AP 3050 Air Pollution

Air Pollution and Global Warming: History, Science, and Solutions

Chapter 5: Acid Deposition

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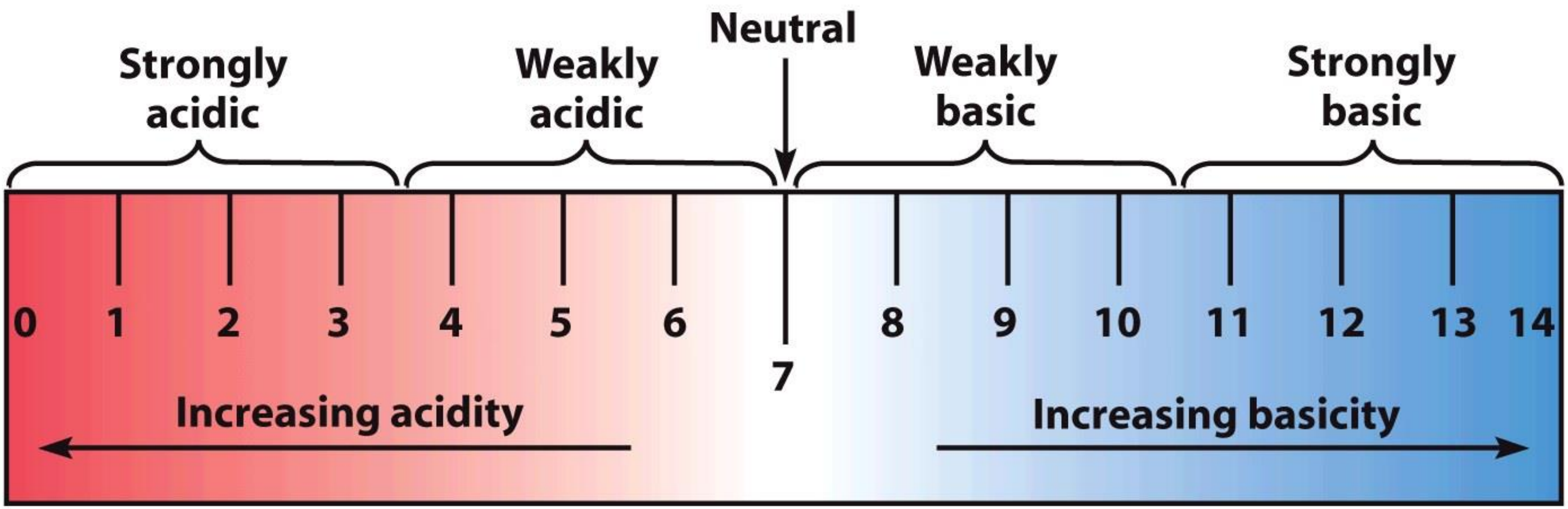
Spring 2024

By Mark Z. Jacobson
Cambridge University Press (2012)

Acid Deposition(酸沈降)

- 指大氣中的酸性物質因重力作用或降雨等過程而落到地表。
- 可分為乾沈降(dry deposition)與濕沈降(wet deposition)，前者有氣體、氣膠及懸浮微粒等，後者如降雨或下雪等。

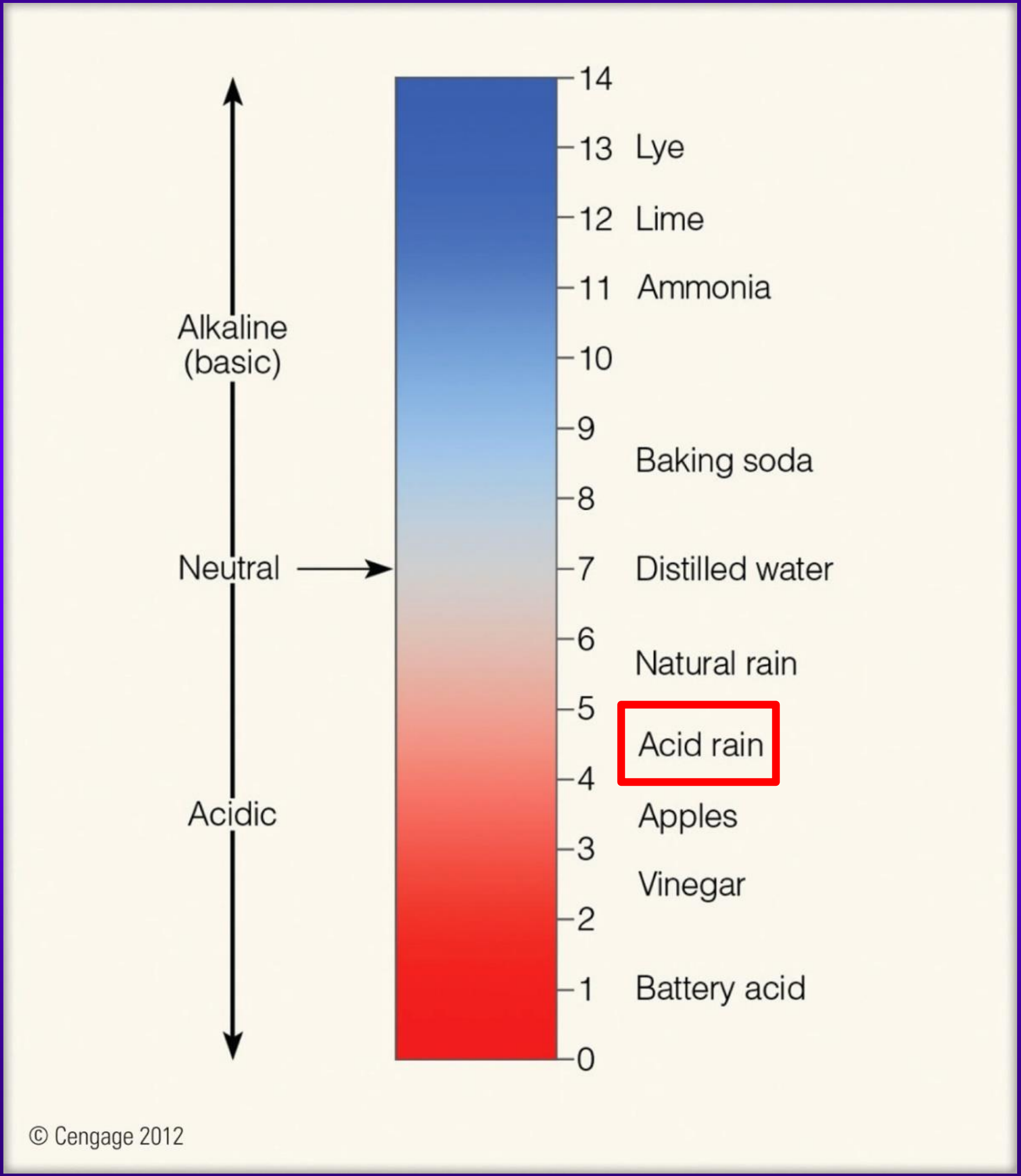
pH Scale(酸鹼值)



Neutral
Strongly acidic
Weakly acidic
Weakly basic
Strongly basic
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Increasing acidity
Increasing basicity

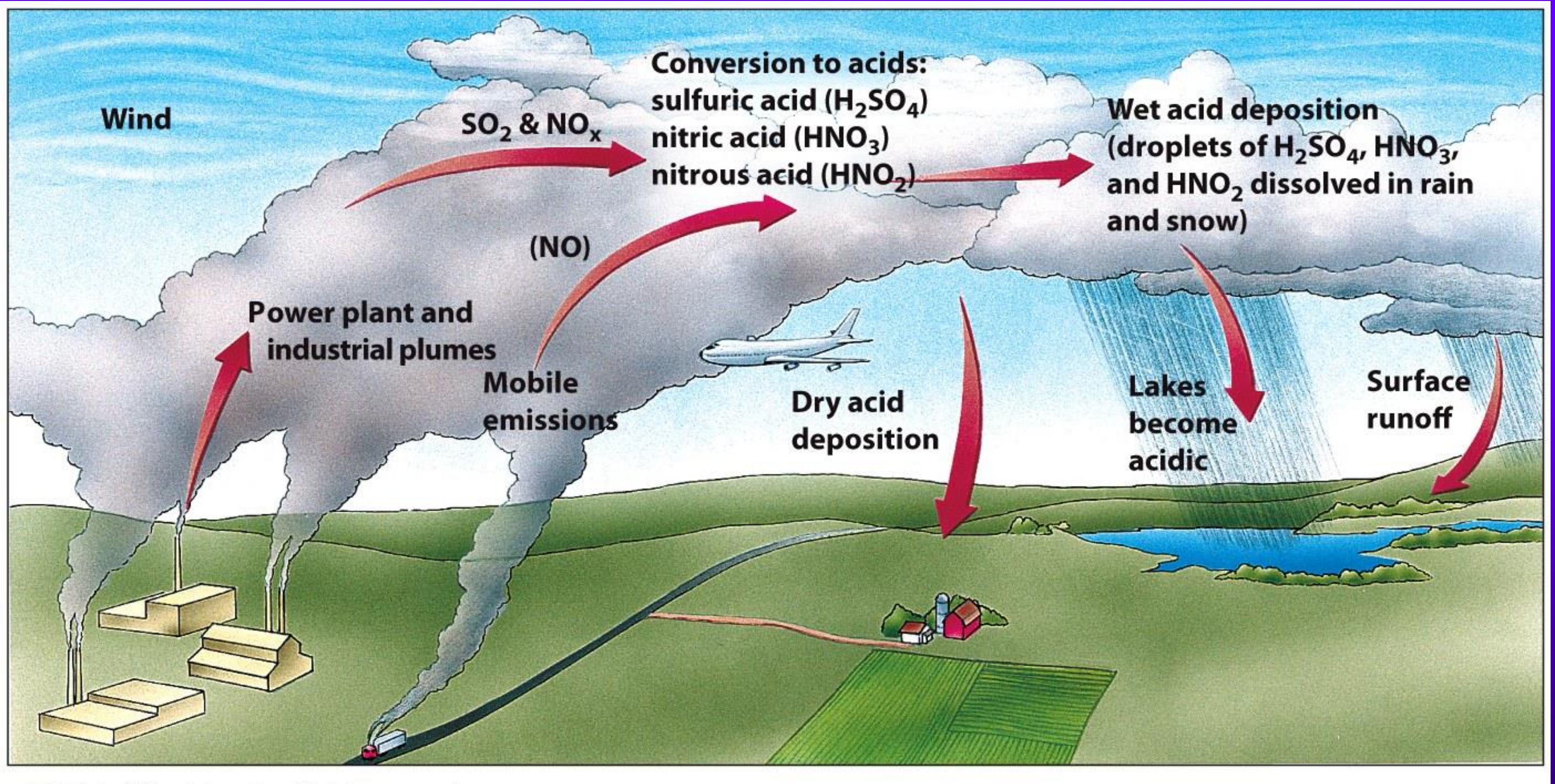
Acid Deposition(酸沈降)

- 因為大氣中的CO_2溶於水中，雨水正常的pH值約為5.6。
- 為了區分酸雨及正常雨水，酸雨之定義為$pH < 5.0$的雨水(ref. Seinfeld, 1986)。



Acid Deposition(酸沈降)

- Sulfur dioxide and nitrogen dioxide emissions react with water vapor in the atmosphere and form acids that return to the surface as either dry or wet deposition.



