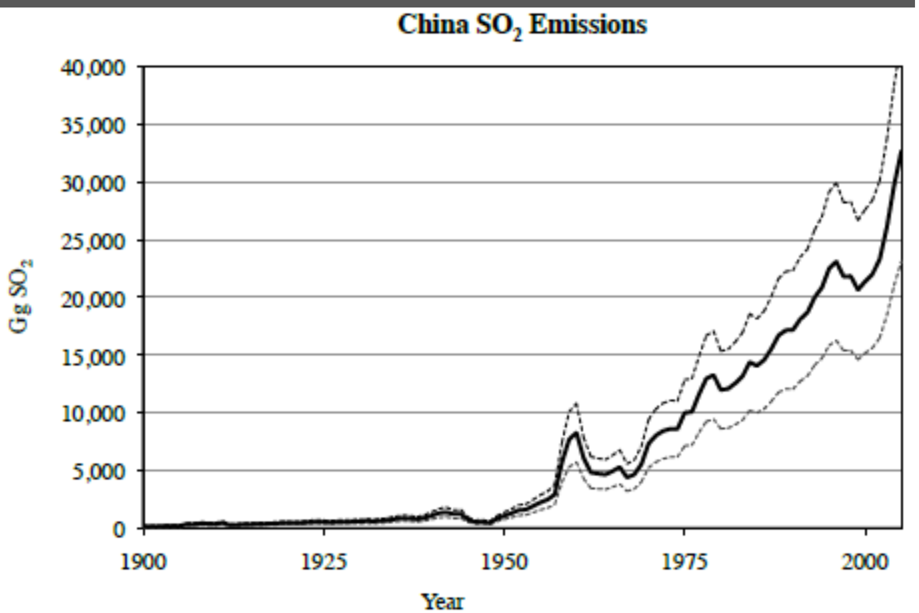


Figure 3–Global sulfur dioxide emissions by meta-region.

1 Gg (gigagram)= 1 Tg = 1 million kg





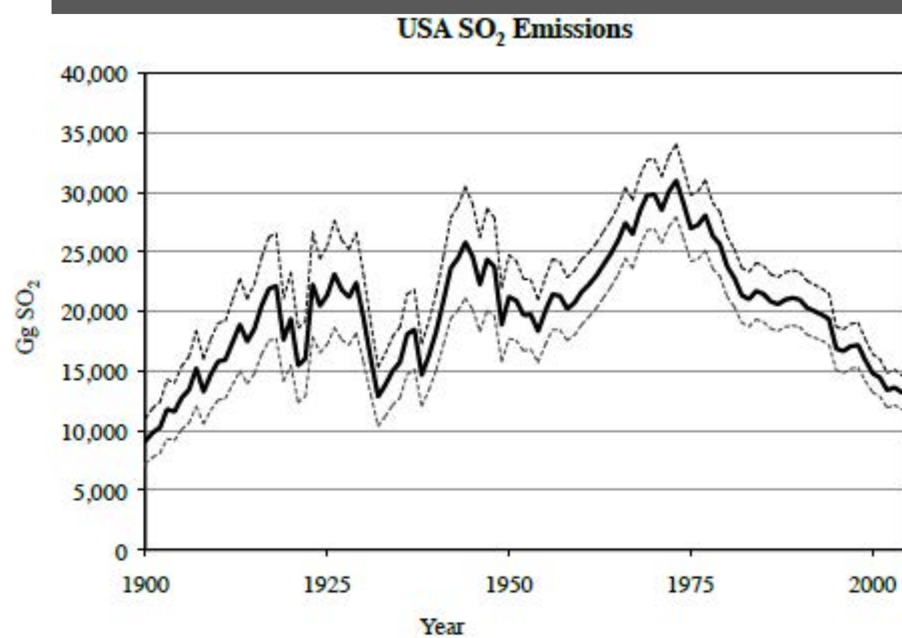


Fig. 3. Sulfur dioxide emissions from fuel combustion and process emissions with central value (solid line) and upper and lower uncertainty bounds (dotted lines). **(a)** Global,**(b)** China, and **(c)** USA. China and USA graphs exclude shipping emissions.

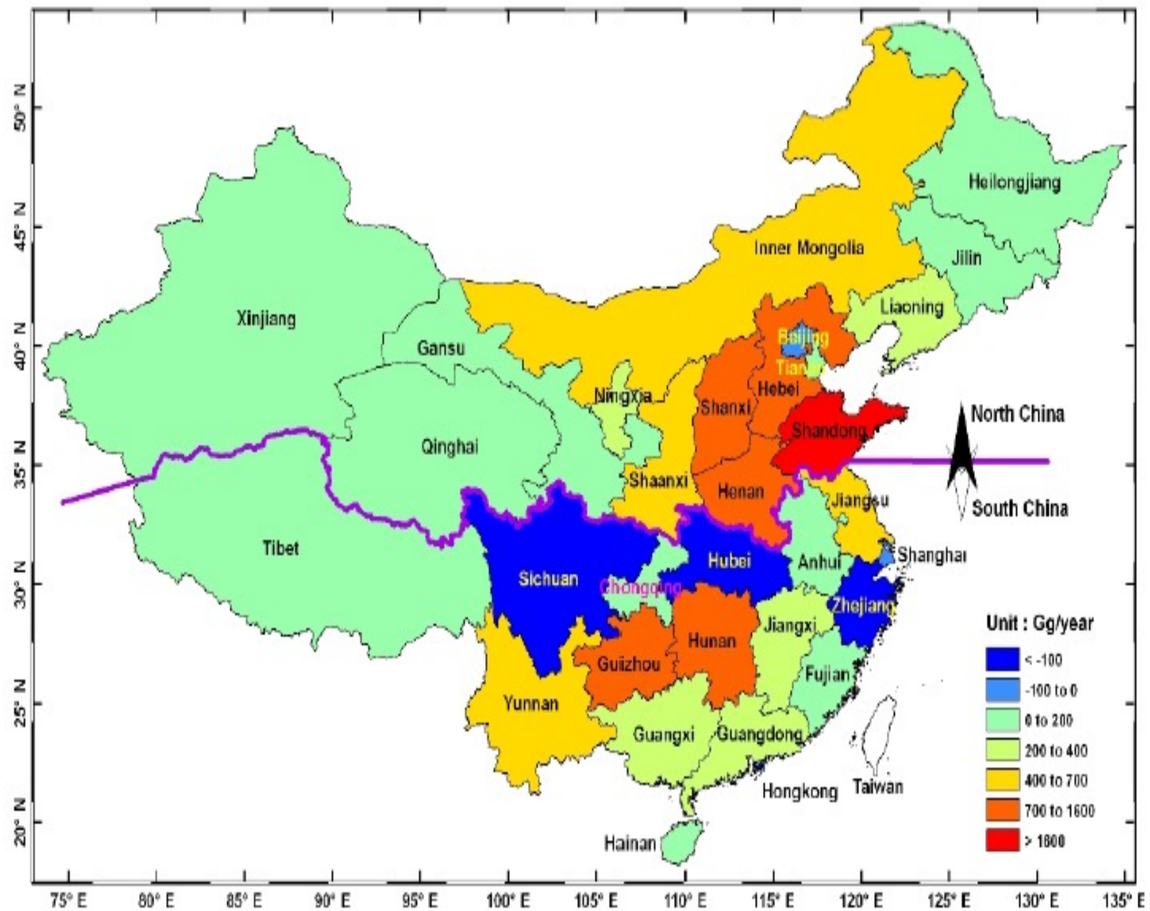


Fig. 3. Provincial change of SO_2 emission in China between 2000 and 2006. Purple solid line indicates the dividing line of north and south China.

