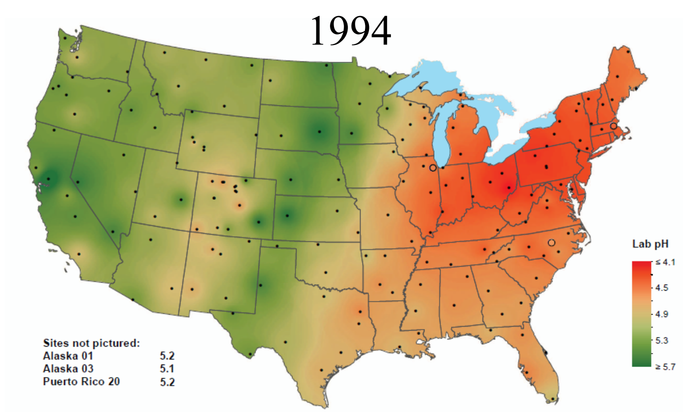
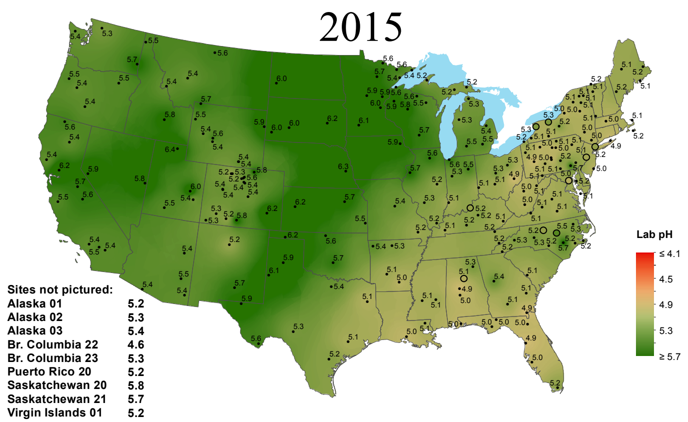
Environmental Impacts of Air Pollution

- Ozone
- Acid rain
- Eutrophication
- Persistent organic pollutants
- Heavy metals (chromium, mercury)





Source: National Acid Deposition Program/National Trends Network,
http://nadp.isws.illinois.edu

Environmental Impacts of Air Pollution

- Atmospheric concentrations are vey low
  - $\sim 10^{-9}$ atm for acid species
  - $\sim 10^{-13}$ atm for mercury
  - $\sim 10^{-12}$ atm for persistent organic pollutants (POP)

- However, the environmental impacts are significant, because of bioaccumulation of the deposited chemical species in the ecosystems.

Acid Rain

- Acid deposition
  - Scavenging of acid species by precipitation (mostly rain), i.e., wet deposition
  - Dry deposition of gaseous and particulate pollutants
  - Deposition of acidic fogs

- Measurements are easier for wet deposition, therefore, the term “acid rain” is widely used. However, dry deposition may be commensurate with wet deposition and it is more accurate to refer to acid deposition.

Environmental Impacts of Acid Deposition

- Impacts on forests and crops: Acidification of soils, which leads to the mobilization of various species. Some nutrients, such as magnesium (Mg) and calcium (Ca) may be lost via runoff, while some toxic species, such as aluminum (Al) may become available to roots. This leads to damage to vegetation with significant loss of trees and crops.
- Impacts on surface waters: Acidification of lakes for example may lead to a loss of plankton, aquatic plants, and fish. Fish-eating birds may also be affected (e.g., impacts on reproduction).
- Impacts on materials (buildings, statues…): erosion of calcareous stones (e.g., chalk stone, some marbles) due to the conversion of calcite to gypsum: $H_2SO_4 + CaCO_3 \Rightarrow CaSO_4 + CO_2 + H_2O$

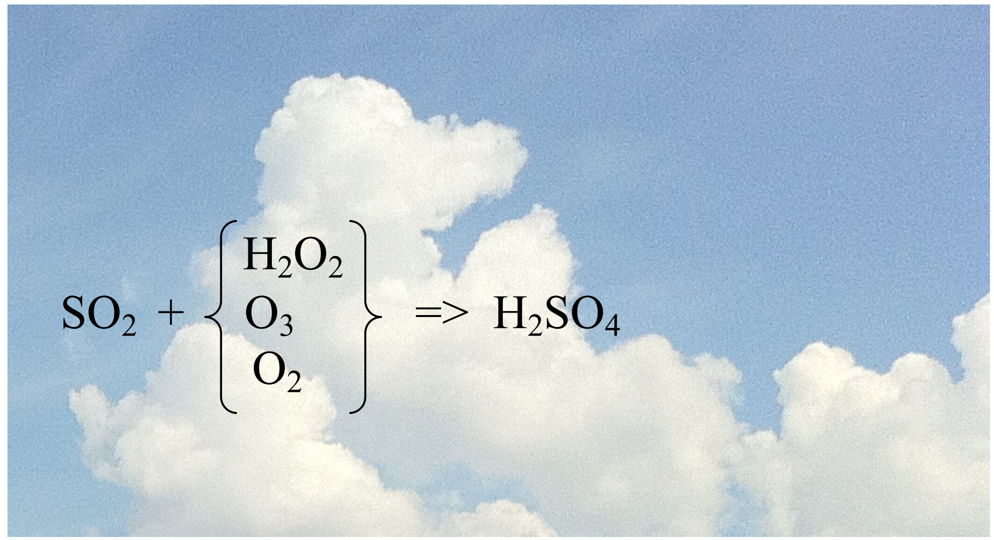
Sources of Acid Deposition

- All combustion processes lead to nitrogen oxides emissions, due to reactions between oxygen and nitrogen at high temperatures: NO and NO_2

- Coals and fuels contain sulfur, which via the combustion process is emitted as sulfur oxides, mostly sulfur dioxide: SO_2