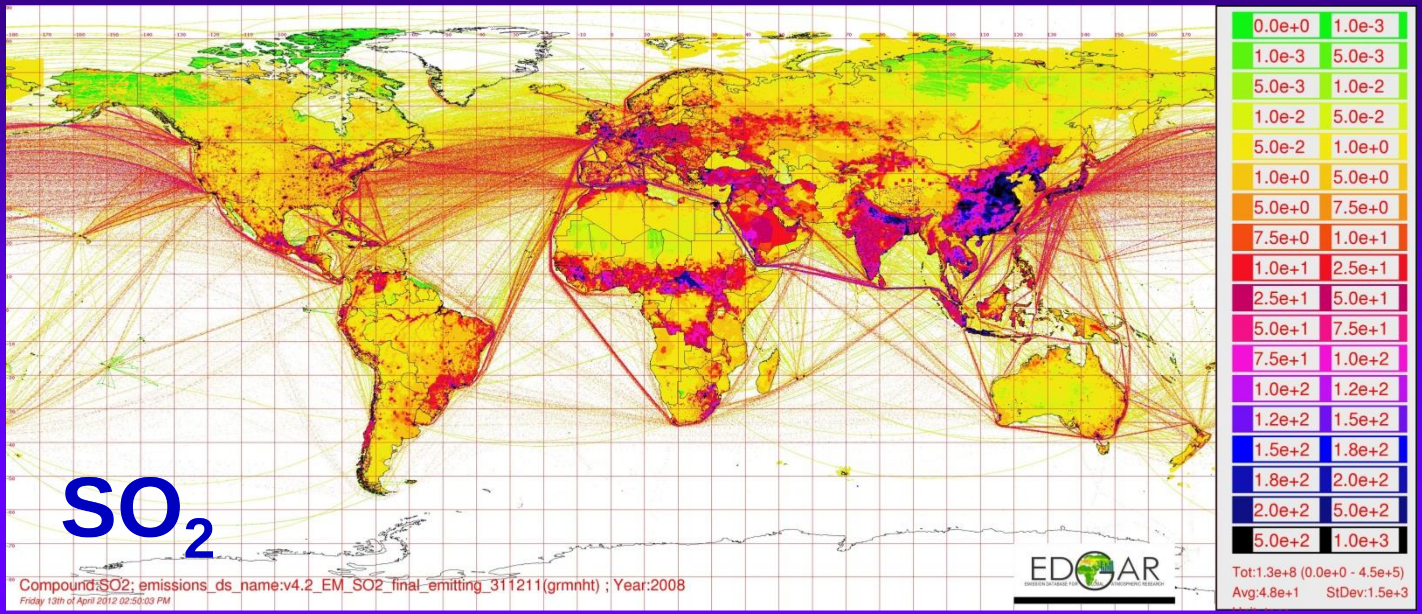
Acid Deposition(酸沈降)

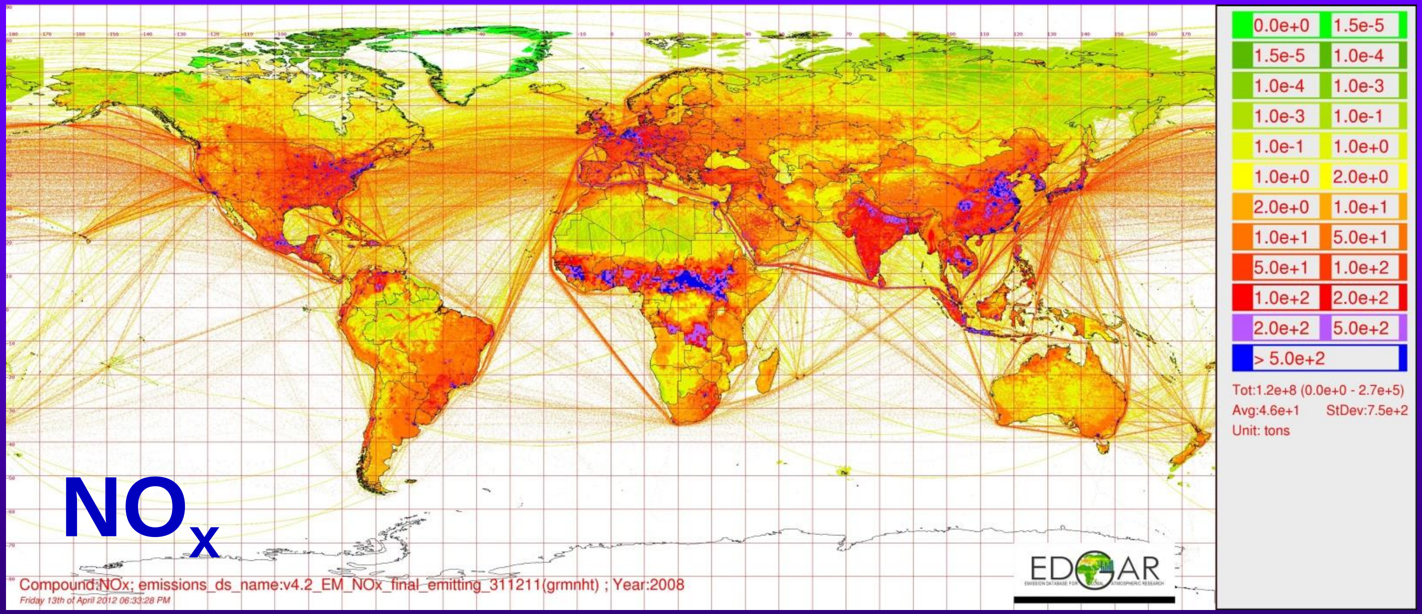
- 自然界的活動，如火山噴發、閃電、森林火災、海洋，以及微生物活動等，便會排放出SO_x及NO_x。
- 但主要來源還是人為排放，如燃煤與交通運輸。
- 燃燒1公噸的煤約可產生10-25公斤的SO_2。
- 全球而言，排到大氣中的SO_2約有80%是人為排放，20%是自然排放 。

Acid Deposition(酸沈降)

- NO_x是高溫下(650°C)的產物。
- 保守估計，人類每年排放近7000萬公噸SO_2到大氣中，1/10最後形成H_2SO_4，相當於500 cc濃硫酸100億瓶。