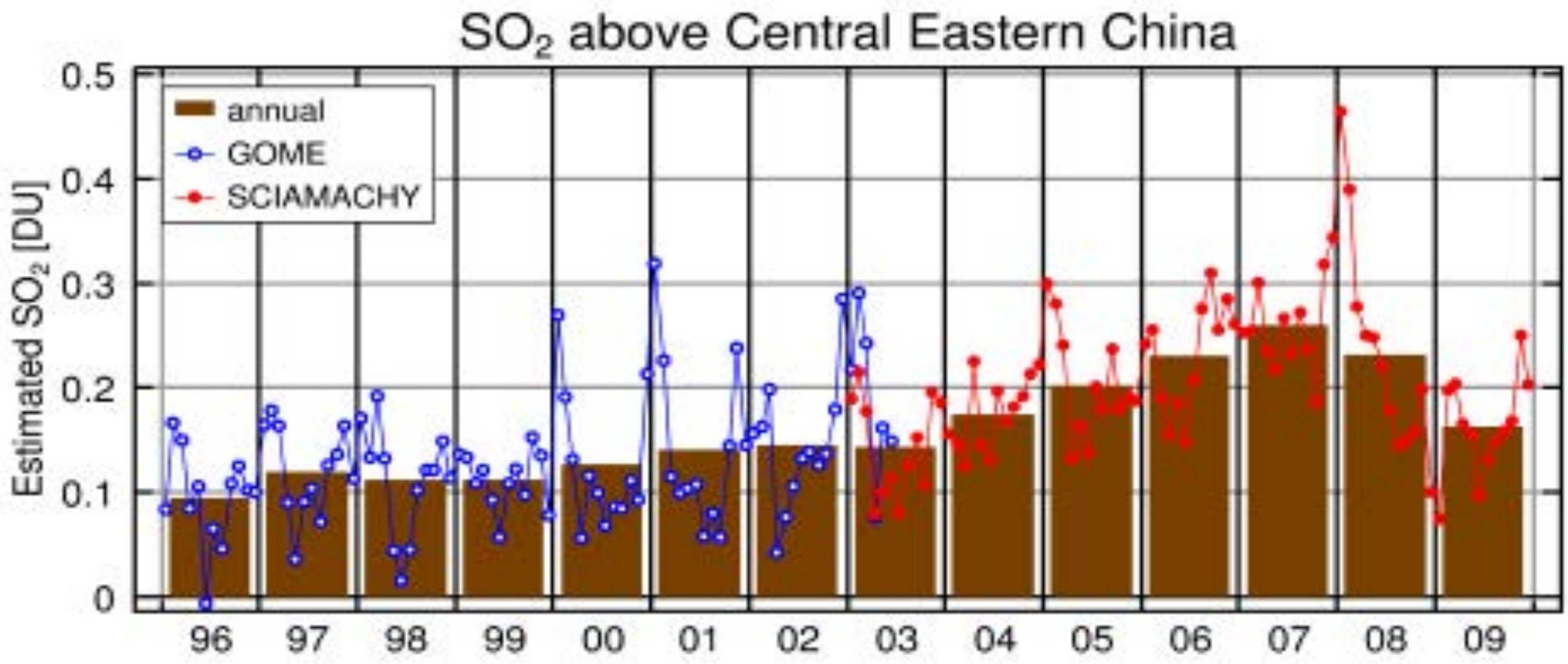


Fig. 9. Monthly (lines) and annual average (bars) estimated sulfur dioxide column over Eastern China as estimated from satellite measurements (Gottwaldov et al., 2010).

1 DU = 2.69 10^{16} molecules/cm^2

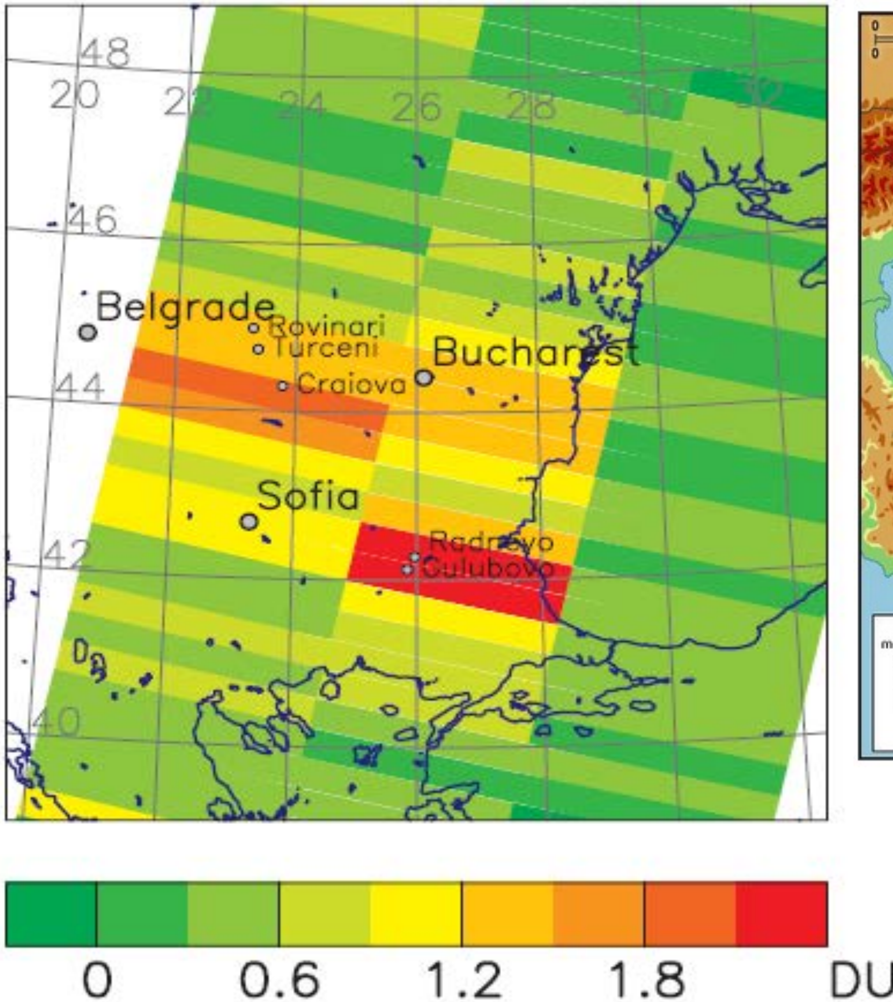
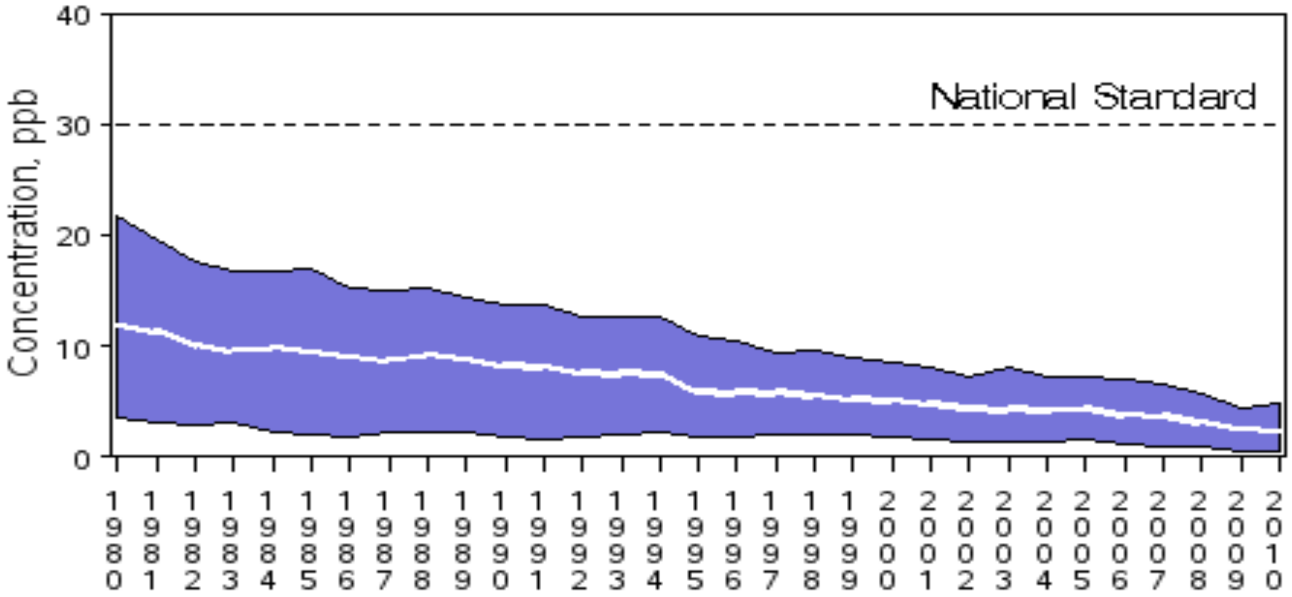


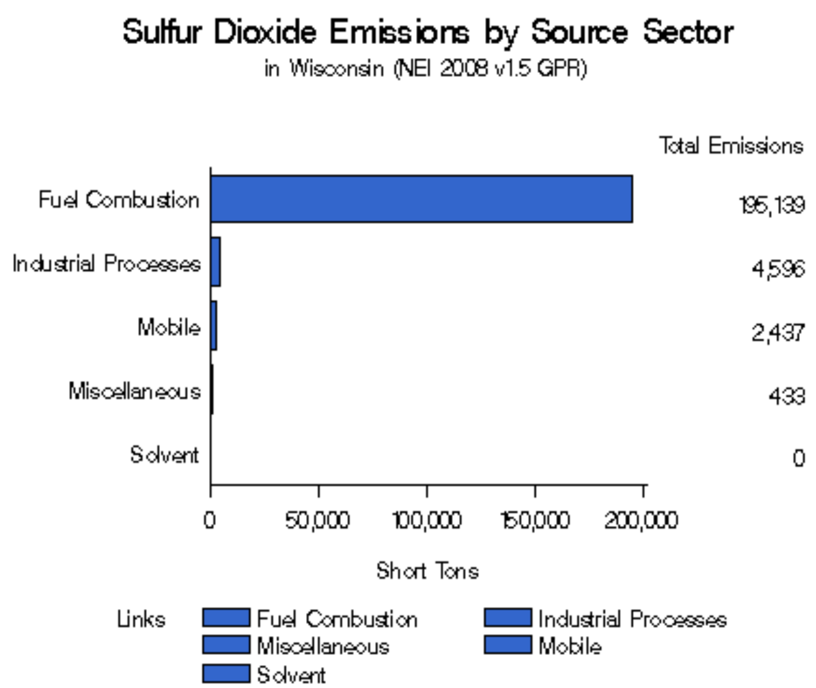
Figure 4. Enhanced SO_2 observed by GOME over the Balkans on 8 February 1998. The small dots indicate the locations of the largest thermal power plants burning lignite in Romania (Turceni, Rovinari, and Craiova, total 5065 MWe) and Bulgaria (Gulubovo and Radnevo, forming the Maritsa-Iztok complex, total 3485 MWe). Together, these plants represent 27 % of the electric power capacity installed in these countries [US Department of Energy].