Sulfuric Acid Formation

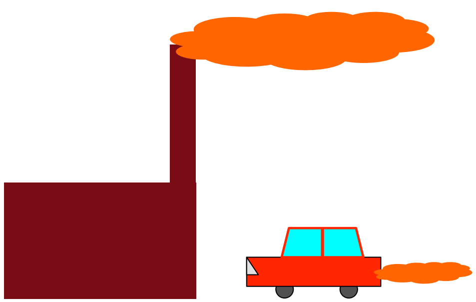
System of non-linear reactions in clouds



$$SO_2 + \left\{ \begin{array}{l} H_2O_2 \\ O_3 \\ O_2 \end{array} \right\} \Rightarrow H_2SO_4$$

$$SO_2 + OH \Rightarrow H_2SO_4 + HO_2$$

SO_2

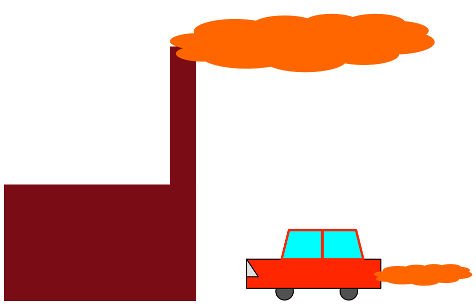


Nitric Acid Formation

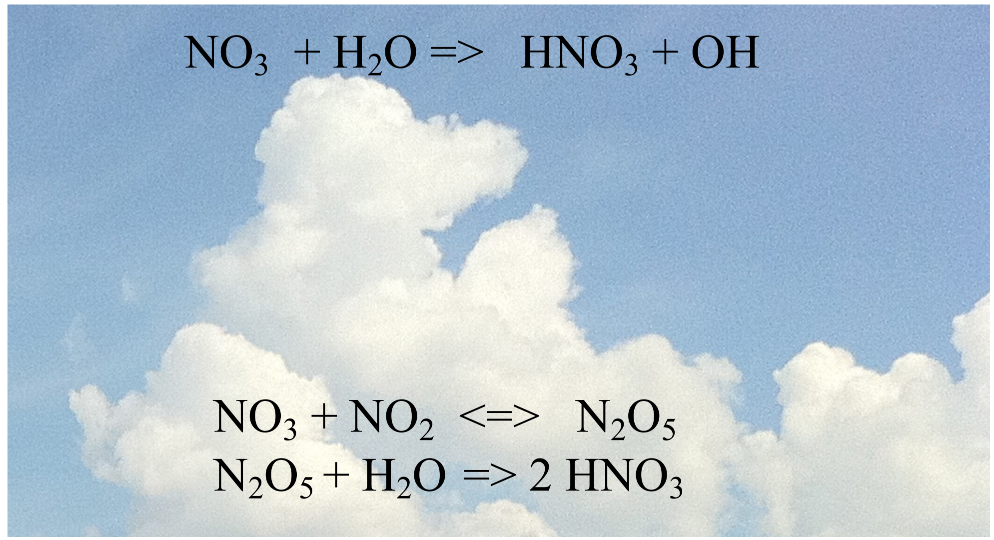
$NO_2 + O_3 \Rightarrow NO_3 + O_2$

$NO_2 + OH \Rightarrow HNO_3$

NO_x



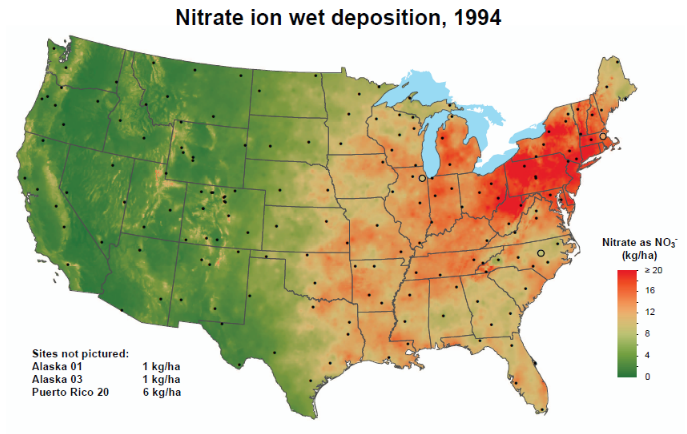
Heterogeneous reactions in clouds

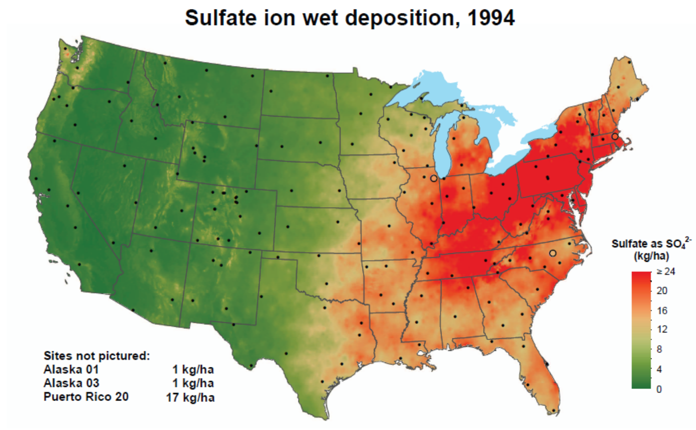


Acid Deposition: Uncertainties

- The chemistry of the formation of sulfuric acid, H_2SO_4, and nitric acid, HNO_3, is well-known but some uncertainties remain:
  - Formation of HNO_3 by heterogeneous chemical reactions on atmospheric particles
  - The presence in space and time of clouds and precipitations (meteorological simulations)

Acid Rain in the United States: 1994





Source: National Acid Deposition Program/National Trends Network, http://nadp.isws.illinois.edu

Acid Deposition: Emission Control

Reducing acid deposition implies reducing the emissions of the gaseous precursors of sulfuric acid and nitric acid, i.e., sulfur dioxide, SO_2, and nitrogen oxides, NO_x, respectively.