2008 Anthropogenic Emissions of SO_2 and NO_x





Changes in Anthropogenic Emissions of SO_2 between 2005 and 2010

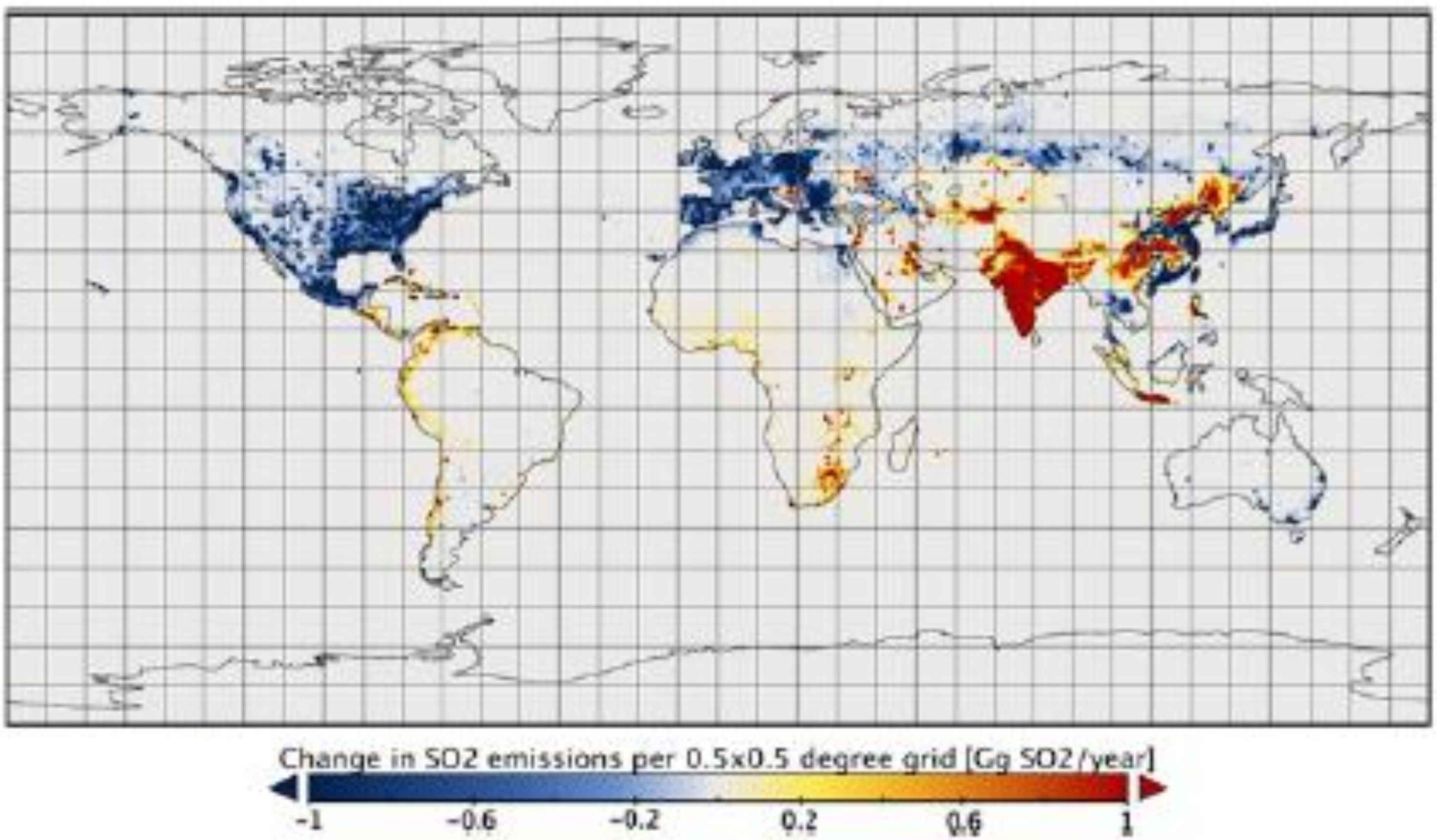
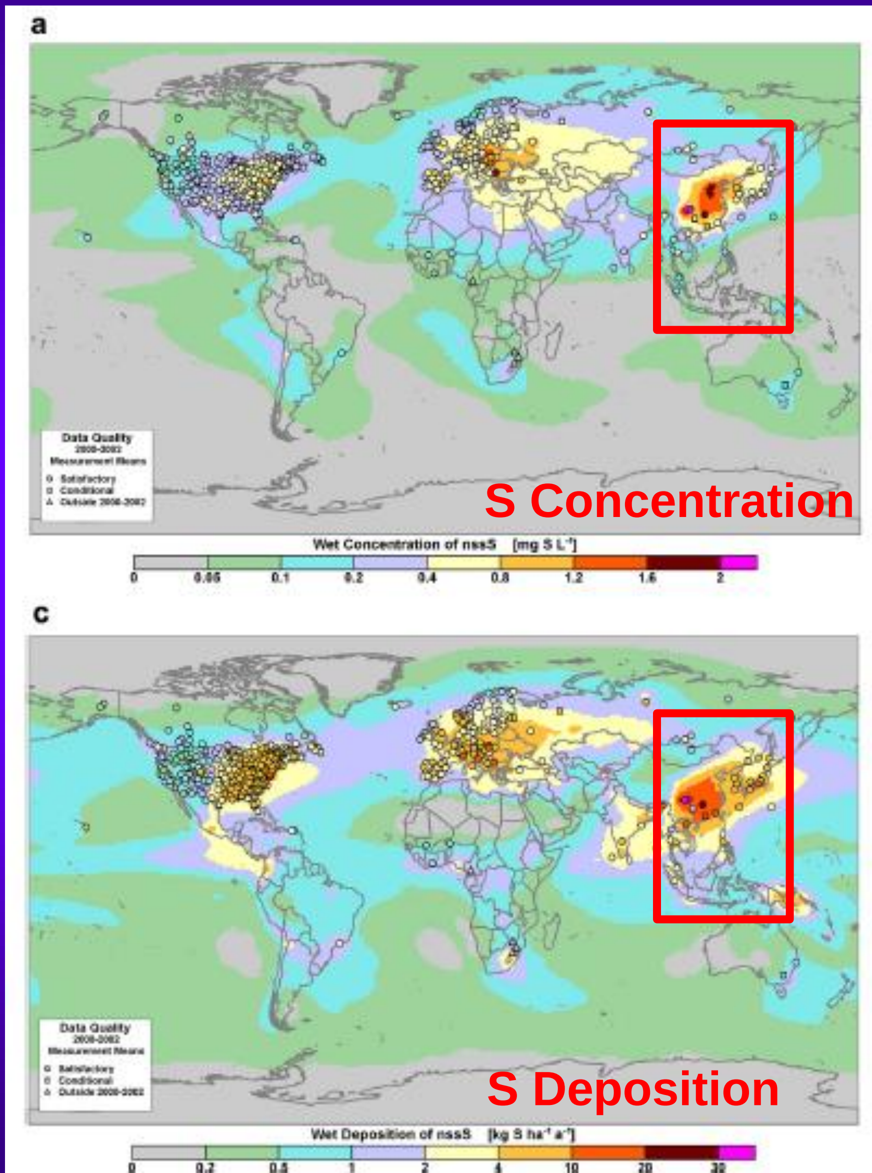
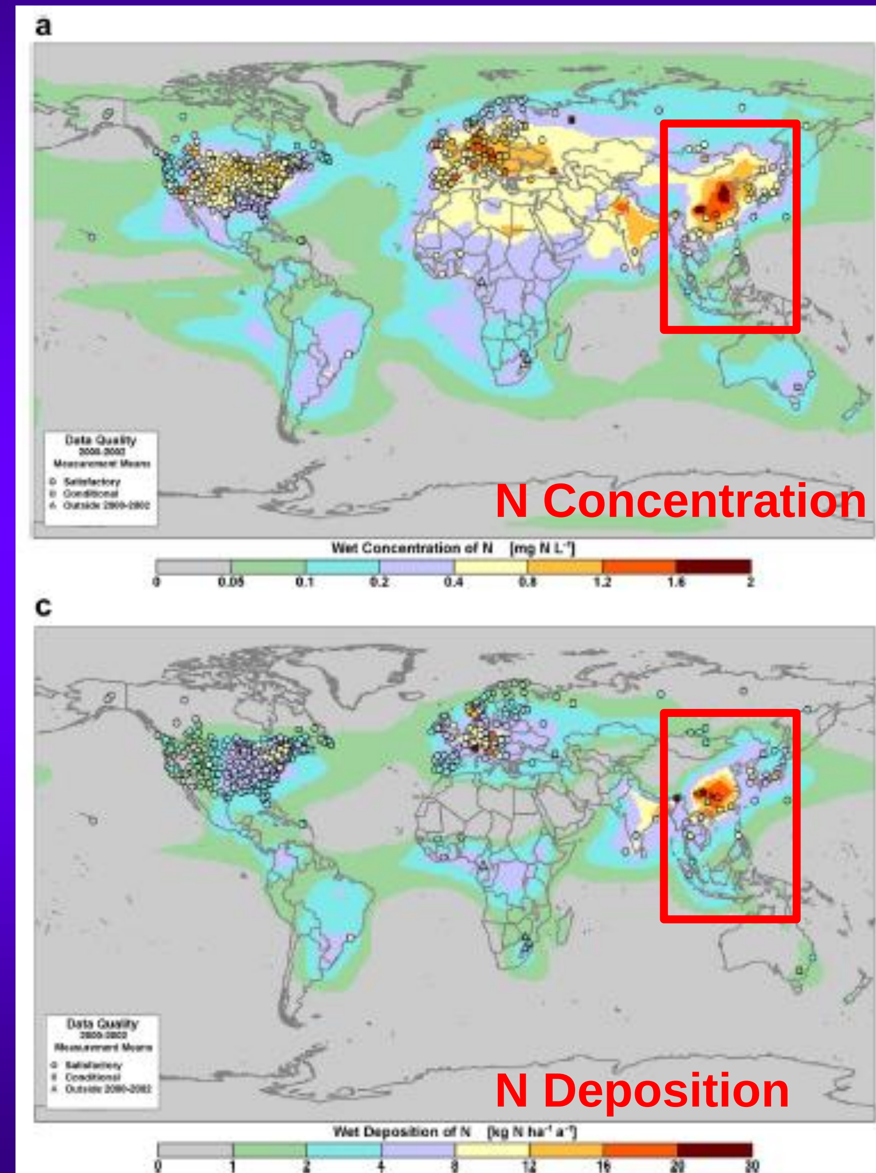


Figure 3. Change in regional distribution of anthropogenic land based SO_2 emissions. Changes indicated as a difference between 2010 and 2005 emissions in 0.5° × 0.5° grids.