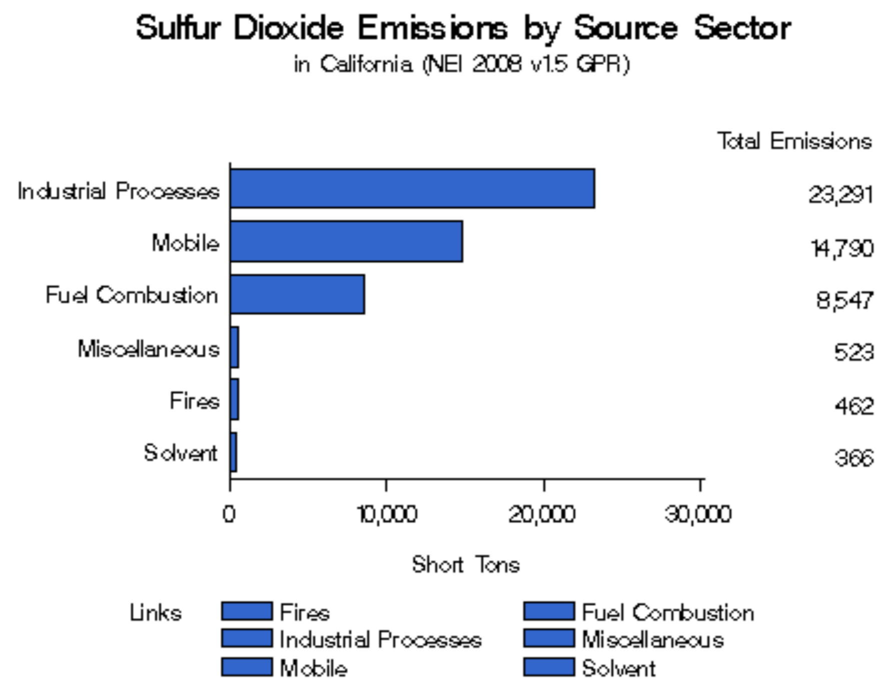
SO2 Air Quality, 1980 - 2010

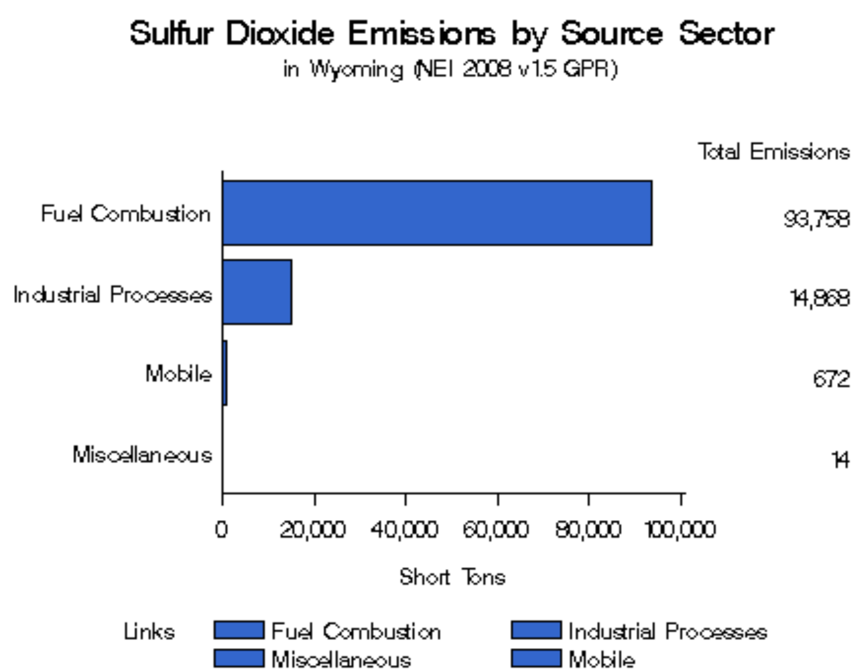
(Based on Annual Arithmetic Average)
National Trend based on 121 Sites

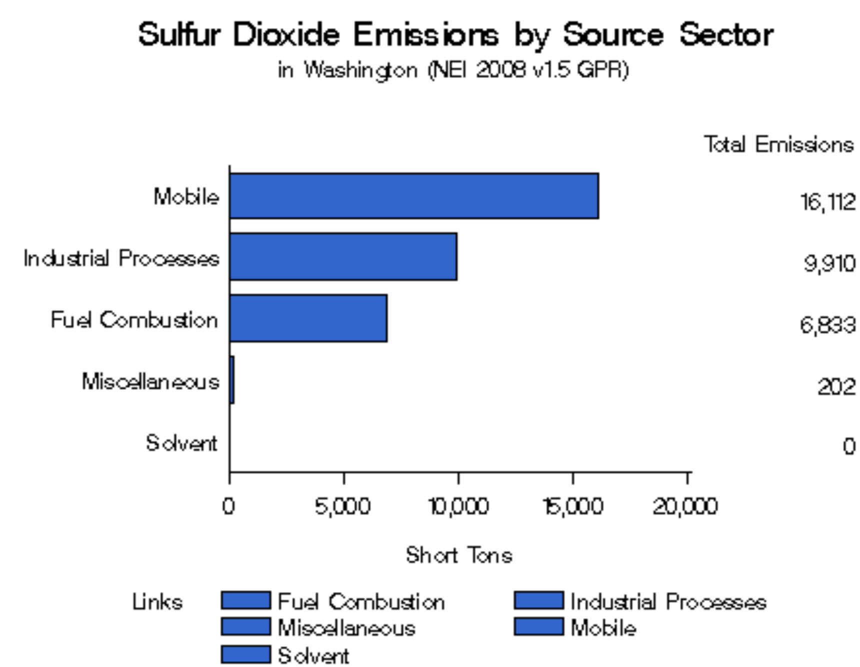


1980 to 2010 : 83% decrease in National Average


Sulfur Dioxide Emissions by Source Sector
in Wisconsin (NEI 2008 v1.5 GPR)
Total Emissions
Fuel Combustion
195,139
Industrial Processes
4,596
Mobile
2,437
Miscellaneous
433
Solvent
0
0
50,000
100,000
150,000
200,000
Short Tons
Links
Fuel Combustion
Industrial Processes
Miscellaneous
Mobile
Solvent


Sulfur Dioxide Emissions by Source Sector
in California (NEI 2008 v1.5 GPR)
Total Emissions
Industrial Processes
23,291
Mobile
14,790
Fuel Combustion
8,547
Miscellaneous
523
Fires
462
Solvent
366
0
10,000
20,000
30,000
Short Tons
Links
Fires
Fuel Combustion
Industrial Processes
Miscellaneous
Mobile
Solvent


Sulfur Dioxide Emissions by Source Sector
in Wyoming (NEI 2008 v1.5 GPR)
Total Emissions
Fuel Combustion
93,758
Industrial Processes
14,868
Mobile
672
Miscellaneous
14
0
20,000
40,000
60,000
80,000
100,000
Short Tons
Links
Fuel Combustion
Industrial Processes
Miscellaneous
Mobile


Sulfur Dioxide Emissions by Source Sector
in Washington (NEI 2008 v1.5 GPR)
Total Emissions
Mobile
16,112
Industrial Processes
9,910
Fuel Combustion
6,833
Miscellaneous
202
Solvent
0
0
5,000
10,000
15,000
20,000
Short Tons
Links
Fuel Combustion
Industrial Processes
Miscellaneous
Mobile
Solvent

Acid Rain

- Dissolved gases in rainfall cause the mixture to become more acidic
- Pure water has a pH of 7.0
- Natural rainfall has a pH of 5.6

  H_2O (liquid) $+CO_2$ (gas) → H_2CO_3 (aqueous)
- Acid rain has a pH of less than 5.6
- Acid fogs with a pH of ~ 1.5 have been observed in Los Angeles

	Environmental Effects	pH Value	Examples
ACIDIC		pH = 0	Battery acid
		pH = 1	Sulfuric acid
		pH = 2	Lemon juice, Vinegar
		pH = 3	Orange juice, Soda
	All fish die (4.2)	pH = 4	Acid rain (4.2-4.4) Acidic lake (4.5)
	Frog eggs, tadpoles, crayfish, and mayflies die (5.5)	pH = 5	Bananas (5.0-5.3) Clean rain (5.6)
NEUTRAL	Rainbow trout begin to die (6.0)	pH = 6	Healthy lake (6.5) Milk (6.5-6.8)
		pH = 7	Pure water
		pH = 8	Sea water, Eggs
		pH = 9	Baking soda
		pH = 10	Milk of Magnesia
		pH = 11	Ammonia
		pH = 12	Soapy water
		pH = 13	Bleach
BASIC		pH = 14	Liquid drain cleaner

What causes acid rain?

