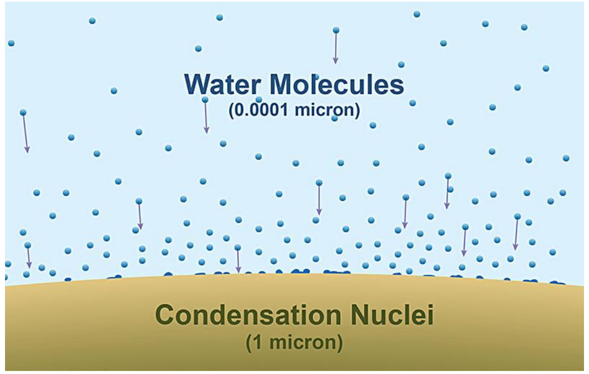
Tropospheric Chemistry - Precipitation

1. Water aerosol formation (clouds, fog, rain, snow)

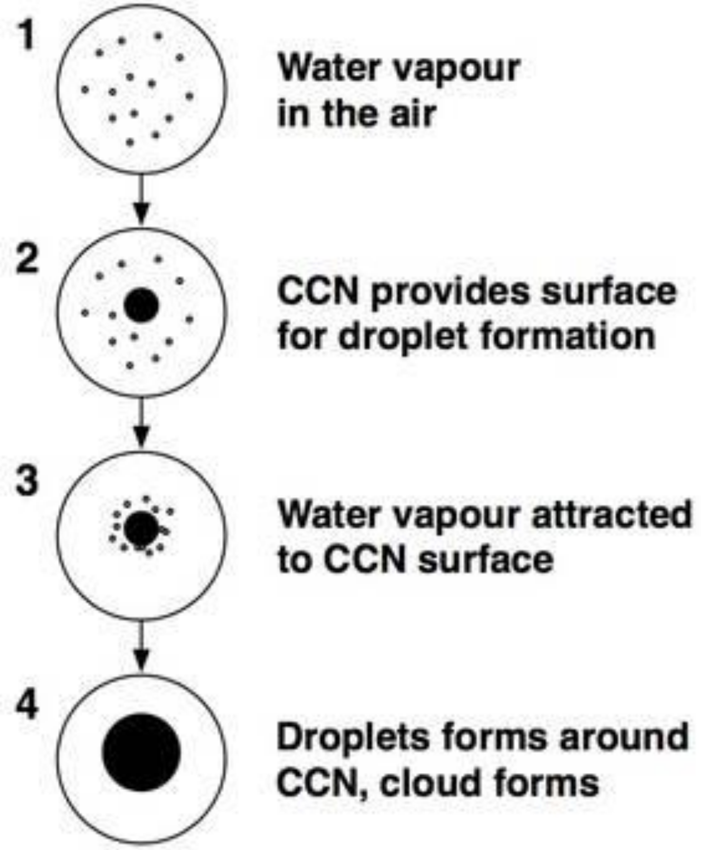
2. Composition of rainwater

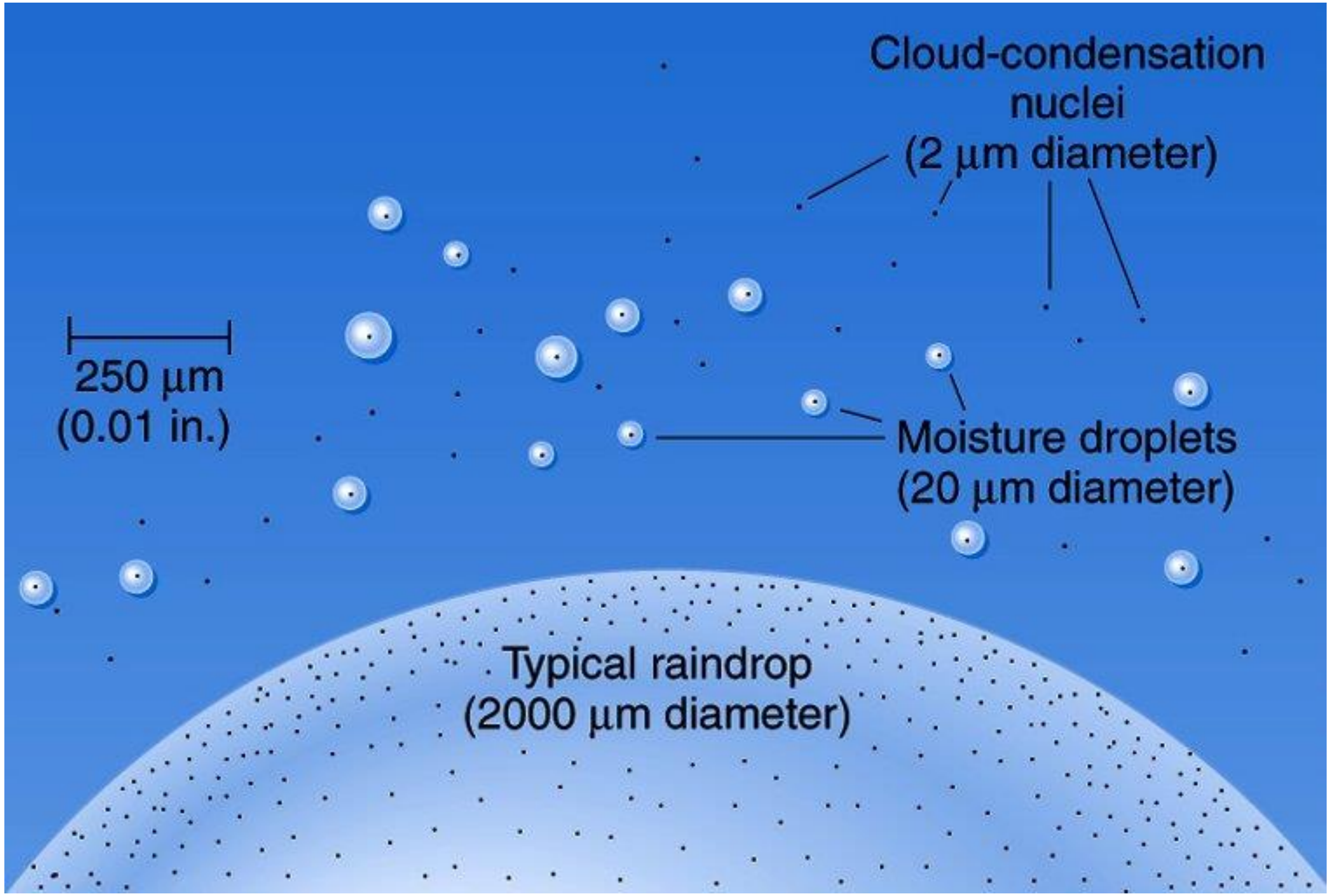
3. Mechanisms of HNO_3 and H_2SO_4 production