Concentration and Deposition Fluxes of S and N



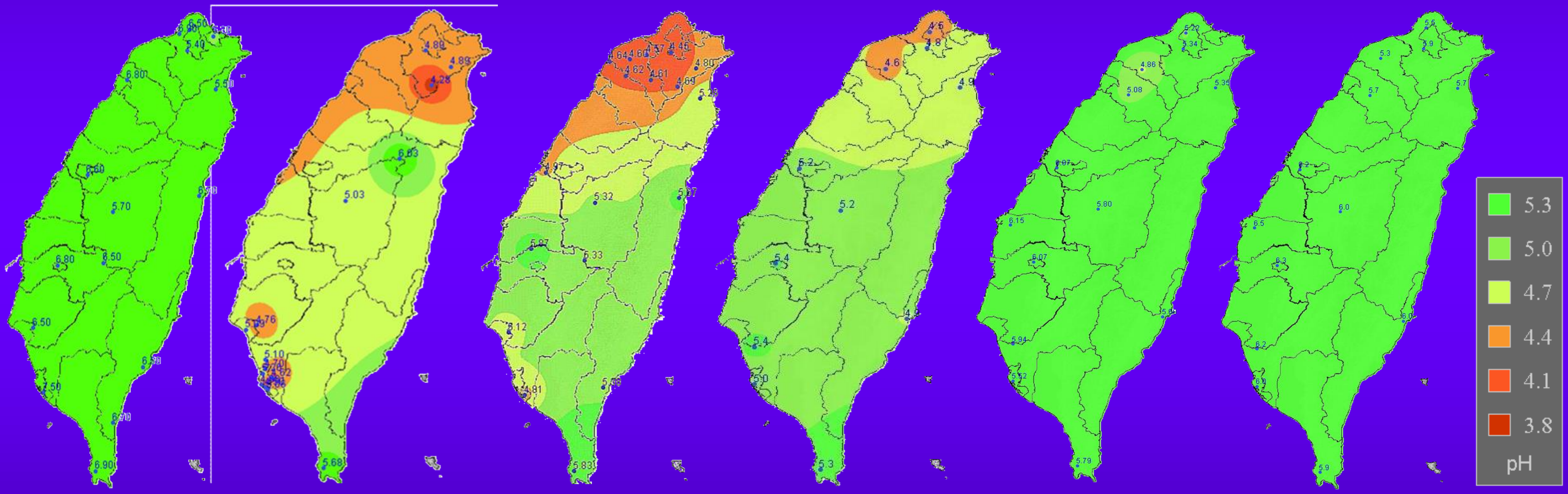


Vet et al., 2014

50年來台灣雨水pH值的變化

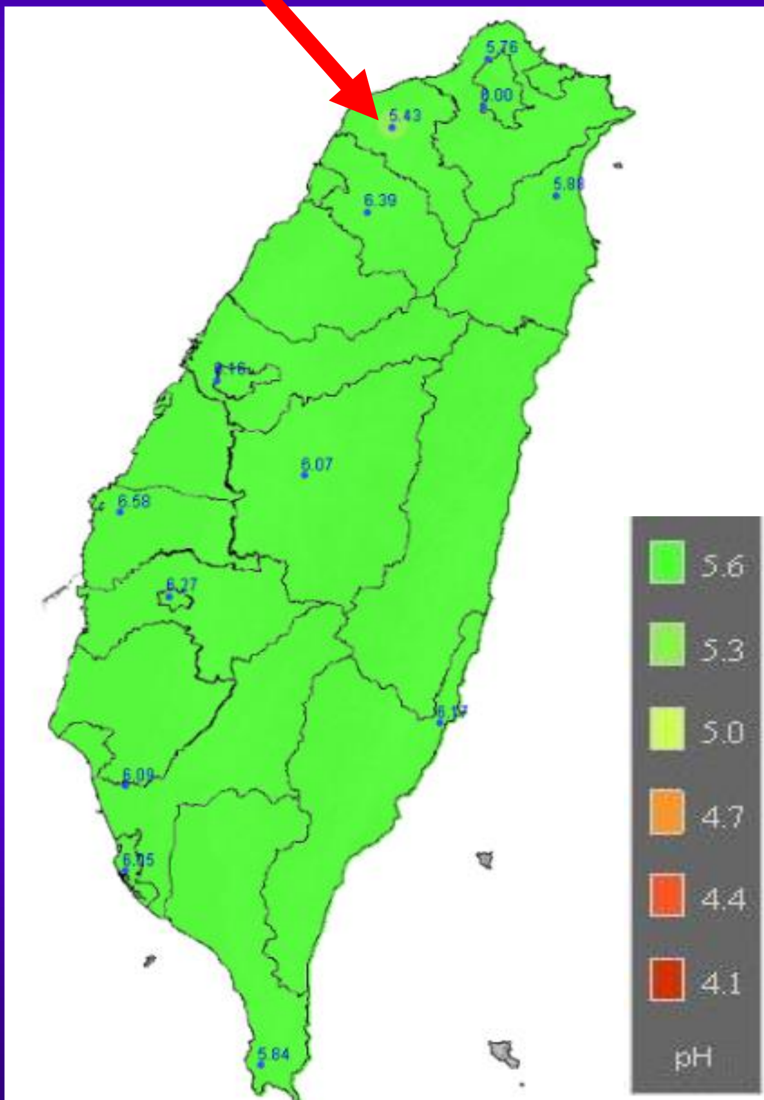
經濟發展 → 惡化 → 採取相關管制作為及徵收空污費後

1970's	1980's	1990's	2004-2010	2011-2020	2021-2023
5.3-6.9	4.3-6.6	4.4-6.3	4.5-5.4	4.9-6.2	5.3-6.2