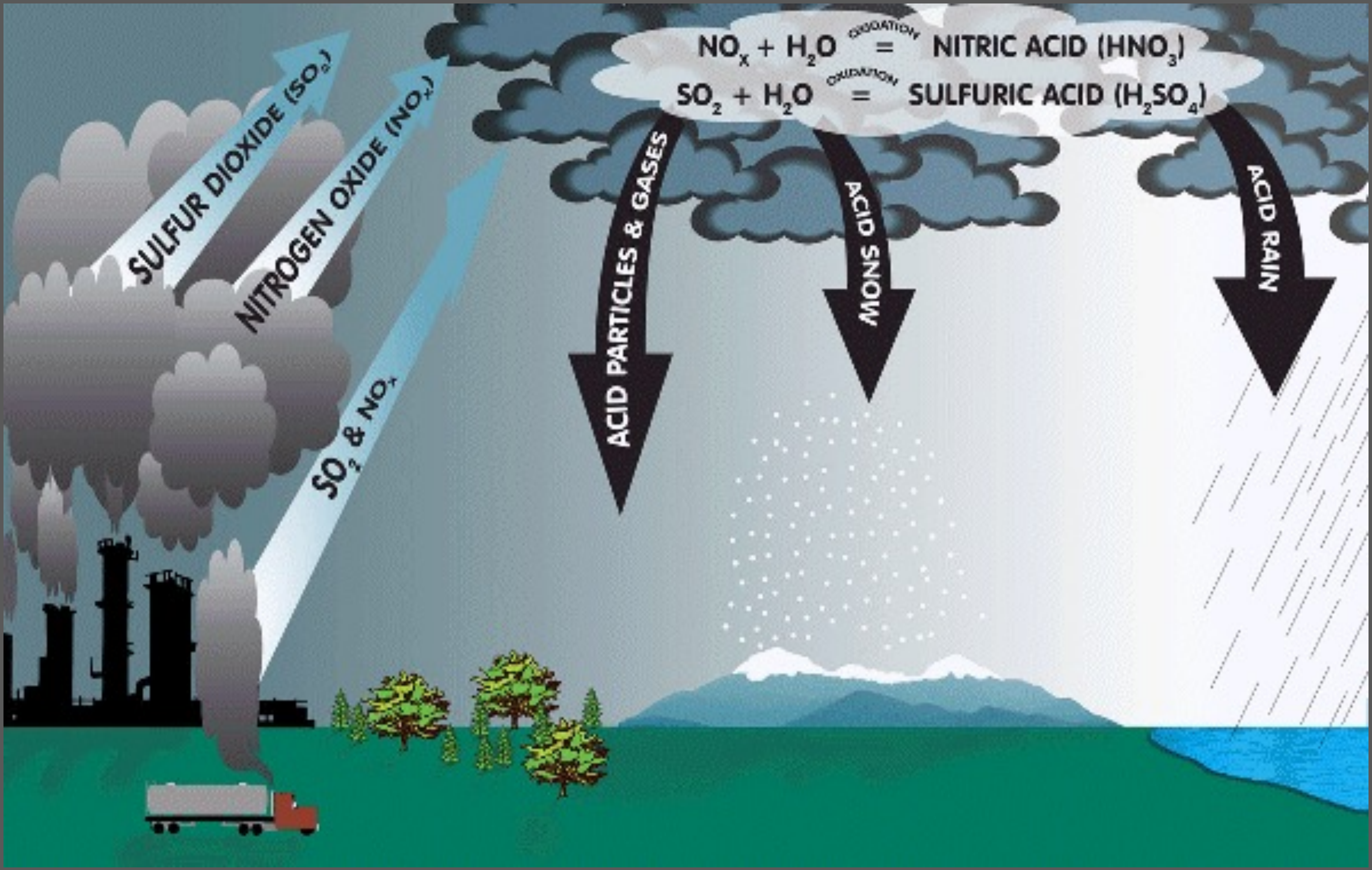
1. Oxides of sulfur (SO_x) and nitrogen oxides (NO_x) emitted from fossil fuel combustion

2. Then water vapor combines with SO_x to make sulfuric acid (H_2SO_4) and nitric acid (HNO_3)

3. These condense into hydrometeors and fall as acid rain, snow, and fog

Air Quality Standards

- In 2010 the EPA revised the primary SO_2 NAAQS by establishing a new 1-hr standard at a level of 75 ppb



$NO_x + H_2O$ OXIDATION = NITRIC ACID (HNO_3)
$SO_2 + H_2O$ OXIDATION = SULFURIC ACID (H_2SO_4)
SULFUR DIOXIDE (SO_2)
NITROGEN OXIDE (NO_x)
SO_2 & NO_x
ACID PARTICLES & GASES
ACID SNOW
ACID RAIN

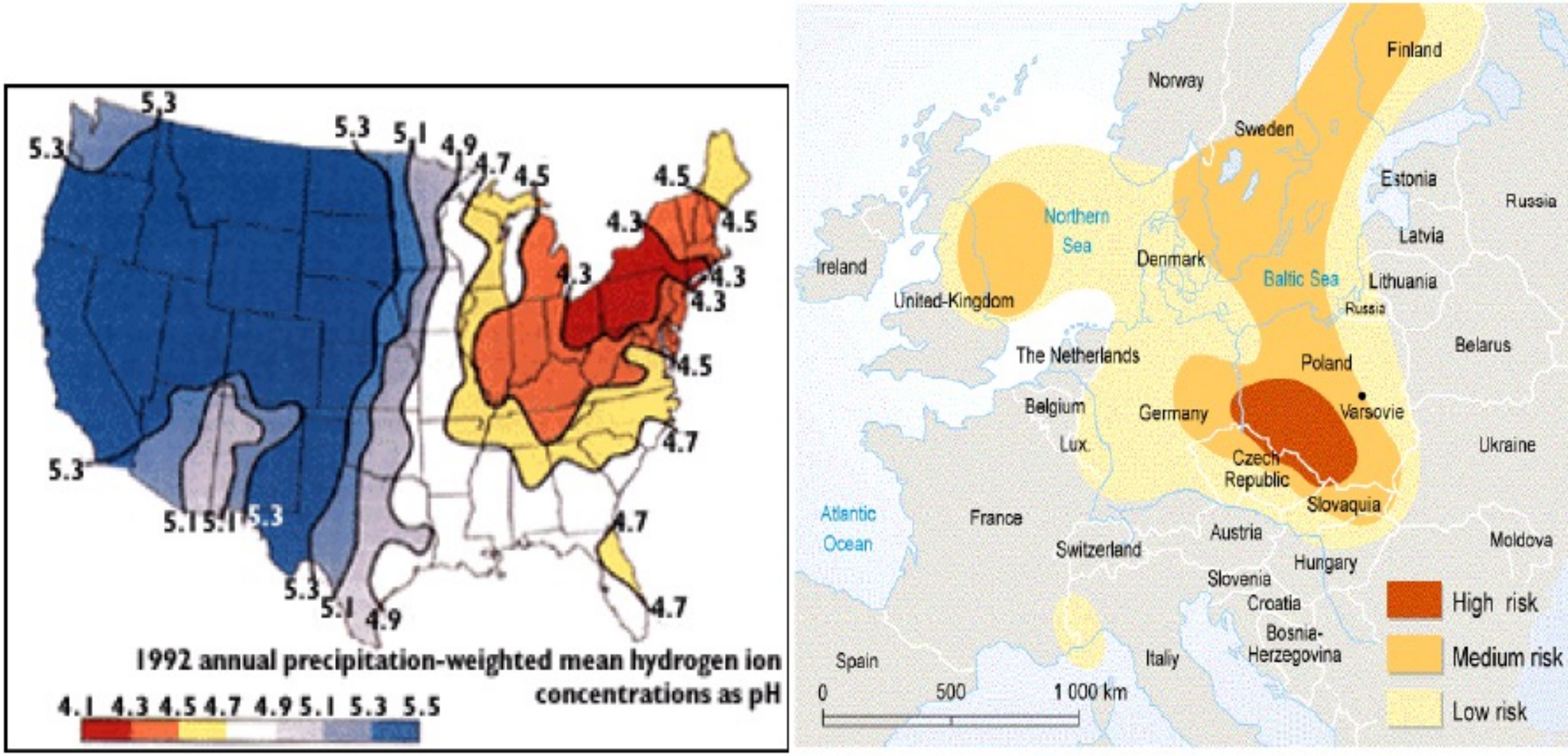
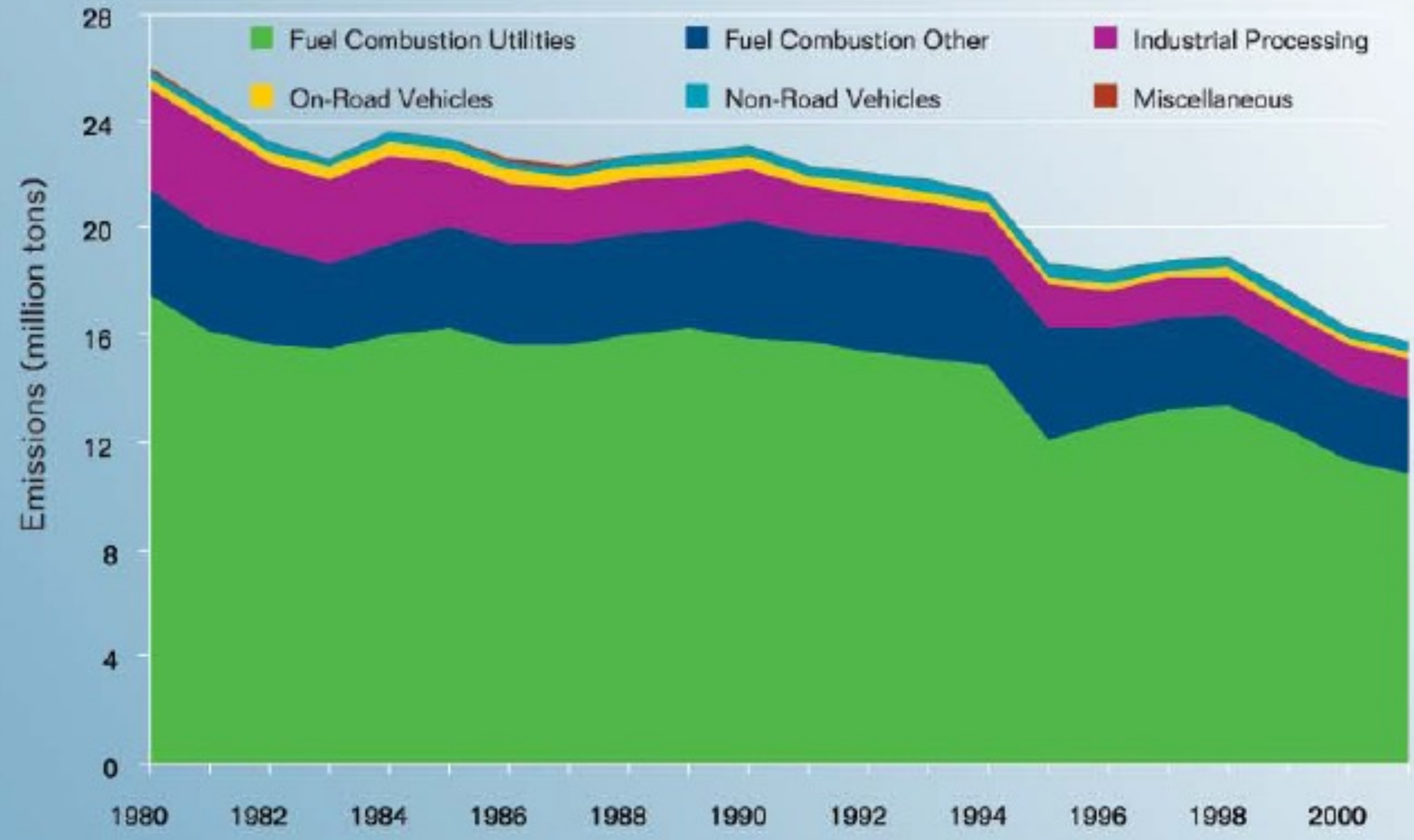