SO_2 emissions may be reduced efficiently by means of a flue gas desulfurization system (FGD), which converts SO_2 into calcium sulfate following its dissolution in water.

$$SO_2 + CaCO_3 + 1/2\ O_2 + 2\ H_2O \Rightarrow CaSO_4\text{-}2\ H_2O + CO_2$$

NO_x emissions may be reduced efficiently with selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) systems, which convert NO to N_2 via reaction with ammonia, NH_3.

$$NO + NH_3 + 1/4\ O_2 \Rightarrow N_2 + 3/2\ H_2O$$

$$NO + NO_2 + 2\ NH_3 \Rightarrow 2\ N_2 + 3\ H_2O$$

Acid Deposition
Public Policy Strategies

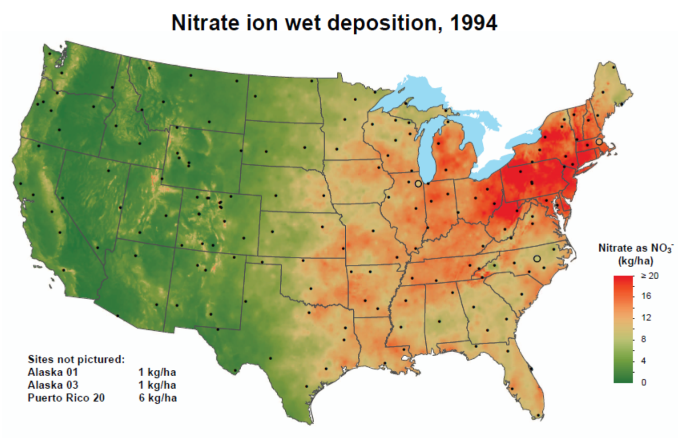
There are two main approaches:

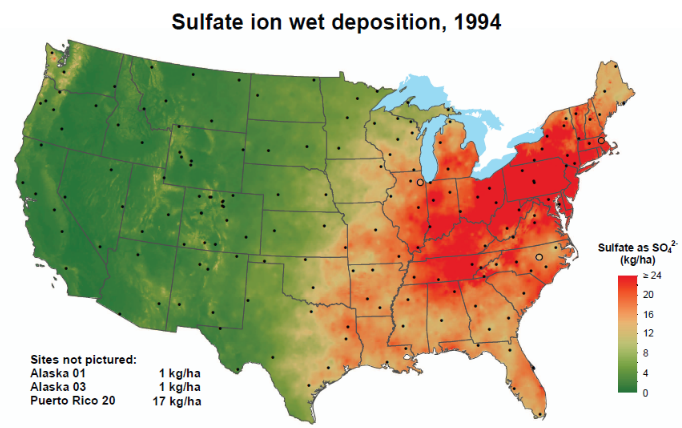
- Emission limits are defined for all sources of a given source category (e.g., coal-fired power plants).

- An emission ceiling is defined for the ensemble of sources of a given source category and industry has the flexibility of the amount of emissions reduction (or not at all) at individual sources, as long as emissions from all sources remain below the emission ceiling. This system is called “cap and trade”.

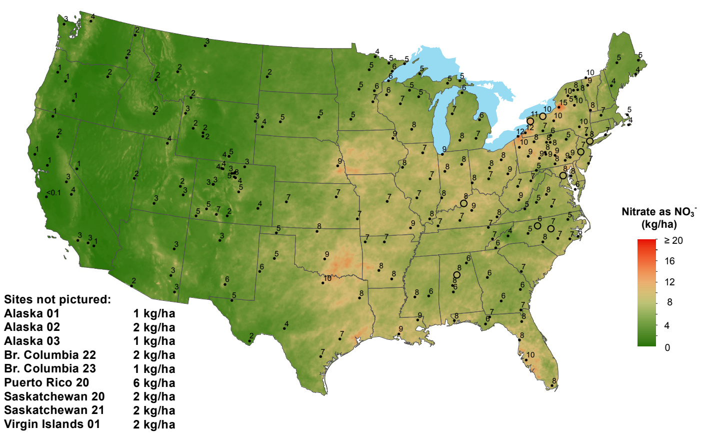
> The “cap and trade” approach has been used in the United States for coal-fired power plants to reduce acid deposition

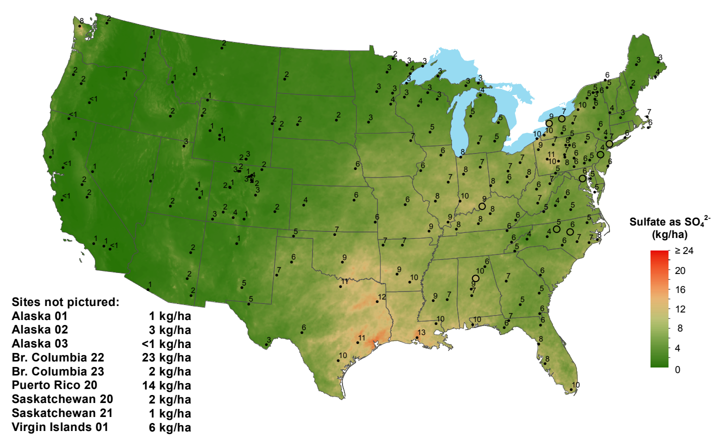
Acid Rain in the United States: 1994 => 2015





1994



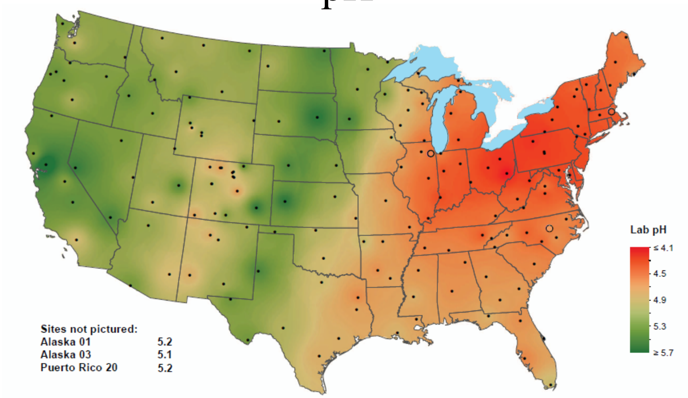


2015

Source: National Acid Deposition Program/National Trends Network, http://nadp.isws.illinois.edu