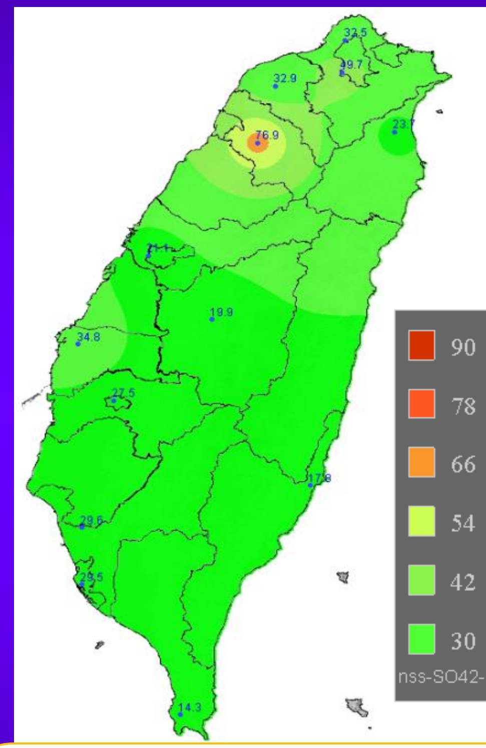


2023年台灣雨水pH值分布圖

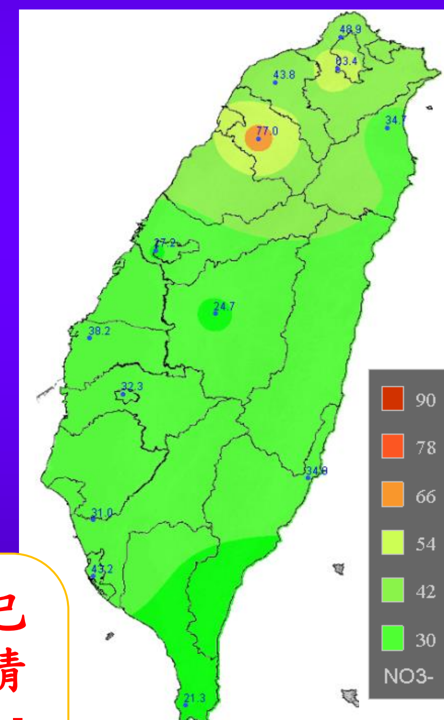
中壢站最低：5.43



nss-SO_4^{2-}
濃度分布圖

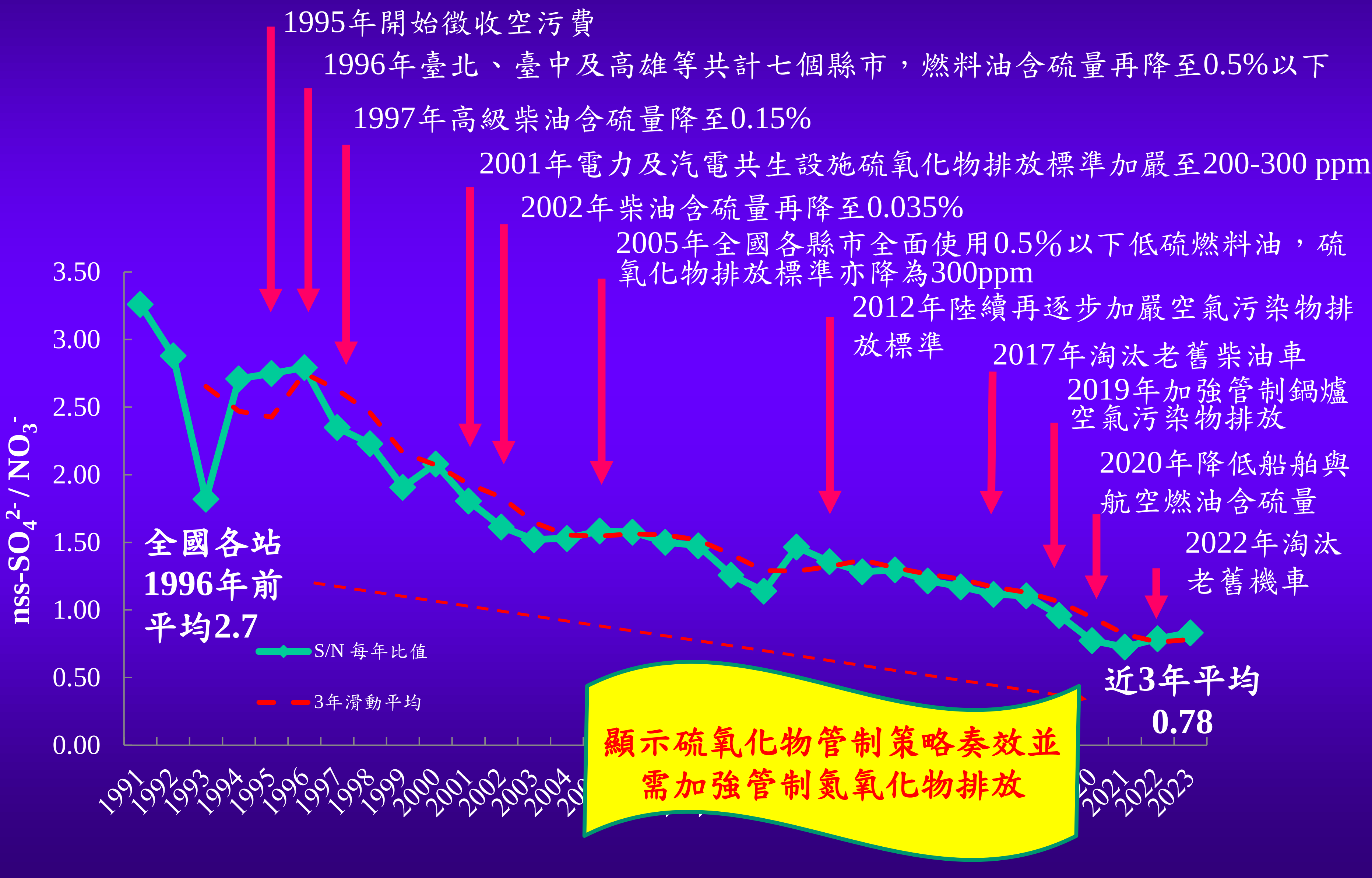


NO_3^-
濃度分布圖



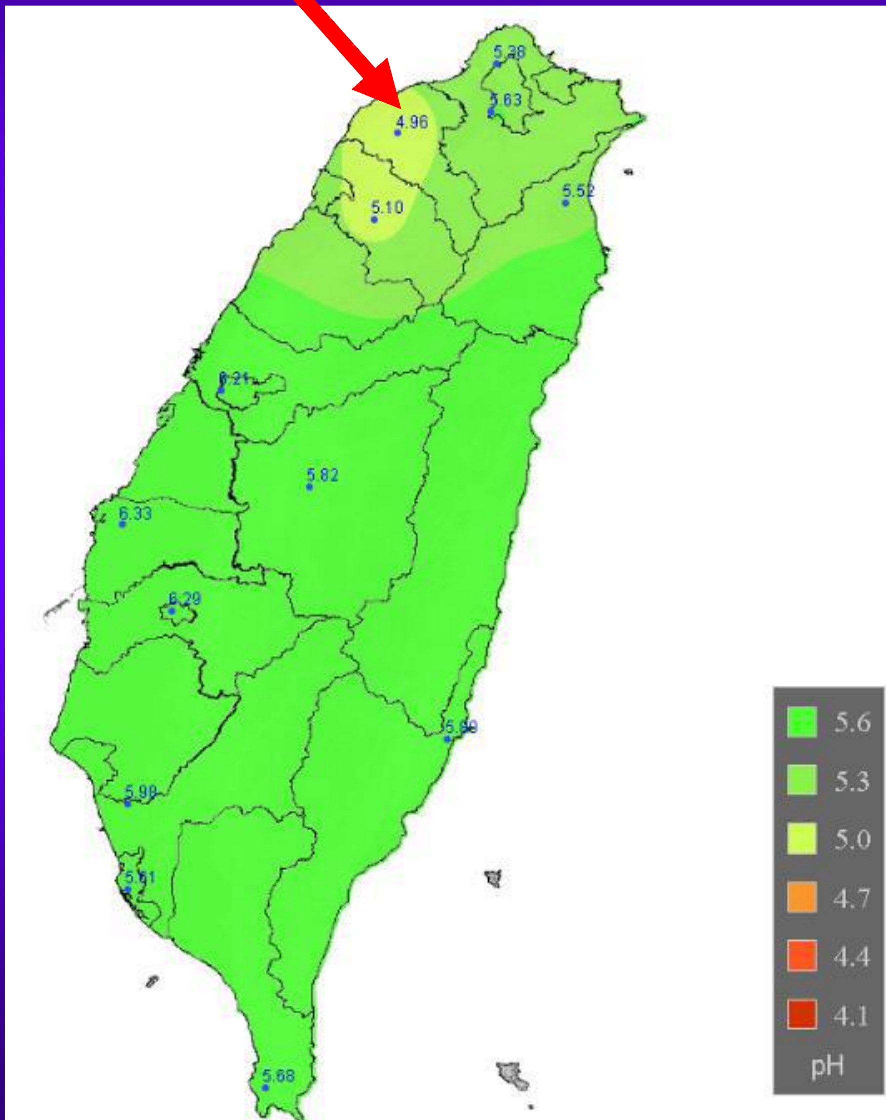
全台雨水pH年平均值均已高於5.0，顯示雨水酸化情形改善，然全數測站NO_3^-濃度高於nss-SO_4^{2-}，顯示氮氧化物管制的必要

$nss\text{-}SO_4^{2-}/NO_3^-$ 變化 VS.空污管制策略



2020年台灣雨水pH值分布圖

中壢站最低：4.96



自由時報

中壢連3年登全台酸雨冠軍 環保局：逐年改善、上半年數據已無酸雨

桃園市設有7座酸雨測站，圖為稽查人員在測站進行酸雨檢測情形。（桃市環保局提供）

2021/08/16 14:03

〔記者李容萍／桃園報導〕環保署在全台設有14個酸雨觀測站，根據統計2020年全台雨水最酸地點就在桃園市中壢測站，pH值只有4.96，不僅是全台唯一pH值低於5.0的測站，更是繼2019、2018年來連續3年拿下全台最酸雨水測站，環保署分析原因，主要是桃園市中壢測站位處東北季風迎風面，加上工廠多、汽機車廢氣排放等移動汙染源等多種因素，才會讓中壢酸雨嚴重。

桃園市政府環保局長呂理德今日受訪表示，為了解市境酸雨情況，環保署於中壢僅設1座監測站，但桃園環保局則設有7測站座酸雨進行監測。在酸雨監測中，顯示環保局有更多、更新的資料來源。

呂理德提到，由桃園市7座酸雨測站長期資料顯示，桃園地區雨水酸化情形改善，今年1至6月監測資料，全市7站pH平均值為5.86，高於環保署酸雨定義之5.0，顯示今年1至6月中壢已不再有酸雨。另2017至2021年6月間pH值數據

History of Acid Deposition

1200s. Coal used in lime kilns and forges produces sulfur and nitrogen oxides that result in sulfuric and nitric acid deposition.

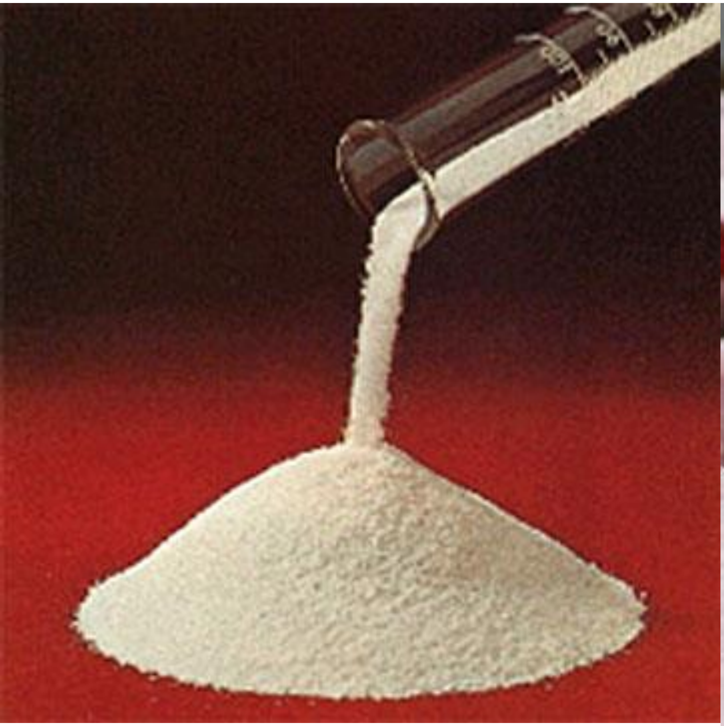
1750s. Expanded use of the steam engine at the beginning of the Industrial Revolution increases sulfuric and nitric acid deposition.

1783. French Academy of Sciences offers a prize to a person who finds the most efficient and economical method to produce soda ash $Na_2CO_3(aq)$, which along with animal fat, is used to make soap.

1789. Nicolas LeBlanc develops two-step soda ash process.

The Rise of Alkali Factories

Soda ash + Animal fat = Soap



Img.alibaba.com

Keetsa.com

www.nutritionfx.com

LeBlanc Process

High temperature

$$2NaCl(s) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + 2HCl(g)$$

Sodium chloride (salt)	Sulfuric acid	Sodium sulfate	Hydrochloric acid

High temperature

$$Na_2SO_4(aq) + 2C + CaCO_3(s) \longrightarrow Na_2CO_3(aq) + CaS(s) + 2CO_2(g)$$

Sodium sulfate	Carbon from charcoal	Calcium carbonate from chalk	Sodium carbonate	Calcium sulfide	Carbon dioxide

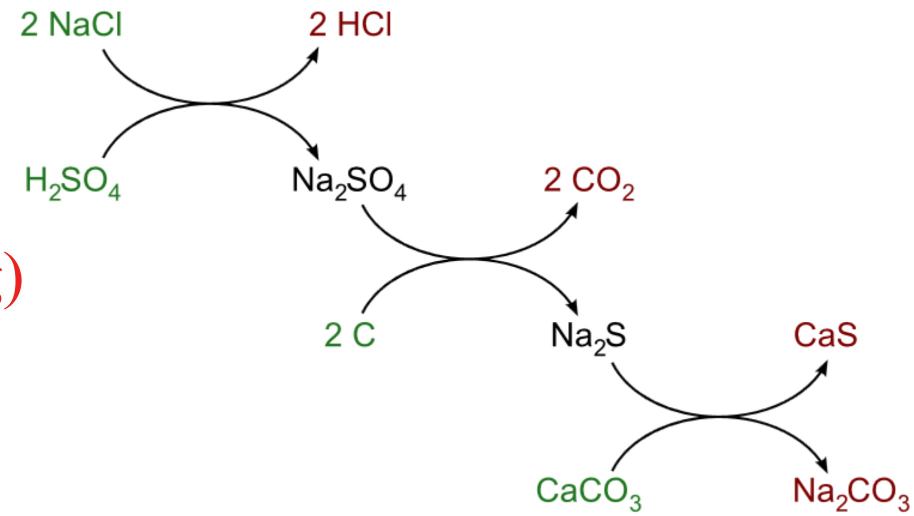
(10.1) - (10.2)

Sulfuric acid produced by burning sulfur and saltpeter in water

$$7S(s)+6KNO_3(s)+4H_2O(aq) \dashrightarrow 3K_2S(s)+6NO(g)+4H_2SO_4(aq)$$

Byproducts of Leblanc Process

$HCl(g)$
evaporated $H_2SO_4(g)$
$NO(g)$, which produces $HNO_3(g)$
Soot (C)
$CO_2(g)$



--> widespread acid deposition due mostly to $HCl(g)$

$CaS(s)$, yellow-gray powder, forms hydrogen sulfide and gypsum

$$CaS(s) + H_2O(aq) \text{ --> } CaO(s) + H_2S(g)$$
$$CaS(s) + O_2(g) + 3H_2O(aq) \text{ --> } CaSO_4\text{-}2H_2O(s) + H_2(g)$$

Piles of gypsum (galligu) still exist near old soda-ash factories.

Gypsum/Galligu Piles

The Rise of Alkali Factories

History of Acid Deposition

1791. LeBlanc patents technique

1793. Loses patent to the state during French Revolution

1806. LeBlanc commits suicide

1838. Liverpool landowner files complaint against an alkali factory: destroyed crops and interfered with hunting.

Early 1860s. William Gossage, who built alkali factory in 1830, develops scrubber for HCl(g) by converting a windmill into a tower, filling tower with brushwood, and letting water drip down the brush as smoke rose from the bottom.

HCl Scrubber Today

www.engpro.com

History of Acid Deposition

1861. Ernst Solvay (1838-1922) develops another way to form soda ash, but it replaces Leblanc process only by 1880s.

1863. Due to devastation from Alkali factories and Gossage's scrubber, the 1863 Alkali Act passes in the U.K.

France. Regulation takes the form of planning laws controlling location of alkali factories.

1866, 1868. Inventions allow chlorine to be recycled for bleaching powder.

1881. U.K. Alkali Act is modified since significant pollution of other chemicals from alkali factories still occurs.

Solvay Process

1861. Solvay rains a salt made of sodium chloride and ammonium down a tower over an upcurrent of CO_2(g). Only inputs: limestone, salt. Only byproduct: calcium chloride.