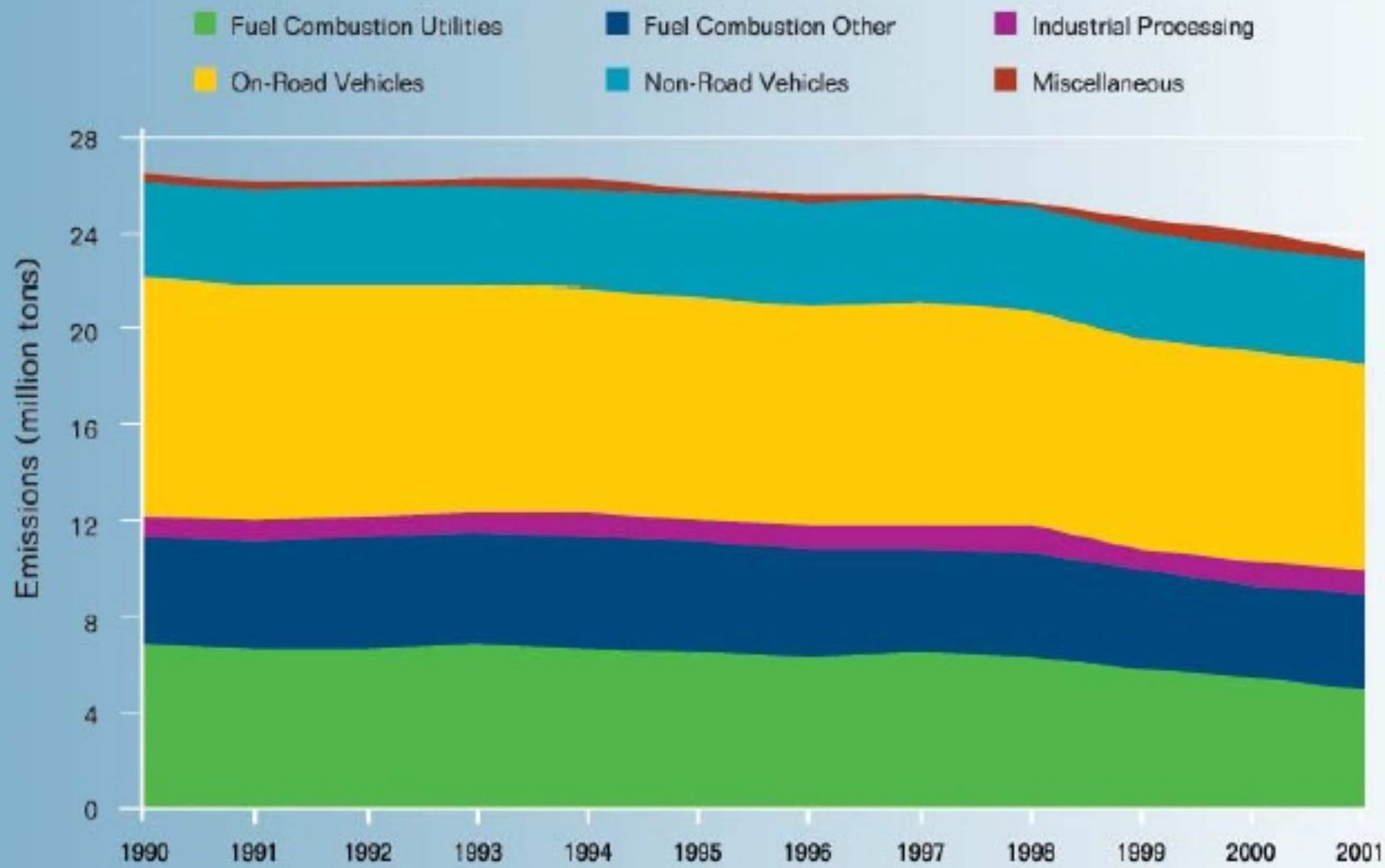
Figure 6.10. Annual mean pH of precipitation in the U.S. during 1992 (left) and risk of ecosystem damage from acid rain in Europe (right).