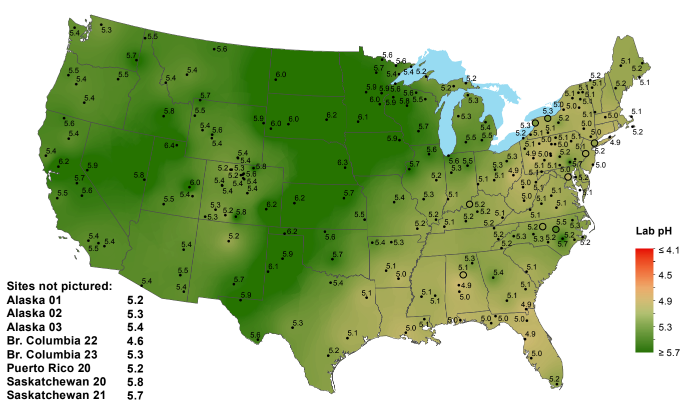
Acid Rain in the United States: 1994 => 2015

pH



1994

2015



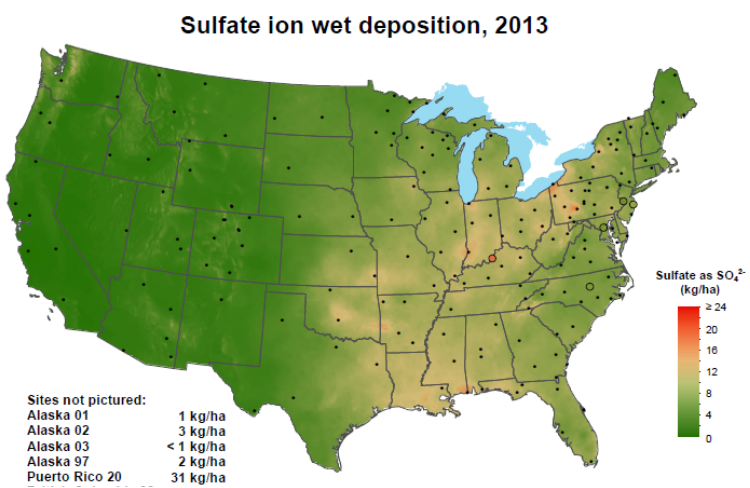
Effect of SO_2 and NO_x coal-fired power plant emission reductions: Significant decrease of acid deposition in the northeastern U.S. and an associated increase in rain pH.

Source: National Acid Deposition Program/National Trends Network, http://nadp.isws.illinois.edu

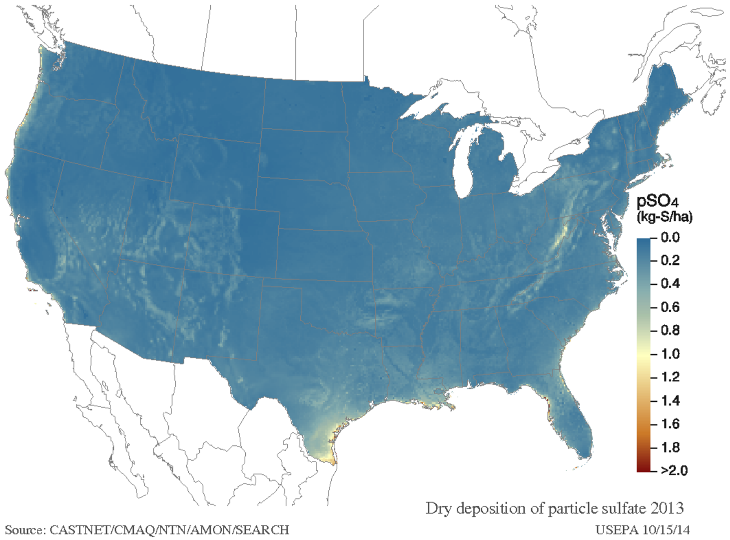
Acid Deposition in the United States
Wet and Dry Deposition

Atmospheric deposition of sulfate
Wet deposition dominates because of the low deposition velocity of particles

Wet deposition of sulfate



Dry deposition of sulfate
(expressed as S; x 3 for sulfate)

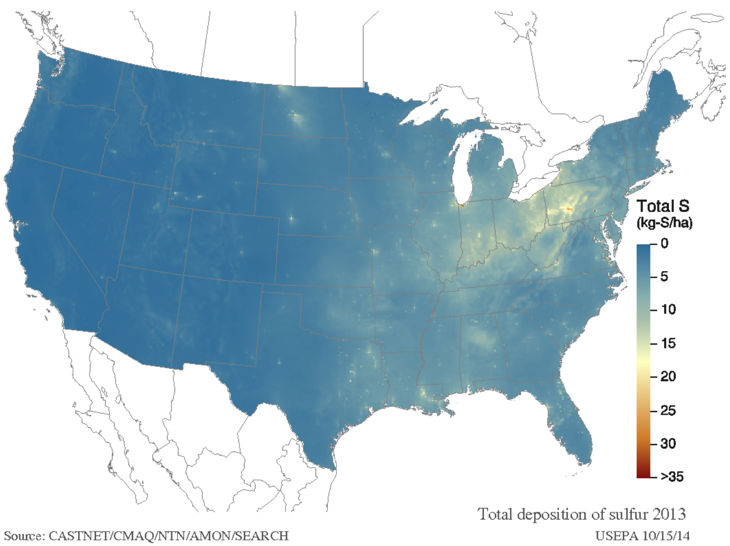


Source: National Acid Deposition Program/National Trends Network,
http://nadp.isws.illinois.edu

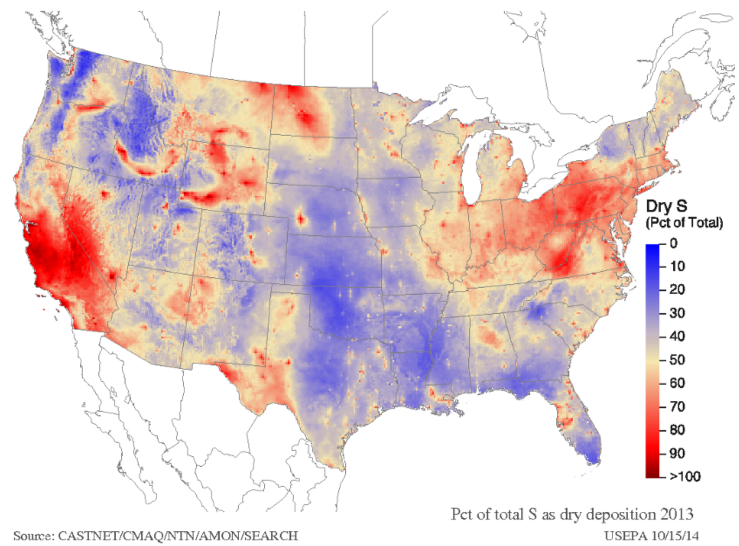
Acid Deposition in the United States
Wet and Dry Deposition