4. Emission controls and abatement technology



1. Water aerosol formation
Cloud Condensation Nuclei (CCN)





Cloud and precipitation chemistry

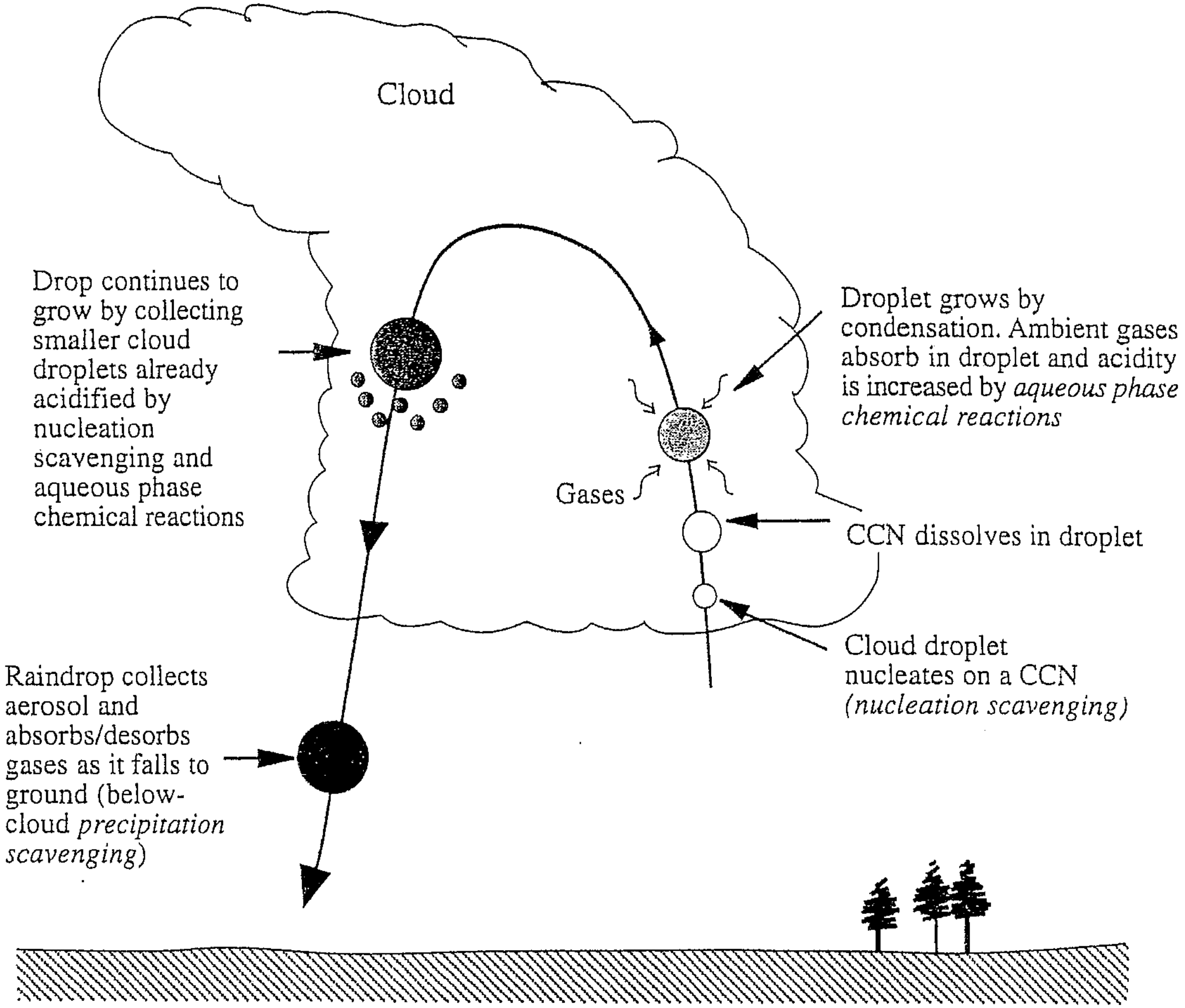


Figure 7.1. Schematic diagram of the processes affecting the chemical compositions of cloud droplets and rain. Not drawn to scale.

<u>**CCNs**</u>

Dust

Soot

Clay

Sea salt

Phytoplankton

Microbes

SVOCs

$AgNO_3$/AgI

Dissolved gases

N_2
O_2

O_3
H_2O_2

$CO_2 \rightarrow$
$SO_2 \rightarrow$