FIGURE 9. SO_2 emissions from all sources
1980–2001



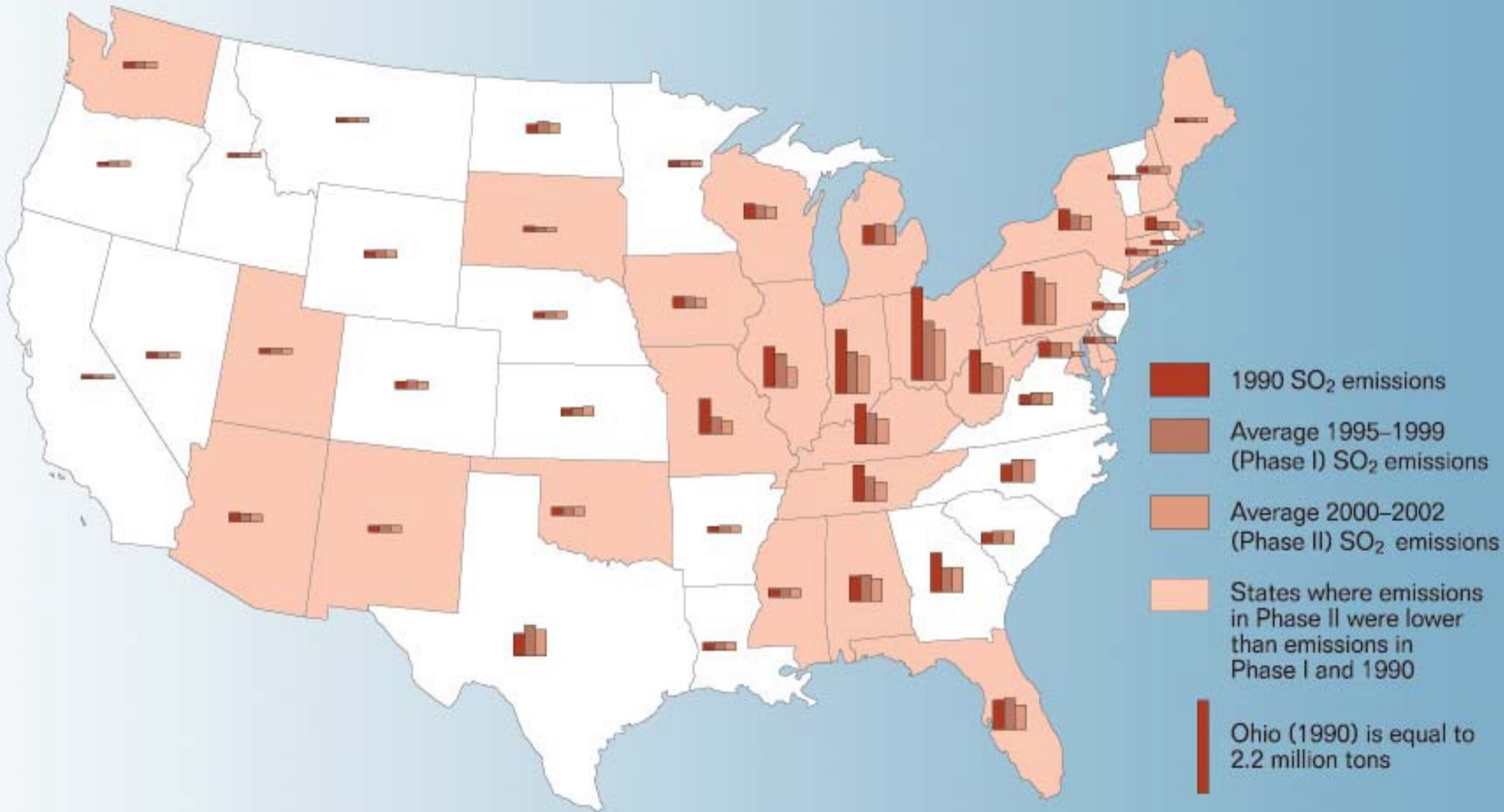
Source: EPA

FIGURE 12. NO_x emissions from all sources 1990–2001



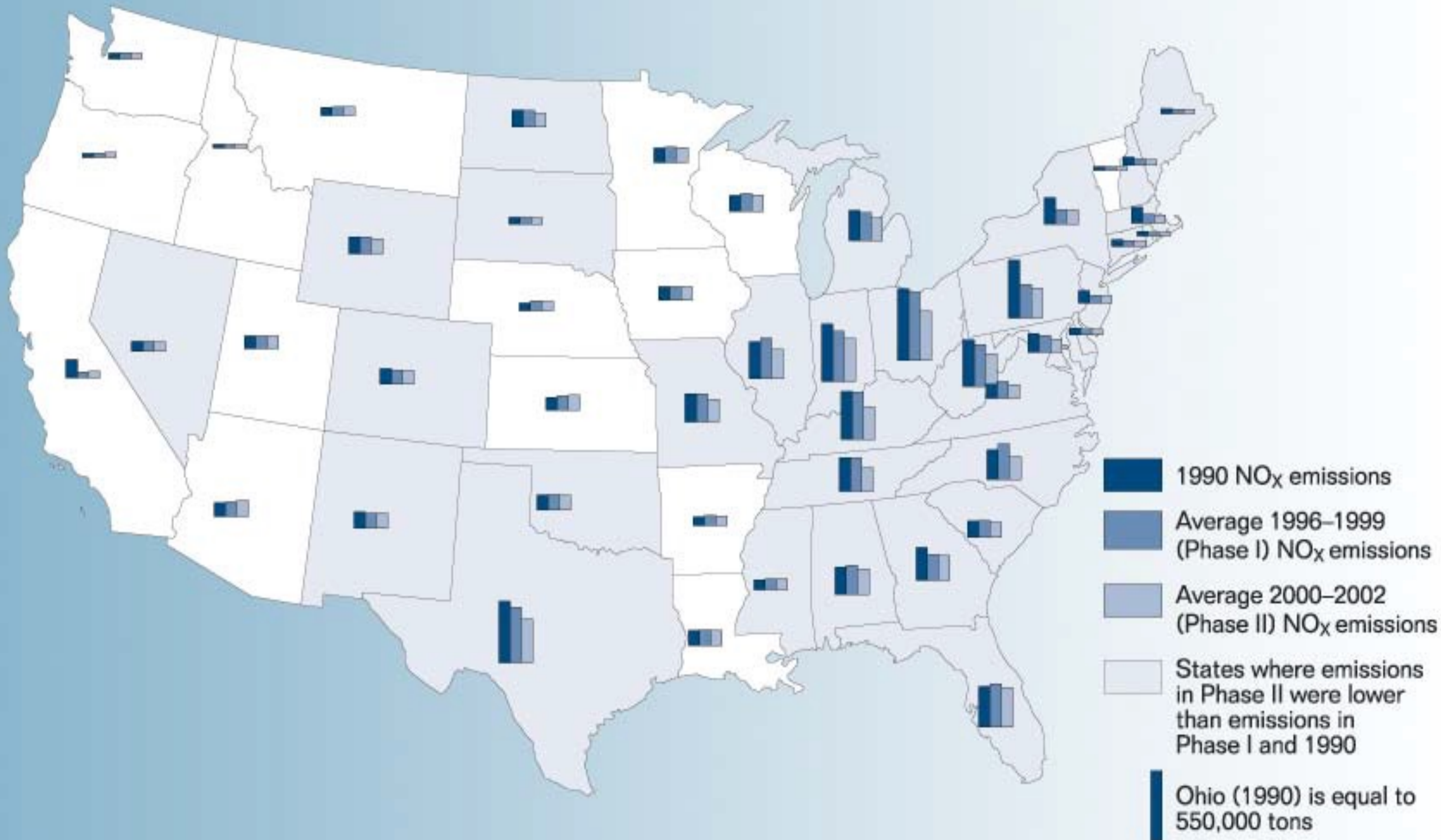
Source: EPA

FIGURE 13. SO_2 emission trends from power generation facilities by state 1990–2002



Source: EPA

FIGURE 14. NO_x emission trends from power generation facilities by state 1990–2002