Atmospheric deposition of sulfur (SO_2 + sulfate)
Dry deposition dominates because of the importance of SO_2 dry deposition

Total deposition of sulfur



Dry deposition percentage

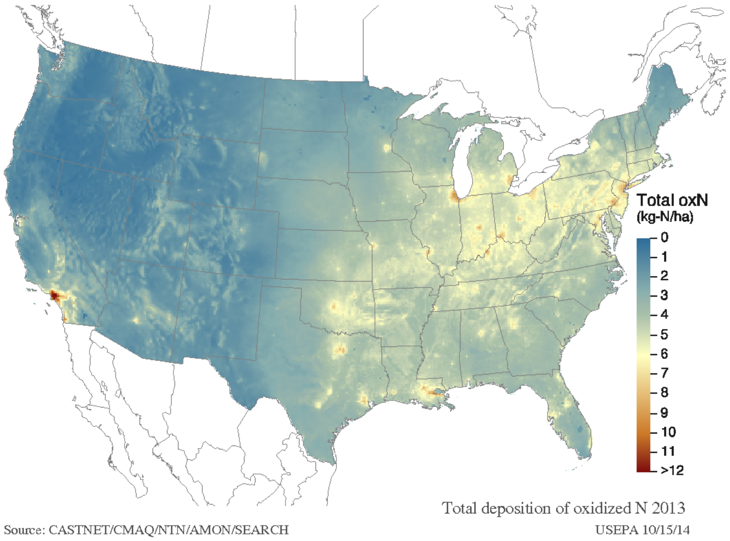


Source: National Acid Deposition Program/National Trends Network,
http://nadp.isws.illinois.edu

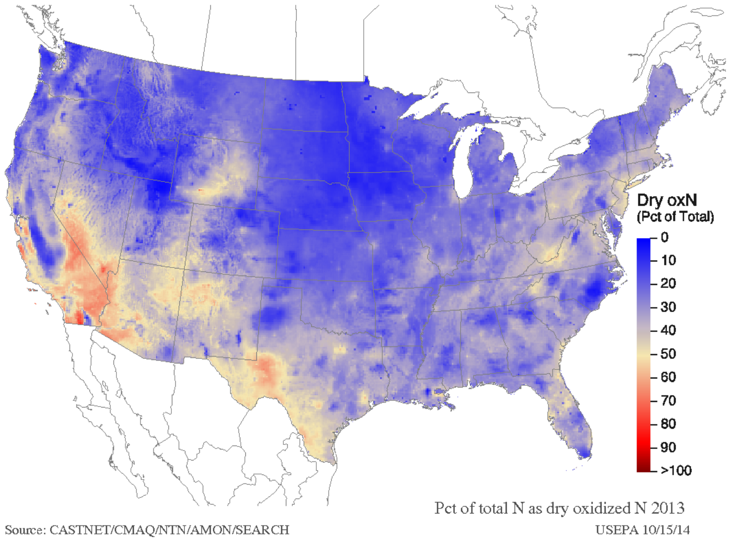
Acid Deposition in the United States
Wet and Dry Deposition

Atmospheric deposition of oxidized nitrogen (HNO_3 and organic nitrates)
Dry deposition dominates in the Southwest
and is commensurate with wet deposition in the East

Total deposition of oxidized nitrogen



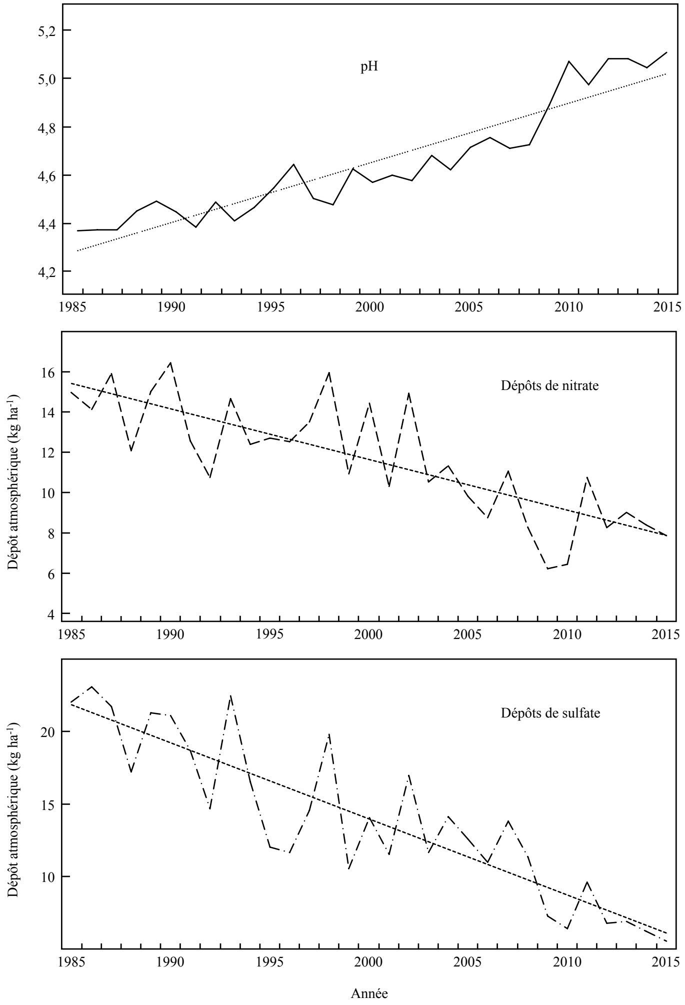
Dry deposition percentage



Source: National Acid Deposition Program/National Trends Network,
http://nadp.isws.illinois.edu

Acid Rain in the United States: 1985 => 2015

Example of wet deposition of sulfate and nitrate at White Face Mountain in New York State from 1985 to 2015: Increase of pH, which results from a significant decrease in sulfate and nitrate wet deposition fluxes.