Production of carbon dioxide

$CaCO_3(s) + heat \text{ --> } CaO(s) + CO_2(g)$

Production of sodium bicarbonate

$NaCl(s)+NH_3(g)+CO_2(g)+H_2O(aq)\text{-->}NaHCO_3(aq)+NH_4Cl(s)$

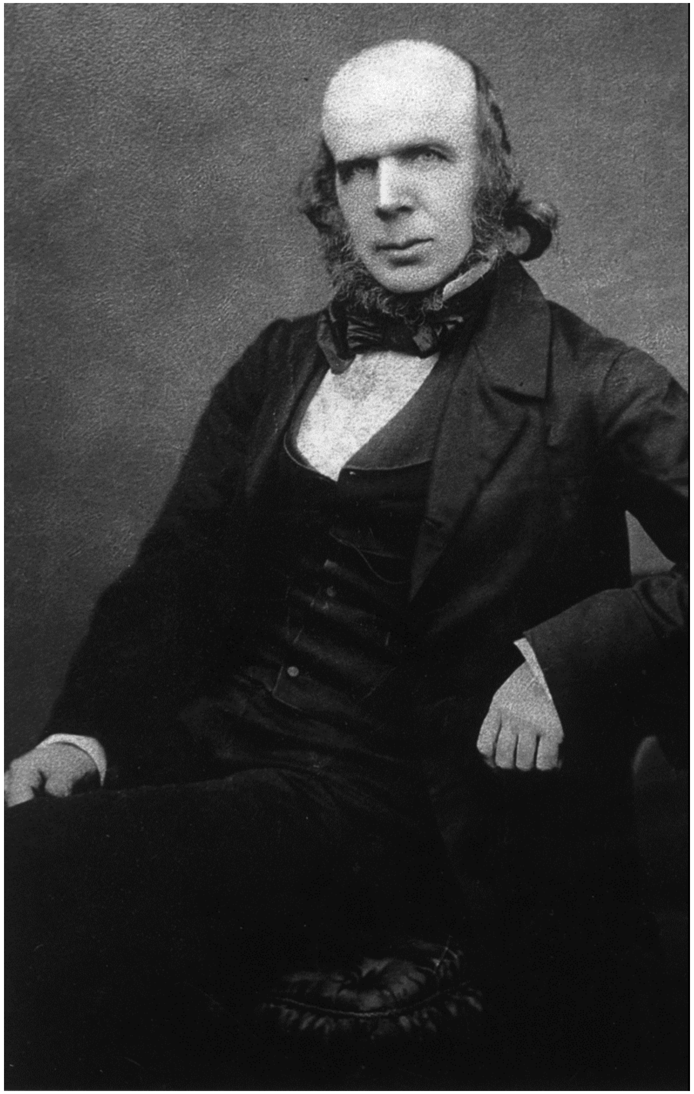
Production of sodium carbonate, recycling of carbon dioxide

$2NaHCO_3(aq) + heat \text{ --> } Na_2CO_3(aq) + H_2O(aq) + CO_2(g)$

Recycling of ammonia

$2NH_4Cl(s) + CaO(s) \text{ --> } 2NH_3(g) + CaCl_2(s) + H_2O(aq)$

Robert Angus Smith (1817-1884)



The first British Alkali Act Inspector,

also publishing a book entitled "*Air and Rain: The beginning of a Chemical Climatology*,"

in which the term of "*acid rain*" was introduced.

Library and Information Centre, Royal Society of Chemistry

Acidity

Measure of the concentration of hydrogen ions (H^+) in solution

$$pH = -\log_{10}[H^+]$$

$[H^+]$ = molarity (M, moles of H^+ per liter of solution)

Higher $[H^+]$ --> lower pH --> more acidic solution

(10.3)

Acidity

In dilute water, the only source of H^+ is

$$H_2O(aq) \rightleftharpoons H^+ + OH^-$$

Liquid water — Hydrogen ion — Hydroxide ion

$[H^+][OH^-] = 10^{-14}\ M^2$ --> $[H^+]=[OH^-]=10^{-7}\ M$

--> $pH = -\log_{10}[10^{-7}M] = 7$

Acid/Base

Acid

Substance that, when added to a solution, dissociates, increasing $[H^+]$, decreasing pH

Strong acid: Substances that dissociate readily (e.g., H_2SO_4, HCl, HNO_3)

Weak acids: Substances that dissociate less readily (e.g., H_2CO_3)

Base (alkalis)

Substances that, when added to a solution, reduce $[H^+]$, increasing pH. (e.g., $NH_3(aq)$, $Ca(OH)_2(aq)$)

pH Scale

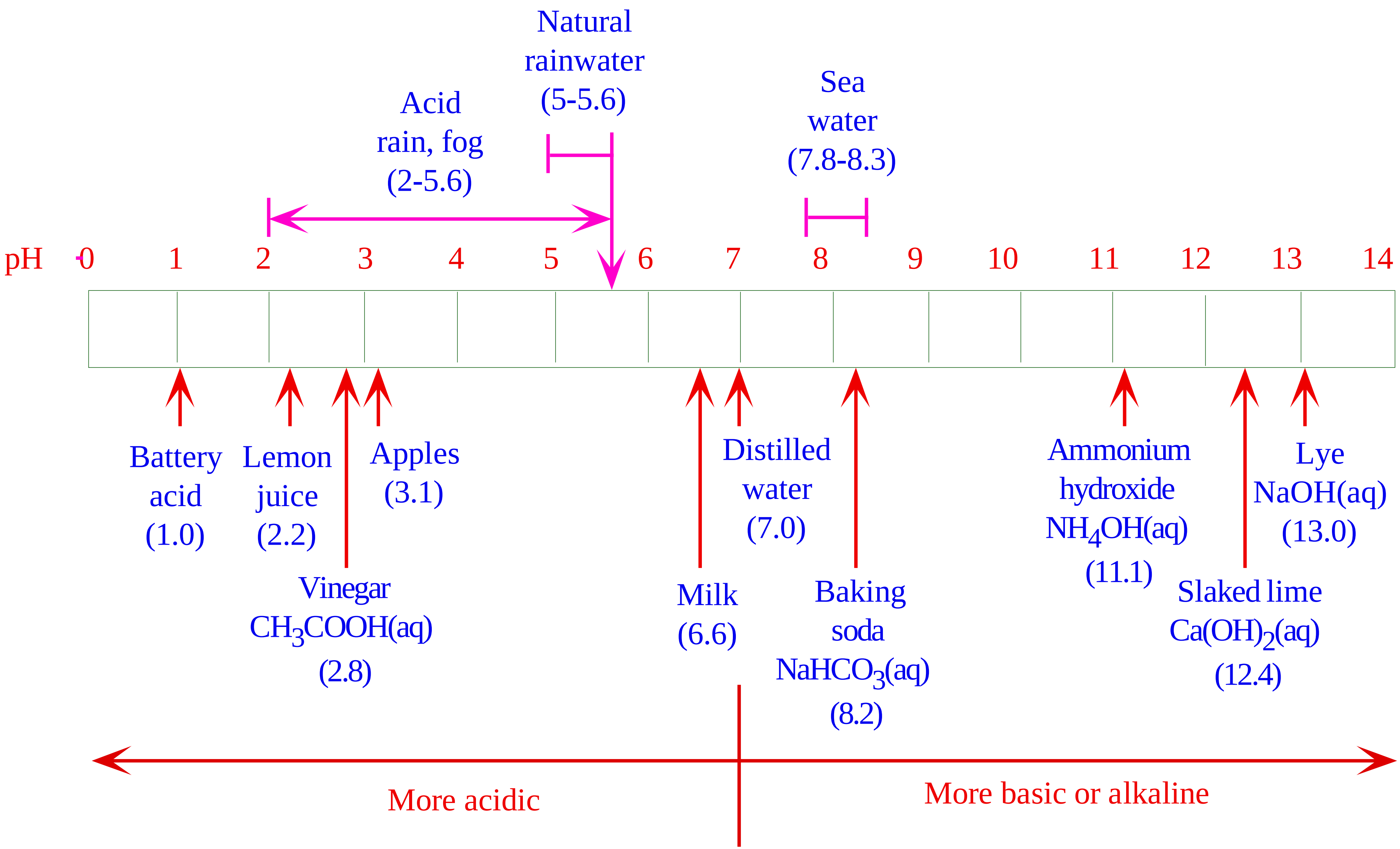


Figure 10.3

Acid Dissociation

Addition of acid to solution increases $[H^+]$, decreasing pH

Carbonic acid

$$CO_2(aq) + H_2O(aq) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$$

Dissolved carbon dioxide; Liquid water; Dissolved carbonic acid; Hydrogen ion; Bicarbonate ion; Hydrogen ion; Carbonate ion

Sulfuric acid

$$H_2SO_4(g) \rightarrow H_2SO_4(aq) \rightleftharpoons H^+ + HSO_4^- \rightleftharpoons 2H^+ + SO_4^{2-}$$

Sulfuric acid gas; Dissolved sulfuric acid; Hydrogen ion; Bisulfate ion; Hydrogen ion; Sulfate ion

(10.5) - (10.6)

Acid Dissociation

Hydrochloric acid

$$HCl(g) \rightleftharpoons HCl(aq) \rightleftharpoons H^+ + Cl^-$$

Hydrochloric acid gas — Dissolved hydrochloric acid — Hydrogen ion — Chloride ion

Nitric acid

$$HNO_3(g) \rightleftharpoons HNO_3(aq) \rightleftharpoons H^+ + NO_3^-$$

Nitric acid gas — Dissolved nitric acid — Hydrogen ion — Nitrate ion

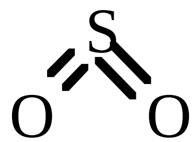
(10.7) - (10.8)

S(IV) and S(VI) Families

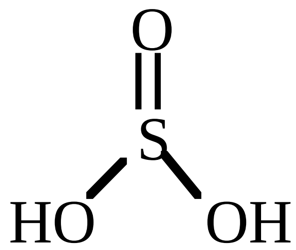
Table 10.1

S(IV) Family

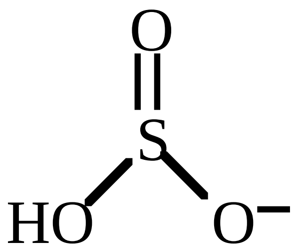
Sulfur dioxide
SO_2(g,aq)



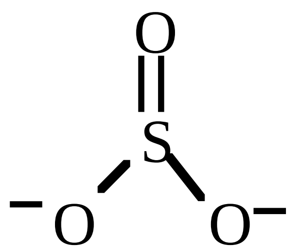
Sulfurous acid
H_2SO_3(aq)



Bisulfite ion
HSO_3^-

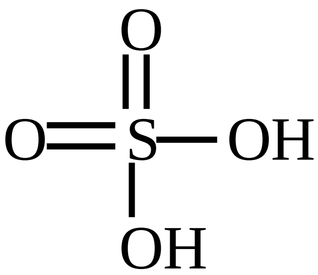


Sulfite ion
SO_3^{2-}

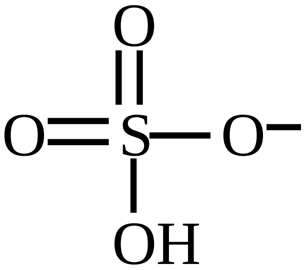


S(VI) Family

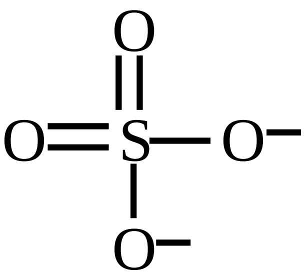
Sulfuric acid
H_2SO_4(g,aq)



Bisulfate ion
HSO_4^-



Sulfate ion
SO_4^{2-}



Mechanisms of Converting S(IV) to S(VI)

Why is converting to S(VI) important?