Source: EPA

Figure 2: Annual Mean Ambient SO_2 Concentration

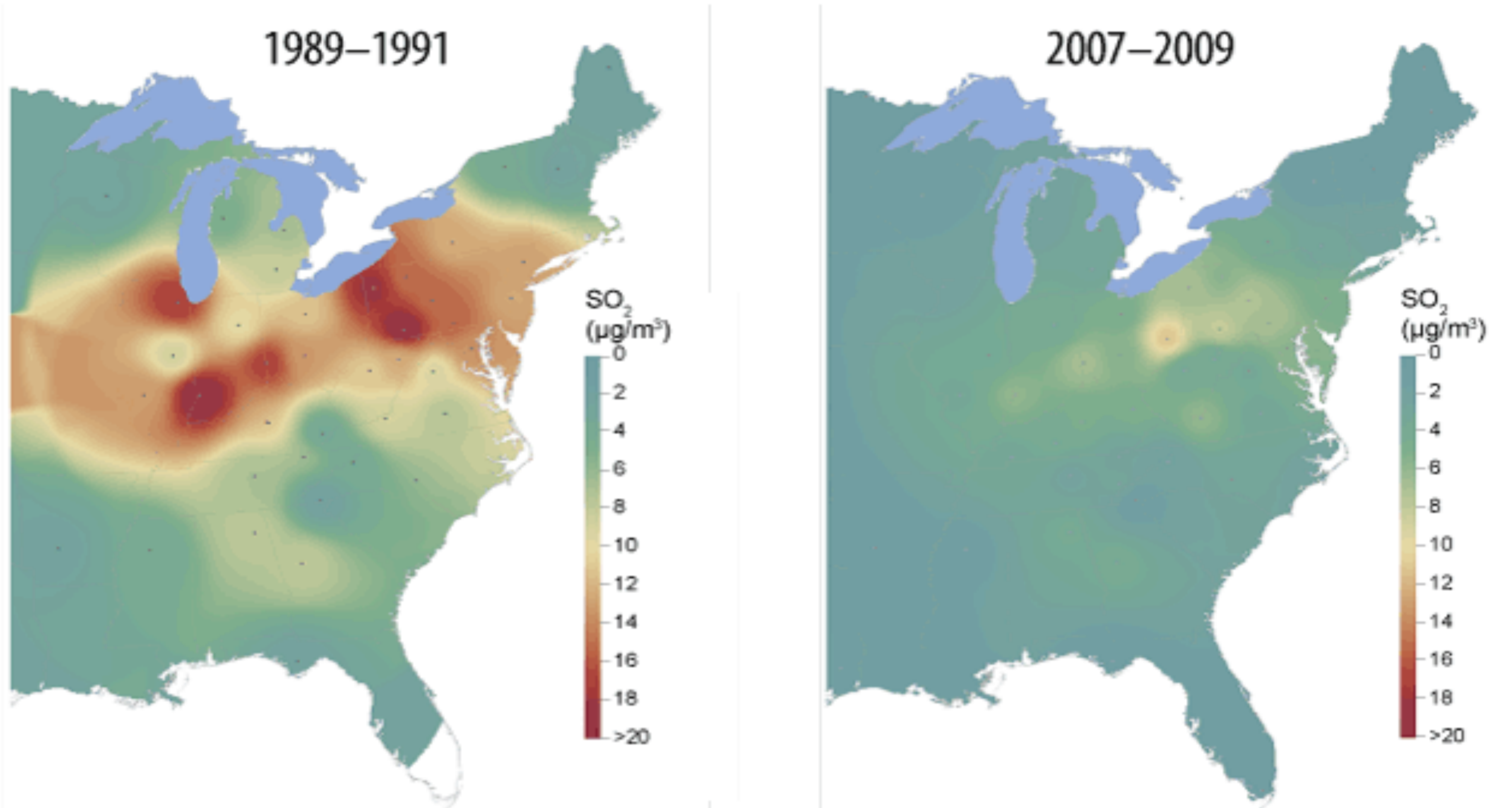


Figure 3: Annual Mean Ambient Sulfate Concentration

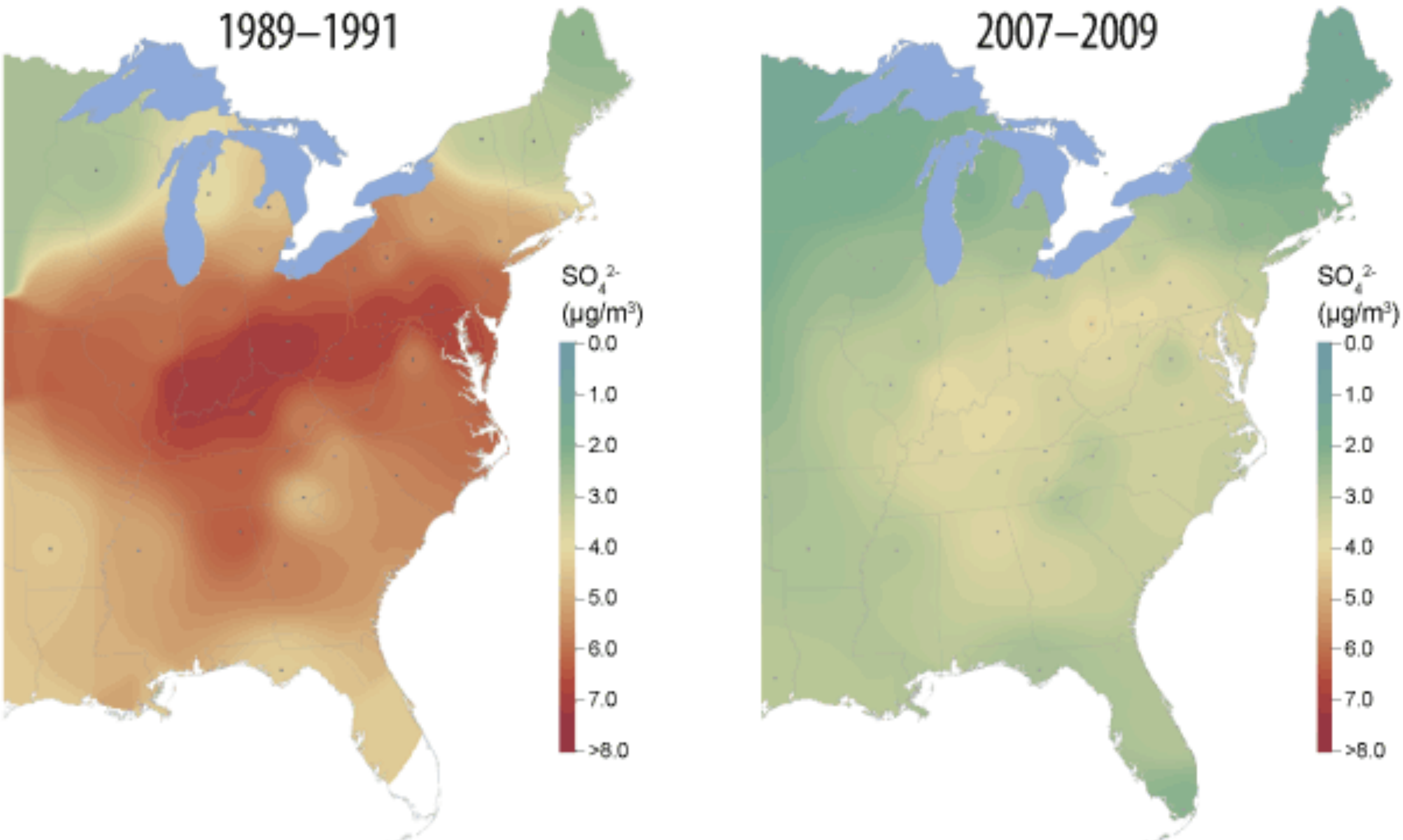
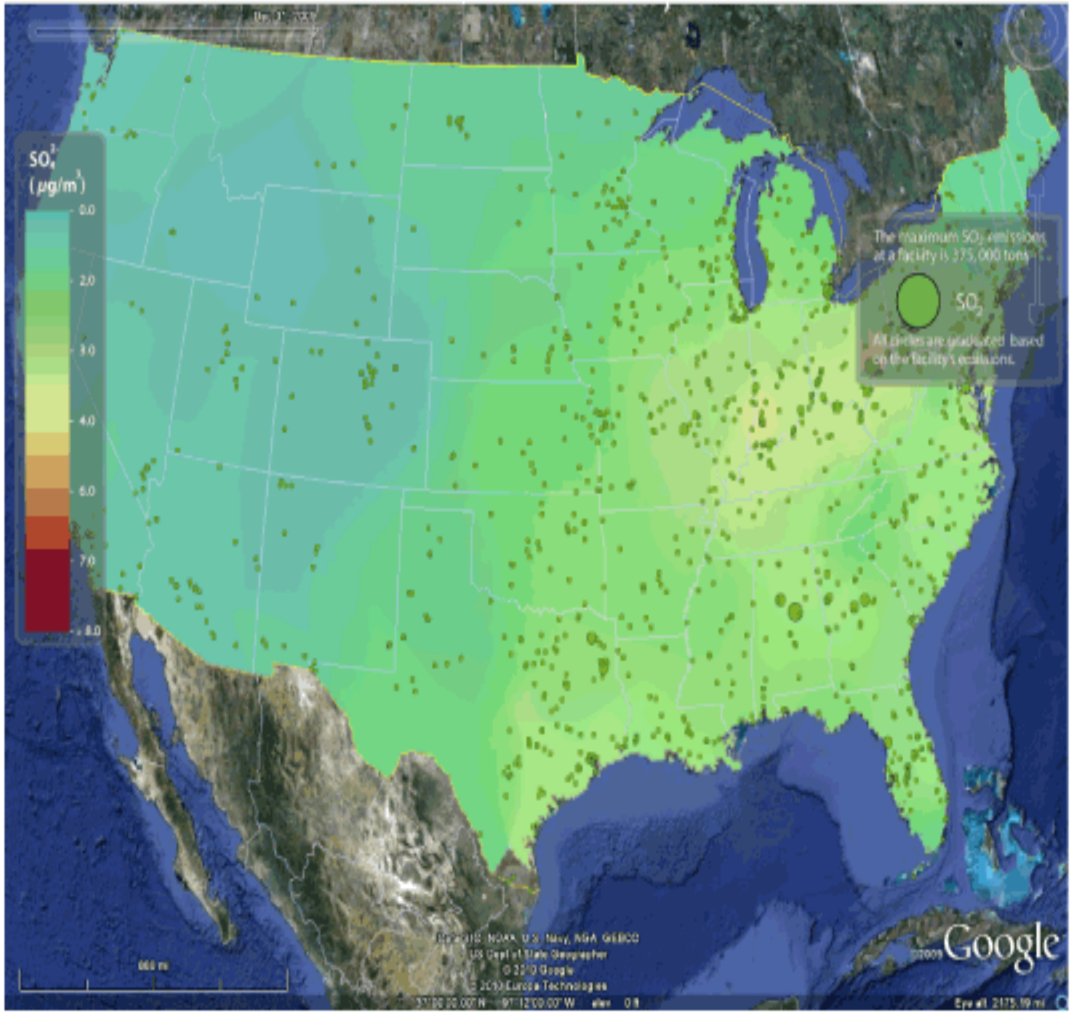
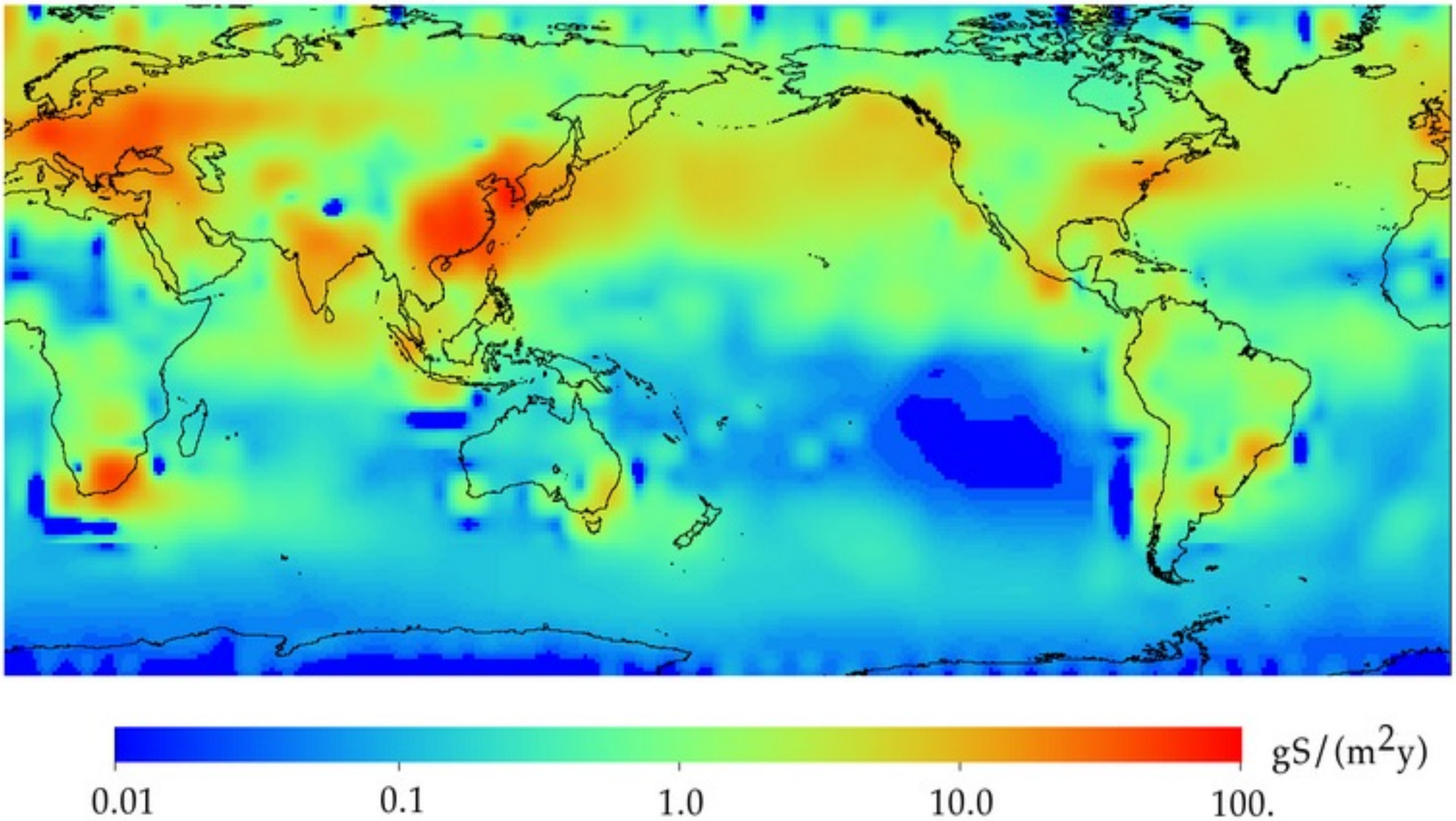


Figure 19: US SO_2 Emissions and Sulfate Concentrations, 2009



Note: This example depicts 2009 SO_2 emissions from ARP sources along with 2009 sulfate concentration data as measured by the CASTNET monitoring program.