Eutrophication

- Direct discharge or atmospheric deposition to surface water bodies of chemical species that favor the growth of aquatic vegetation: phosphates and nitrogenous species

- The growth of aquatic vegetation leads to a decrease in the availability of sunlight at lower depths of the water body, thereby leading to a decrease in photosynthesis and available oxygen.

Eutrophication
Atmospheric Deposition of Nitrogenous Species

- The main atmospheric nitrogenous species that are deposited to surface waters include:
  - Nitric acid (HNO_3)
  - Ammonia (NH_3)
  - Organic nitrates (e.g., PAN)
  - Nitrogen oxides (NO_x)

- These nitrogenous species behave as fertilizers. For example, ammonium nitrate is a fertilizer that is widely used for crops.

Eutrophication
Atmospheric Deposition of Nitrogenous Species

Example of Escambia Bay in Florida

(Vijayaraghavan et al., *J. Air Waste Manage. Assoc.*, 2010)

- Contributions of nitrogenous species to atmospheric deposition to Escambia Bay were calculated to be as follows:
  - Nitric acid (HNO_3): 56 %
  - Ammonia (NH_3): 29 %
  - Organic nitrates (including PAN): 7 %
  - Nitrogen oxides (NO_x): 8 %

- Therefore, inorganic nitrate and ammonia dominate atmospheric deposition of nitrogen.

Eutrophication
Nitrogen Emission Control

- The control of nitrogen oxide emissions is typically being driven by regulations on ozone and acid rain.

- Ammonia emission control requires addressing emissions from agriculture.

Persistent Organic Pollutants (POP)

- Rachel Carson publishes “Silent Spring” in 1962
- Several scientific articles document the adverse effects of pesticides on birds:
  - Radcliffe, *Nature*, **215**, 208-210, 1967
  - Prest, Jefferies, and Moore, *Environ. Pollut*., **1**, 3-26, 1970
  - etc.

Persistent Organic Pollutants (POP)

- Environmental effects in animals
  - Weakening of egg shells
  - Perturbation of the endocrine system
  - Weakening of the immune system

- Health effects
  - Some POP lead to adverse health effects in humans
  - Some POP are carcinogenic

Persistent Organic *Pollutants* (POP)

- POP are organic pollutants that are mostly cyclic compounds (in some cases aromatic) with chlorine atoms (but not all)

- They tend to accumulate in the food chain, i.e., their concentration in a living organism increases by several orders of magnitude compared to their concentration in the corresponding environmental medium.

Persistent Organic *Pollutants* (POP)

- Examples of adverse health effects of dioxins in humans:
  - Dioxin ingestion may lead to chloracne
  - An increase in some types of cancers was observed in the populations located in the area contaminated by dioxin (2,3,7,8-TCDD) after the 1976 industrial accident in Seveso, Italy (Berlazzi et al., *Am. J. Epidemiology*, 2001 ; Pesatori et al., *Environ. Health*, 2009).

Persistent *Organic* Pollutants (POP)

The Stockholm Convention identified twelve POP that must be eliminated or have their emissions decreased significantly ("Dirty dozen")

- Pesticides
  - Aldrin
  - Chlordane
  - DDT
  - Dieldrin
  - Endrin
  - Heptachlor
  - Mirex
  - Toxaphene
- Fungicide
  - Hexachlorobenzene
- Species with dielectric properties
  - PCB
- Combustion products
  - Dioxins and furans

Persistent *Organic* Pollutants (POP)

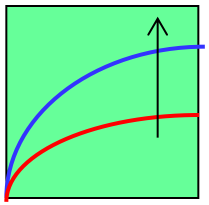
Other POP include for example:

– Hexachlorocyclohexanes (e.g., lindane)
- Hexabromobiphenyl
- Chlordecone
- Polycyclic aromatic hydrocarbons (PAH)
- etc.

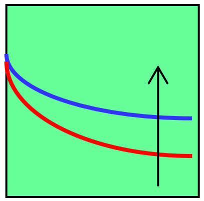
Persistent Organic Pollutants (POP)

- Lifetime
  - Several days in the atmosphere
  - Several years in soils and waters

- For a given emission rate, the environmental concentration increases with the lifetime.



- For a given initial environmental concentration, the degradation time increases with the lifetime.



Time

POP: Grasshopper Effect

- Semi-volatile pollutants such as persistent organic pollutants (POP) have a volatility, which varies with temperature. They will deposit more readily when the temperature is low as they are mostly present in the particulate phase. When the ambient temperature increases, their gas/particle partitioning will tend to shift toward the gas phase and they will be reemitted as gases.
- A succession of deposition and reemission steps of a semi-volatile pollutant is called the “grasshopper effect”, because the pollutant may be transported over long distances (several thousands of kilometers) via a series of deposition/reemission “hops”: This is the grasshopper effect.
- It is observed over regions where temperature decreases either with increasing latitude or increasing altitude.

POP: Emission Control

- Ban of the chemical: e.g., some pesticides, such as lindane in France
- Emission control technologies: e.g., dioxins and furans from incinerators with activated carbon