$SO_3 \rightarrow$
$NO \rightarrow$
$NO_2 \rightarrow$

$CH_2O \rightarrow$
$HCl \rightarrow$

Inorganic salts

Na^+ Cl^-

K^+ and Ca^{2+}

NH_4^+

SO_4^{2-}

NO_3^-

Ground level clouds: Fog

→ enriched conc of dissolved ions

Water aerosol droplets evaporate

Closer to land based sources (e.g., NOx, SOx)

Oxidation rxns enhanced by presence of

- O_3
- R-O-O (VOCs and BVOCs)

2. Composition of Rain

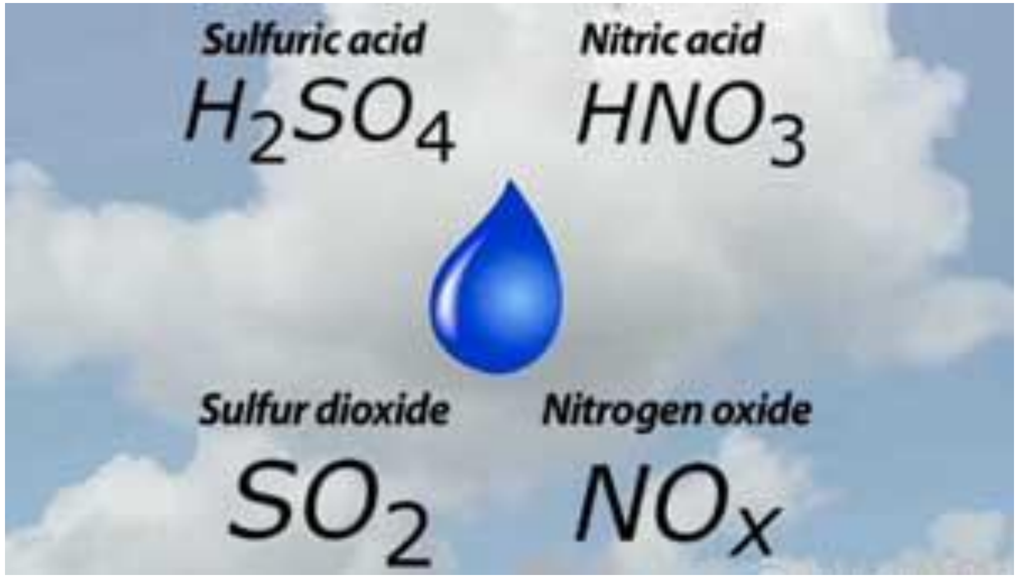
Typical chemical composition of precipitation in μequiv/L*