Source: EPA, 2010



Distribution of sulfur oxide deposition, year 2025

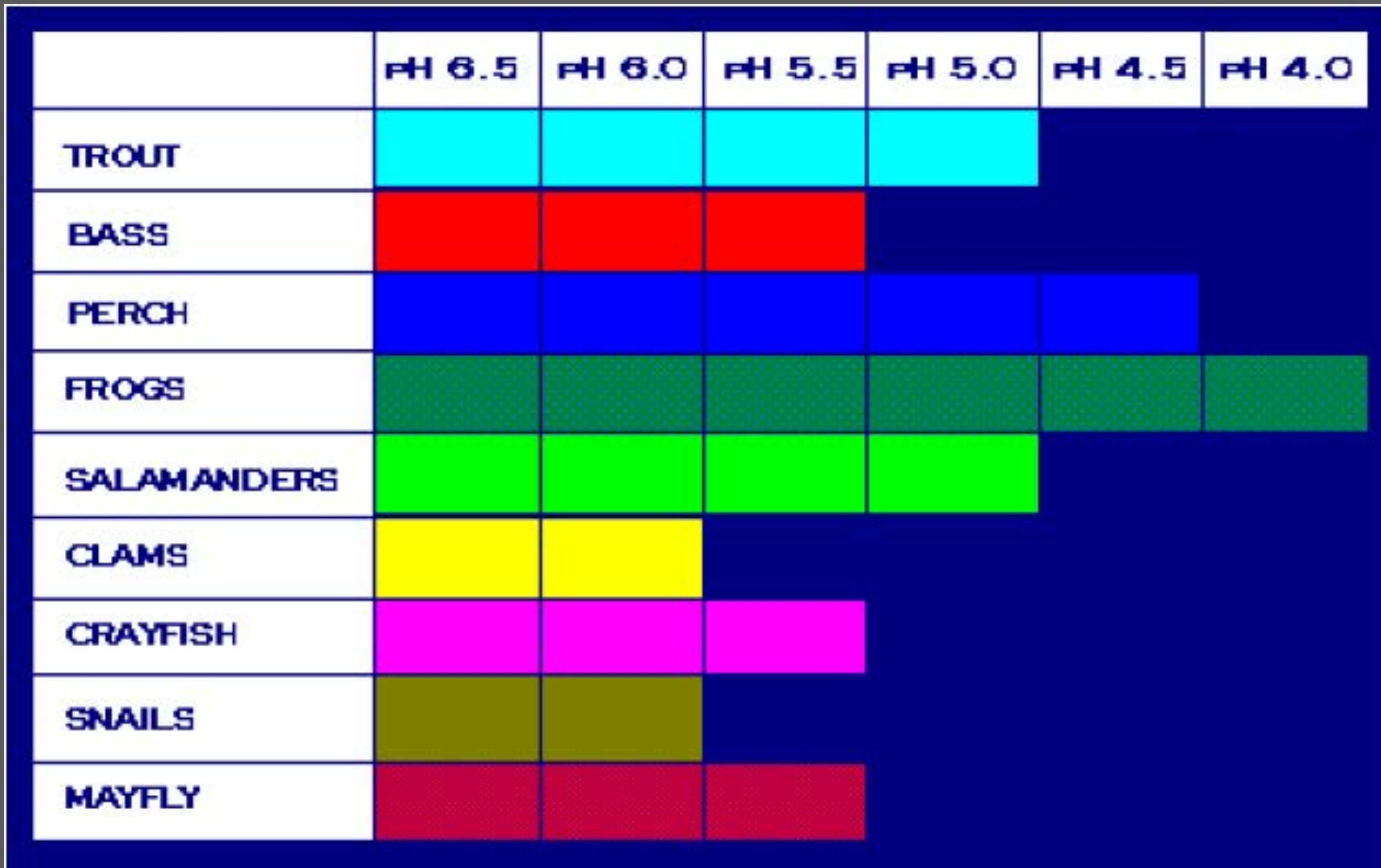
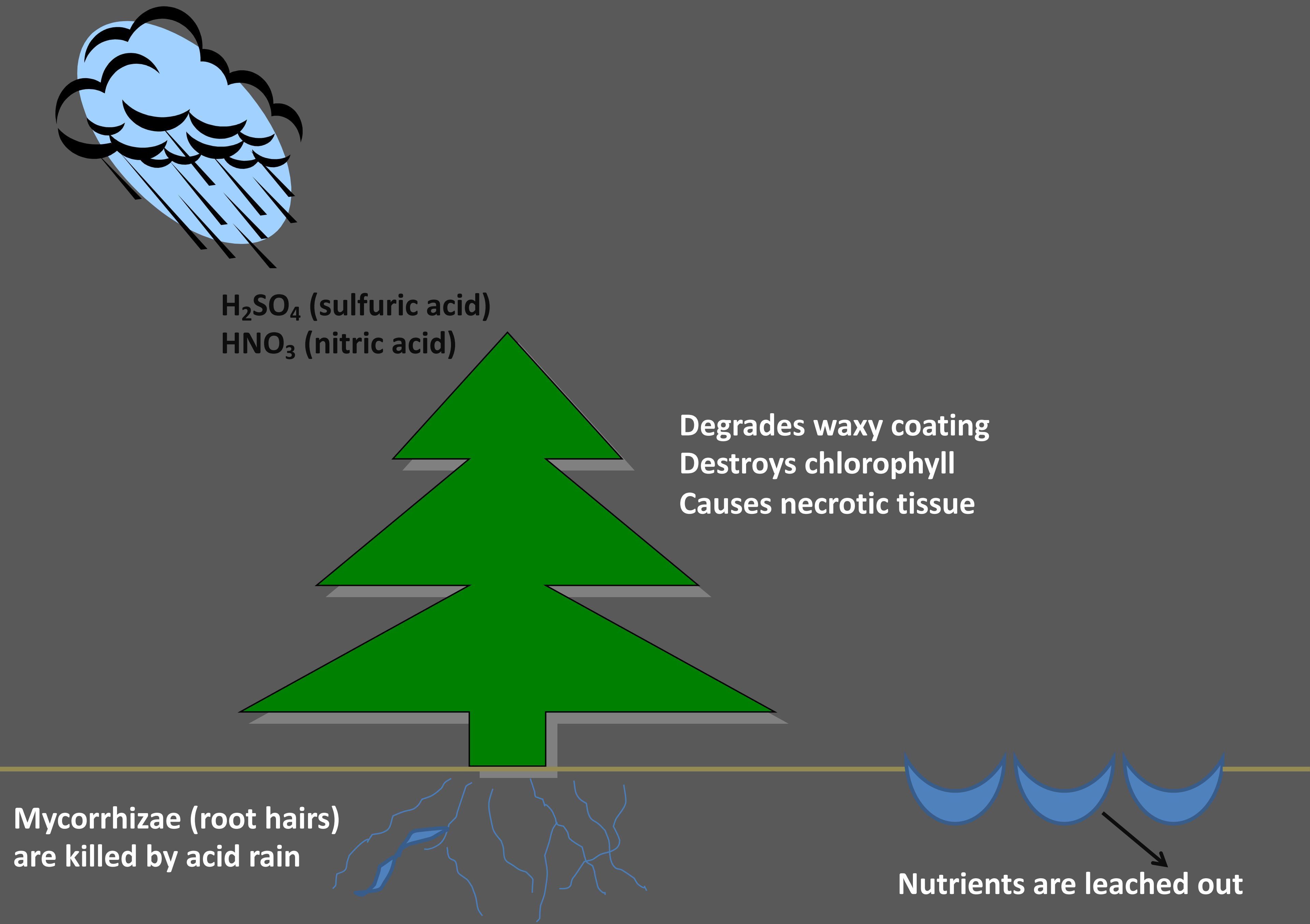


Figure 6.11. Range of pH tolerated by selected aquatic organisms.



H_2SO_4 (sulfuric acid)
HNO_3 (nitric acid)
Degrades waxy coating
Destroys chlorophyll
Causes necrotic tissue
Mycorrhizae (root hairs)
are killed by acid rain
Nutrients are leached out

Acid rain and statue degradation

- **Calcium carbonate, the main component of marble and limestone, is not soluble in water.**
- **Acids contained in acid rain transform $CaCO_3$, by chemical reactions, into soluble salts which are washed away, giving rise to the formation of holes on the surface of artifacts**

Leshan Buddha in China, 2005, sandstone blackened and corroding from acid rain. Photo by Ariel Steiner

Figure over the portal of a castle in Westphalia, Germany, Photographed in 1908 (left) and again in 1968 (right)

Summary

- Anthropogenic aerosols reflect 2-10 W m^{-2} of solar energy back to space across N. America and Eurasia
- Acid rain - SO_x and NO_x form sulfuric acid (H_2SO_4) and nitric acid (HNO_3) which dissolve into rain and snow and fall out
- Acid rain contributes toward increased ocean acidity, but the primary cause is increasing atmospheric CO_2 dissolving into the ocean

NASA movie of aerosol types blowing around the planet for one year

https://gmao.gsfc.nasa.gov/research/aerosol/modeling/nr1_movie/