Heavy Metals

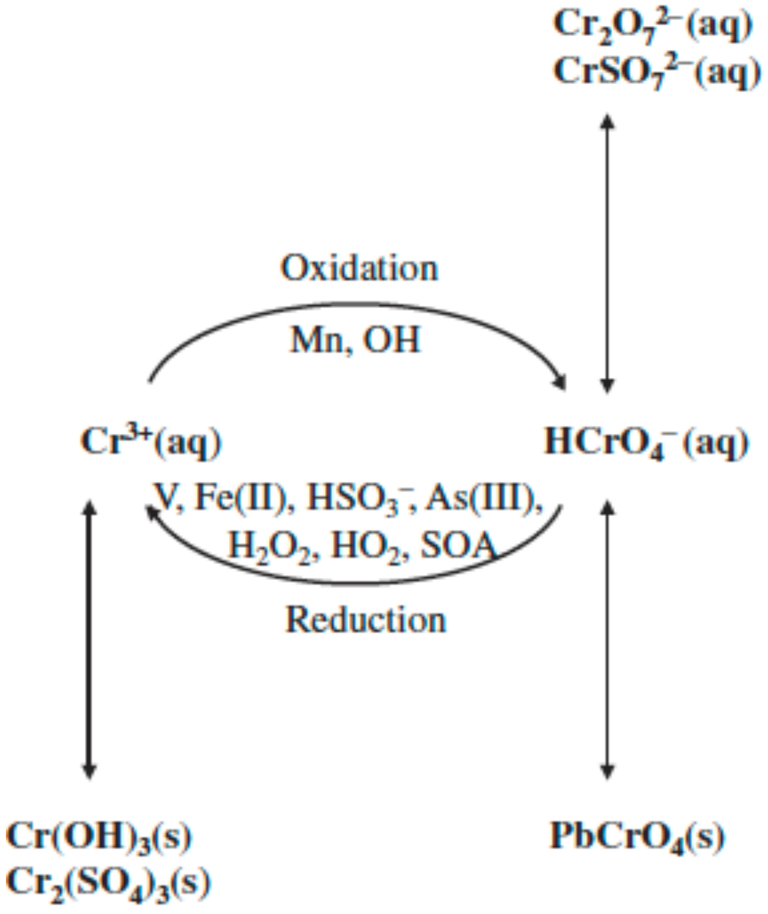
- Heavy metals: It is not a scientific definition, as it may include some metalloids (e.g., arsenic).

- Many heavy metals lead to adverse health effects for humans (e.g., mercury, chromium, arsenic, lead, cadmium) or the environment (e.g., mercury, copper).

- For some metals, their toxicity depends on their chemical speciation:
  - Chromium (Cr): the hexavalent form, Cr(VI), is carcinogenic, whereas the trivalent form, Cr(III), is not.
  - Mercury (Hg): the organic form, monomethyl mercury (MMHg), bioaccumulates readily in the food chain, whereas the inorganic forms do not.

Chromium

Chromium may undergo oxidation and reduction in the atmosphere. Overall, atmospheric conditions favor the reduction of the carcinogenic hexavalent form, Cr(VI), to the non-carcinogenic trivalent form, Cr(III).



Mercury

- Mercury is considered to be neurotoxic by several organizations (WHO, U.S. EPA, etc.).
- In the ambient environment, mercury presents adverse health effects mostly under its organic form (monomethyl mercury).
- Monomethyl mercury is found in surface waters that are located far away from mercury sources; therefore, the origin must be atmospheric deposition.
- Mercury is emitted in the atmosphere in its inorganic form. It is transformed into organic mercury in soils and surface waters (lakes, rivers, oceans).

Mercury Emissions

Natural emissions: oceans, volcanoes, mercury-rich rocks (cinnabar)

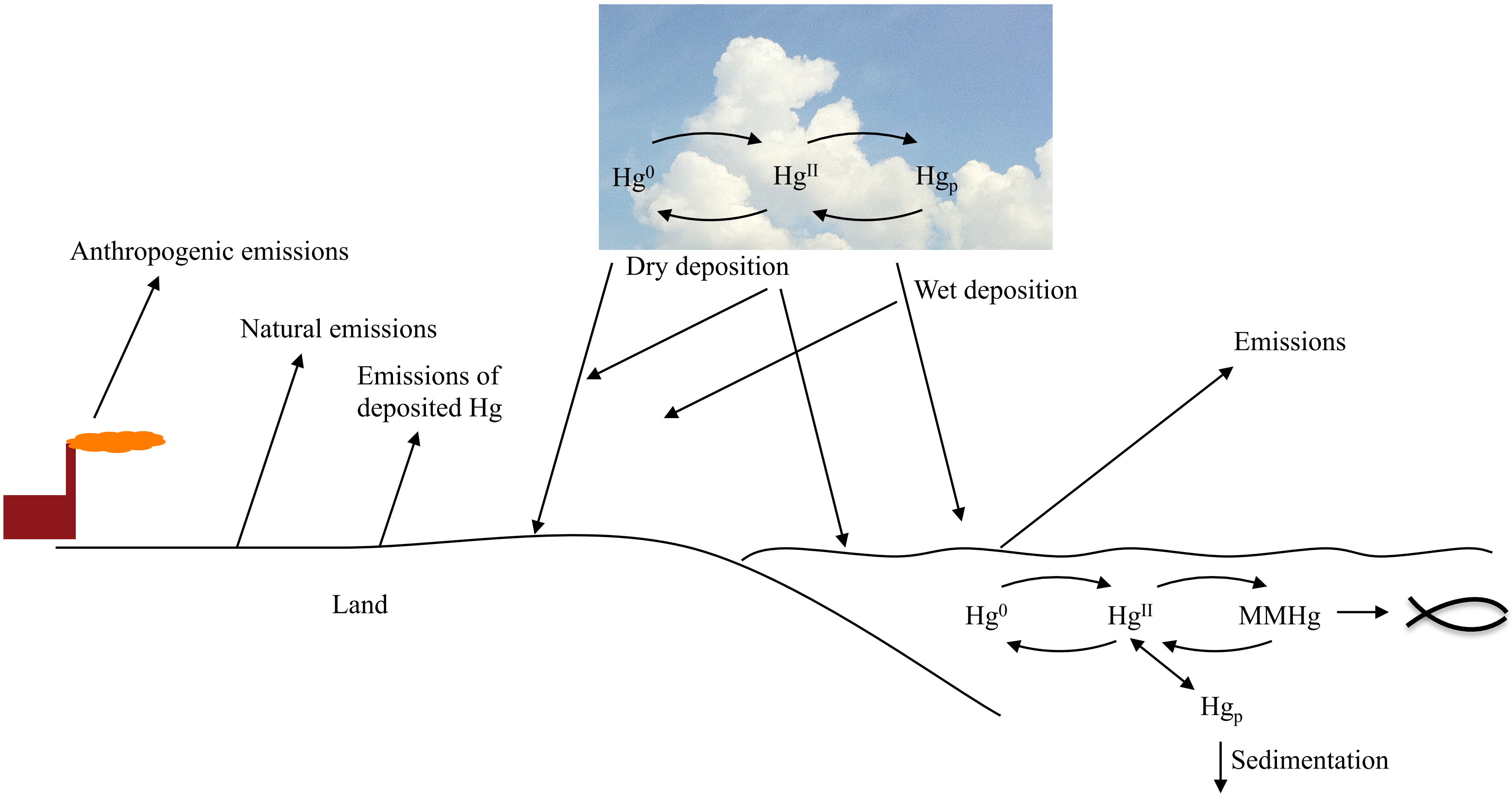
Anthropogenic emissions: coal combustion, waste incineration, chlorine production, gold mining, fungicides and bactericides