It allows sulfuric acid to enter or form within cloud drops and aerosol particles, increasing their acidity

Mechanisms

1. Gas-phase oxidation of SO_2(g) to H_2SO_4(g) followed by condensation of H_2SO_4(aq)

2. Dissolution of SO_2(g) into liquid water to form H_2SO_3(aq) and its dissociation products, which convert chemically to H_2SO_4(aq) and its dissociation products.

Gas-Phase Oxidation of S(IV) to S(VI)

$$SO_2(g) \xrightarrow{+\dot{O}H(g),\ M} H\dot{S}O_3(g) \xrightarrow[\dot{H}O_2(g)]{+O_2(g)} SO_3(g) \xrightarrow{+H_2O(g)} H_2SO_4(g)$$

Sulfur dioxide — Bisulfite — Sulfur trioxide — Sulfuric acid

(10.9)

Aqueous-Phase Oxidation of S(IV)

Step 1. S(IV) dissolution and dissociation

$$SO_2(g) \rightleftharpoons SO_2(aq)$$

Sulfur dioxide gas — Dissolved sulfur dioxide

$$SO_2(aq) + H_2O(aq) \rightleftharpoons H_2SO_3(aq) \rightleftharpoons H^+ + HSO_3^- \rightleftharpoons 2H^+ + SO_3^{2-}$$

Dissolved sulfur dioxide — Liquid water — Sulfurous acid — Hydrogen ion — Bisulfite ion — Hydrogen ion — Sulfite ion

(10.10) - (10.11)

Aqueous-Phase Oxidation of S(IV)

Step 2. S(IV) oxidation by hydrogen peroxide in solution

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

Bisulfite ion — Dissolved Hydrogen peroxide — Sulfate ion

Alternate Step 2. S(IV) oxidation by ozone in solution

$$SO_3^{2-} + O_3(aq) \longrightarrow SO_4^{2-} + O_2(aq)$$

Sulfite ion — Dissolved ozone — Sulfate ion — Dissolved oxygen

(10.12) - (10.13)

Production of Nitric Acid Gas

$$\dot{O}H(g) + \dot{N}O_2(g) \xrightarrow{M} HNO_3(g)$$

Hydroxyl radical | Nitrogen dioxide | Nitric acid

(10.14)

Effects of Acid Deposition

- 酸沈降的危害至少有下列6項：
  - 湖泊酸化 (pH < 6.0)
  - 水生生物死亡
  - 土壤酸化
  - 森林凋萎
  - 建築物侵蝕
  - 人體健康受威脅

Effects of Acid Deposition

Lakes and streams

Lake pH decreased 1 pH unit between the 1950s and 1960s in Scandinavia. 25,000 out of 90,000 lakes in Sweden were acidified in the 1970s. 17,000 of these were due to anthropogenic pollution.

Fish and microorganisms are sensitive to pH.

Plants

Acids damage trees at their roots and erodes cuticle wax.

Acidified water carries away minerals.

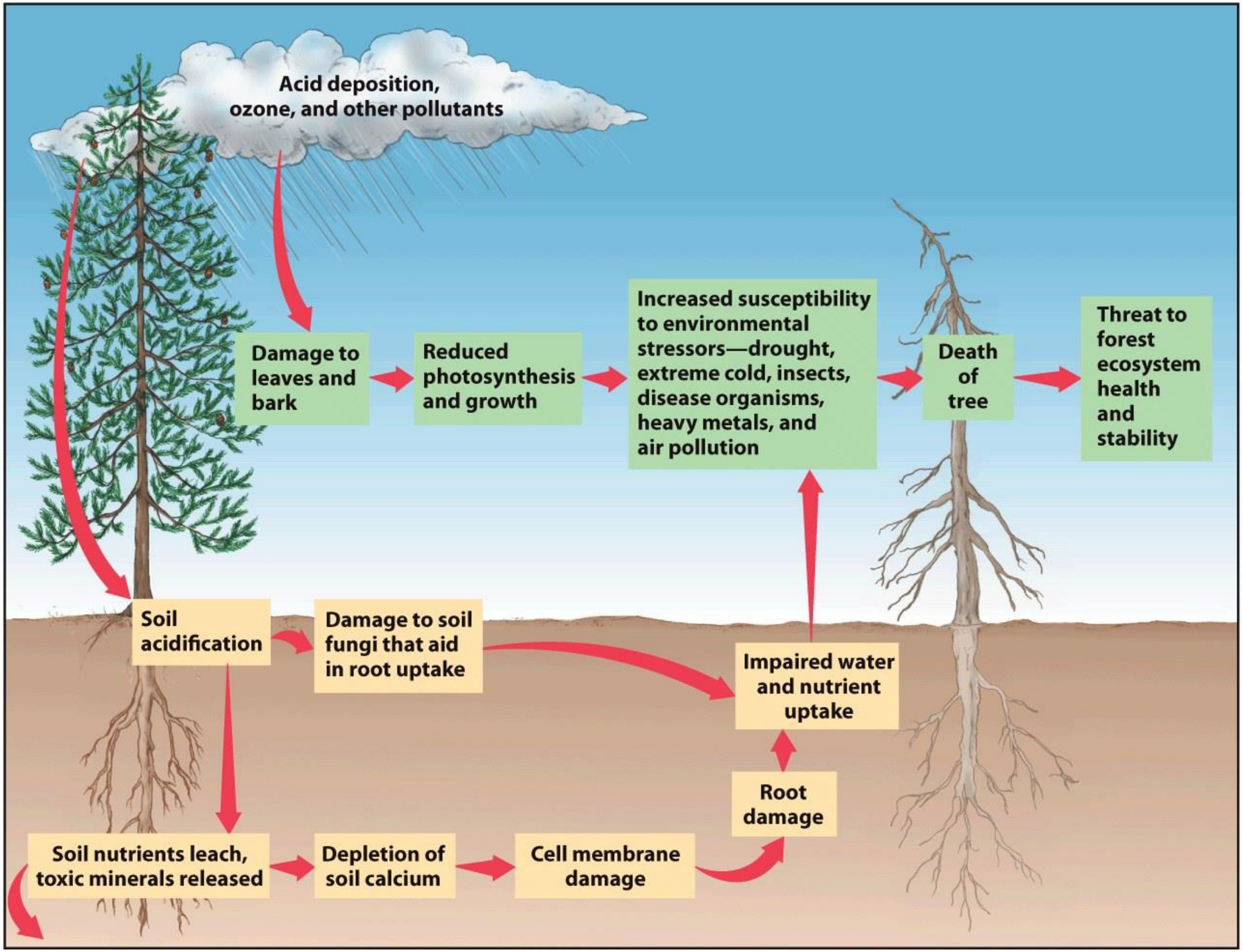
Acids release metals Al^{3+}, Fe^{3+} from the minerals $Al(OH)_3(s)$, $Fe(OH)_3(s)$. Metals are toxic to roots.

Effects of Acid Deposition

- Declining Aquatic Animal Populations
  - Aluminum toxicity
- Thin-shelled eggs prevent bird reproduction
  - Calcium is unavailable in acidic soil
- Forest decline
  - (right) Black Forest in Germany

Hans Reinhard/Bruce Coleman, Inc./Photoshot Holdings Ltd.

Acid Deposition and Forest Decline



Dead Norway Spruce, Nacetin Forest, Czech Republic, 1995

Dead Spruce, Mt. Mumlava, Czech Republic

Acidified Forest, Oberwiesenthal, Germany (1991)

Neutralizing Acids

Add ammonium hydroxide to a lake

$$NH_4OH(aq) + H^+ \rightleftharpoons NH_4^+ + H_2O(aq)$$

Ammonium hydroxide	Hydrogen ion	Ammonium ion	Liquid water

Add slaked lime to a lake

$$Ca(OH)_2(aq) + 2H^+ \rightleftharpoons Ca^{2+} + 2H_2O(aq)$$

Calcium hydroxide	Hydrogen ion	Calcium ion	Liquid water

Calcium carbonate is a natural neutralizing agent in soil

$$CaCO_3(s) + 2H^+ \rightleftharpoons Ca^{2+} + CO_2(g) + H_2O(aq)$$

Calcium carbonate	Hydrogen ion	Calcium ion	Carbon dioxide gas	Liquid water

(10.15) - (10.17)

Liming of a Lake in Sweden

Neutralizing Acids

Sea salt is a natural neutralizing agent near the coast

$$NaCl(s) + H^+ \rightleftharpoons Na^+ + HCl(g)$$

Sodium chloride	Hydrogen ion	Sodium ion	Hydrochloric acid

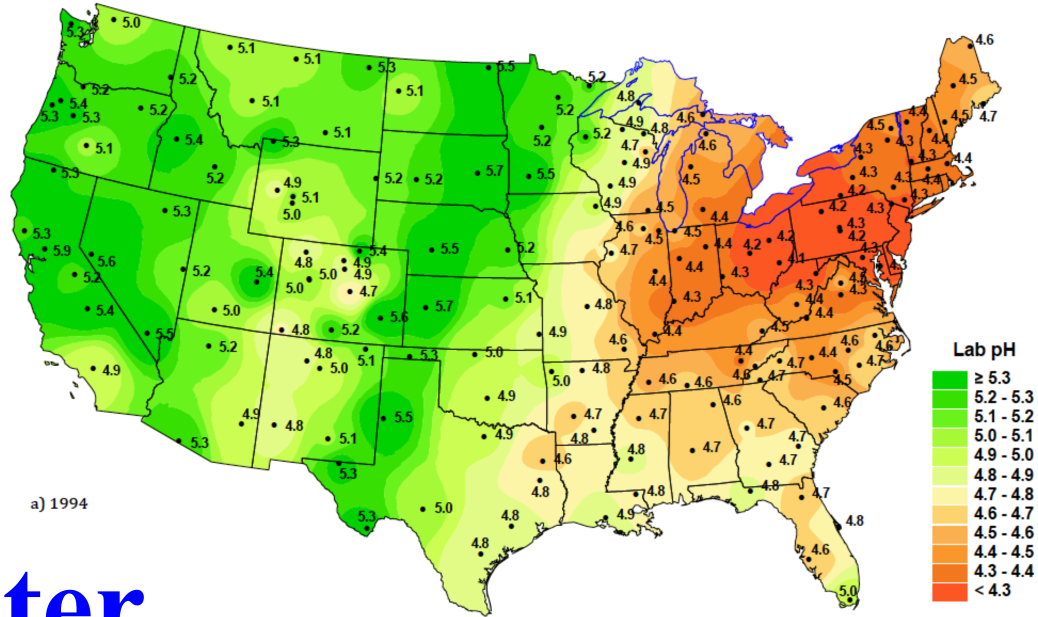
Ammonia is a neutralizing agent

$$NH_3(aq) + H^+ \rightleftharpoons NH_4^+$$

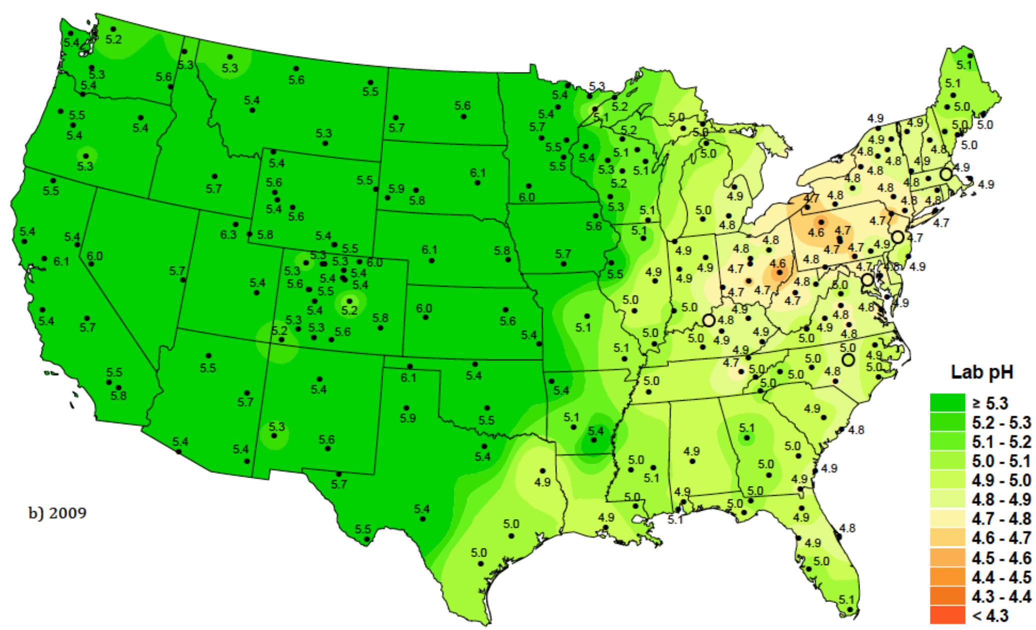
Dissolved ammonia	Hydrogen ion	Ammonium ion

(10.19) - (10.20)

U.S. Rainwater pH



1994



2009

U.S. National Atmospheric Deposition Program/National Trends Network

Effects of Acid Deposition

Materials

The addition of sulfuric acid to marble or limestone produces gypsum, which forms a crust that creates pits when rain loosens the crust.

Crusting of marble and limestone

$$CaCO_3(s) + 2H^+ \rightleftharpoons Ca^{2+} + CO_2(g) + H_2O(aq$$

Calcium carbonate	Hydrogen ion		Calcium ion	Carbon dioxide gas	Liquid water

$$Ca^{2+} + SO_4^{2-} + 2H_2O(aq) \rightleftharpoons CaSO_4\text{-}2H_2O(s)$$

Calcium ion	Sulfate ion	Liquid water		Calcium sulfate dihydrate (gypsum)

(10.17) - (10.18)

Sandstone Figure in 1908 and 1968, Westphalia, Germany

Herr Schmidt-Thomsen

Recent Regulation of Acid Deposition

1970. U.S. Clean Air Act Amendments

1977. U.S. National Atmospheric Deposition Program

1979. Geneva Convention on Long-Range Transboundary Air Pollution

1985. Sulfur Protocol (Helsinki, EC, 30% reduction)

1988. Nitrogen Oxide Protocol

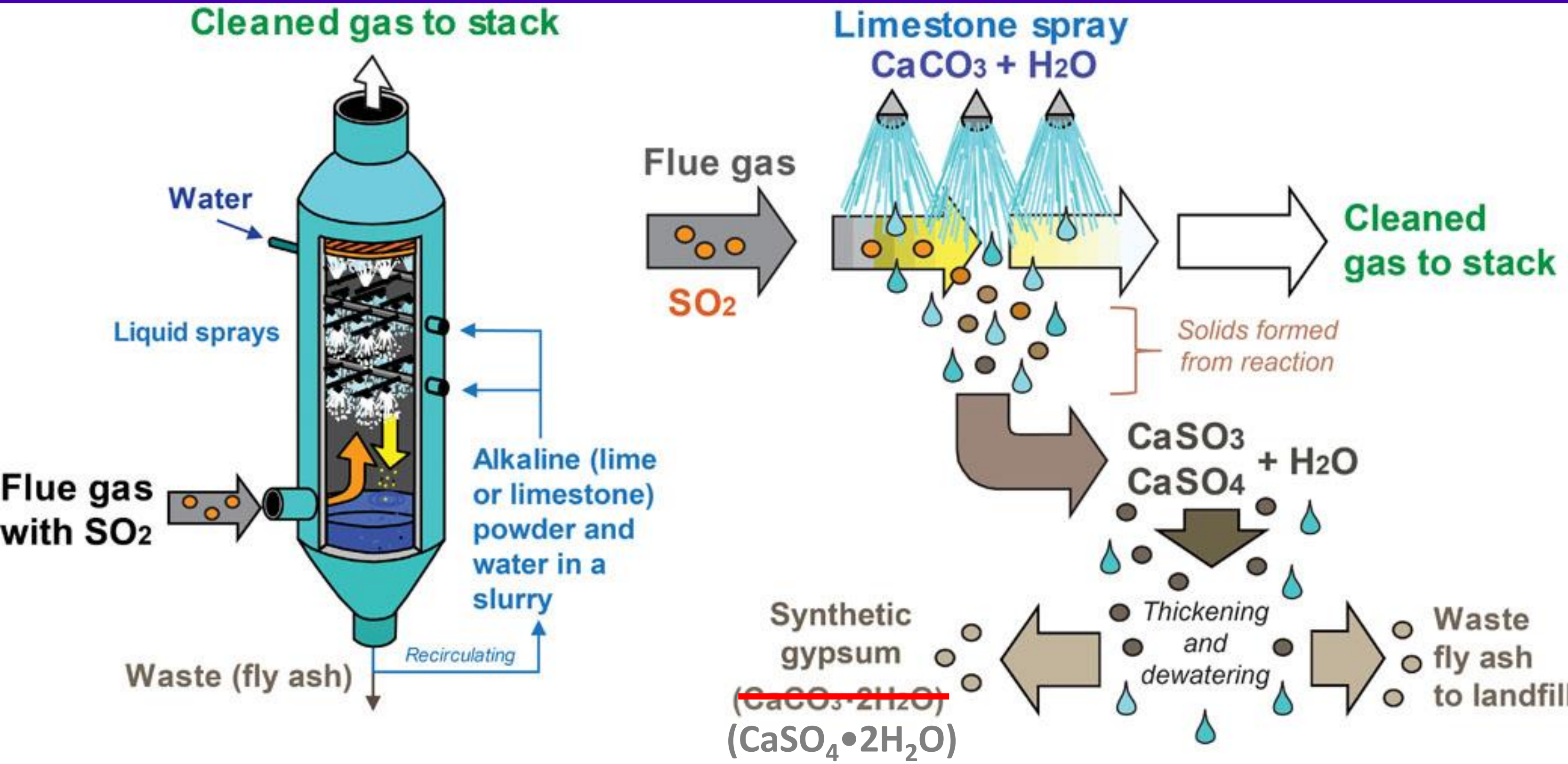
1990. U.S. Clean Air Act Amendments

1994. Second Sulfur Protocol (Oslo)

Methods of Controlling Emission

- Control of sulfur dioxide:
  - Change to low-sulfur fuel
  - Desulfurization before combustion, such as coal washing
  - Flue-gas desulfurization(排煙脫硫技術), such as wet scrubber and dry scrubber

Flue-Gas Desulfurization (FGD)



Controlling Air Pollution

- Control of nitrogen oxides:
  - 燃燒改善
    - 少量過剩空氣(Excess Air Combustion)
    - 二段式燃燒(Two Stage Combustion)
    - 排氣循環(FGR)
    - 燃燒器設計之改良(Low NOx Burner)
  - 控制設備
    - 選擇性非觸媒還原設備(SNCR)
    - 選擇性觸媒還原設備(SCR)

Politics of Acid Deposition

- Acid deposition is so hard to combat is that it does not occur only in the locations where the gases that cause it are emitted.
- It is entirely possible for sulfur and nitrogen oxides released in one spot to return to the ground hundreds of kilometers from their sources.
- Cap-and-trade(總量管制與交易制度）
  - 設定限制地區或國家污染物的最高排放水準(上限)，並要求受管制的排放源必須取得排放權才能排放。公司或政府管轄區如有多餘的排放權，可以賣給排放權不敷使用的單位。