Reemissions of deposited atmospheric mercury: grasshopper effect

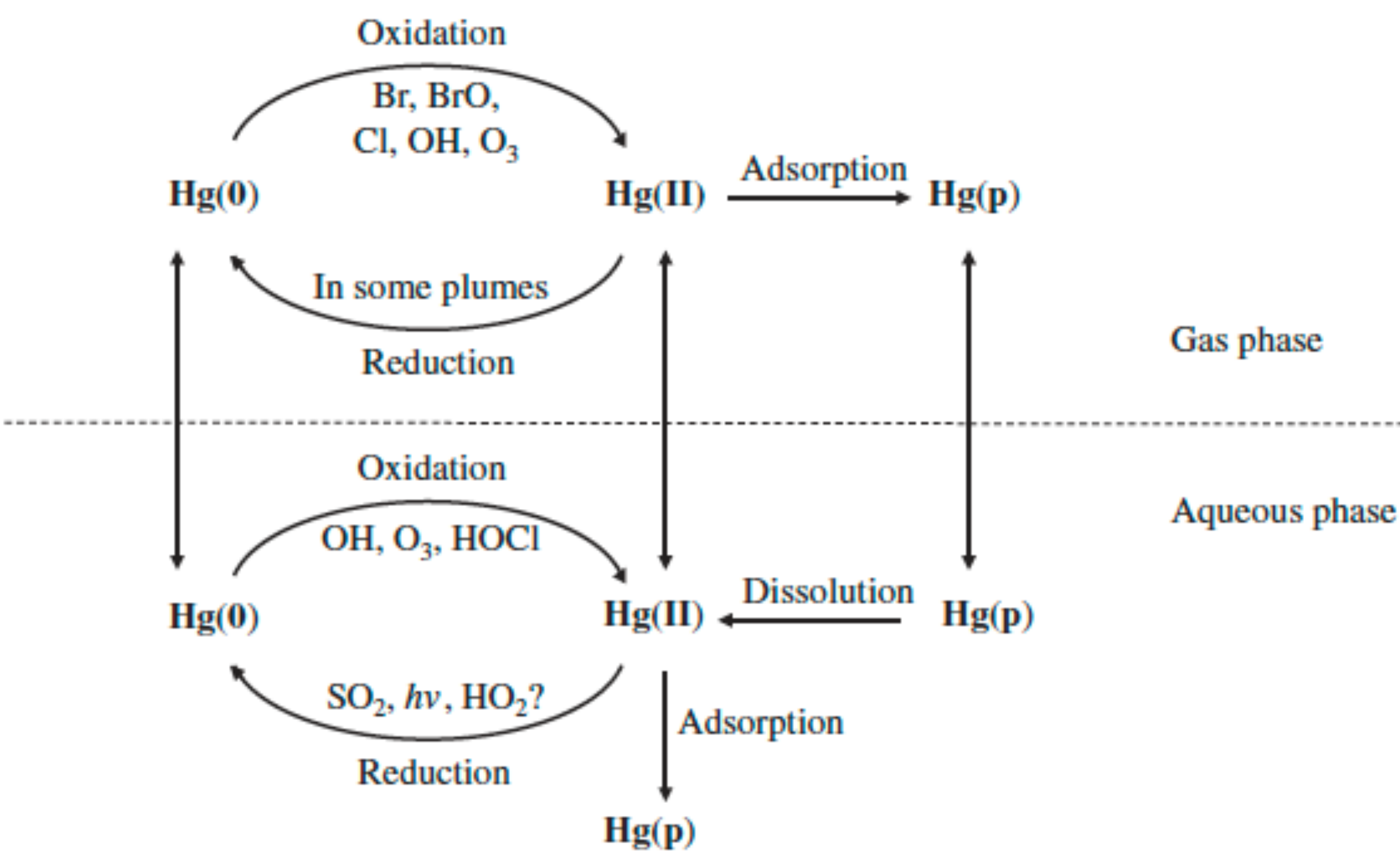
Current emissions = 6000 to 7000 tons per year

Current emissions / Preindustrial emissions ≈ 3

Mercury Cycle



Chemical Transformation of Atmospheric Mercury



Mercury Regulations in the United States

- The Clean Air Interstate Rule (CAIR) was proposed in 2005; CAIR was based on a cap-and-trade approach (similar to what was done for acid rain precursors). This law was rejected by a court in 2008 because it was not consistent with the Clean Air Act amendments of 1990.

- In 2011, the Mercury & Air Toxics Standards (MATS) were promulgated for coal-fired power plants. All coal-fired power plants must control their mercury emissions (unlike under CAIR). MATS should lead to an overall emission reduction of 74 %.

- The current (2019) federal administration plans not to regulate mercury emissions from old power plants, arguing that the health benefits estimated during the development of MATS were overestimated, because co-benefits (due to other pollutants than mercury) should not be taken into account.

Mercury Emission Control

- Mercury emissions may be directly controlled using activated carbon injection.

- The contaminated activated carbon must then be disposed of in an environmentally-sound manner.

- Power plants that use SCR for NO_x emission control and FGD for SO_2 emission control obtain some co-benefits because mercury emissions are then partially controlled: the SCR oxidizes Hg(0) to Hg(II) and the water-soluble Hg(II) is efficiently scavenged by the FGD scrubber.