* concentrations reported as μequiv/L = μmol/L x #equiv/mol, where an equivalent is defined on the basis of charge (i.e., for divalent ions, there are 2 equivs per mol)

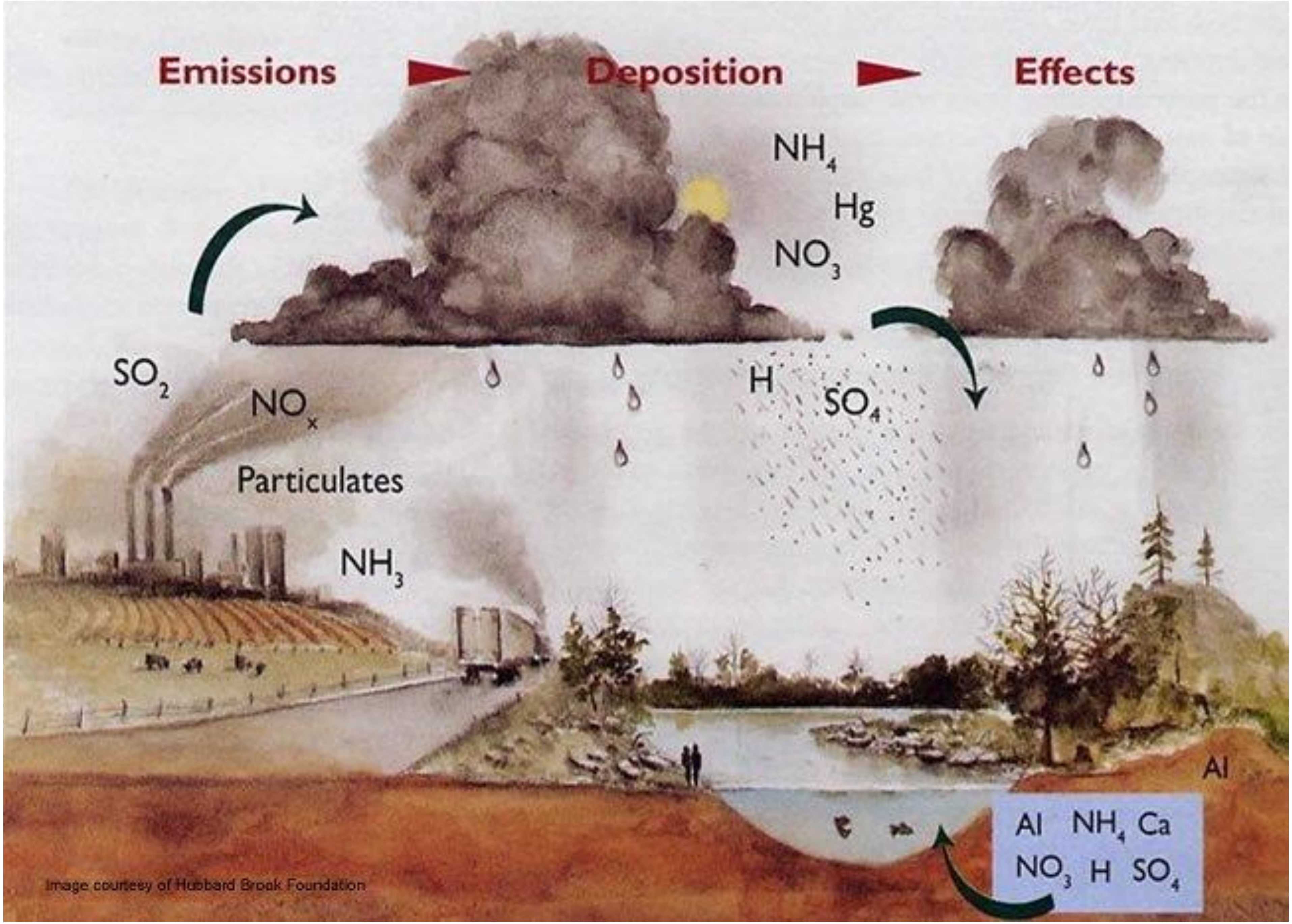
for SO_4^{2-} = 245 μmol/L x 2 equiv/mol = 490 μequiv/L

	Alaska Rainfall	California Rainfall	Bay of Fundy Fog
SO_4^{2-}	10	19	490
NO_3^-	2	24	160
Cl^-	5	22	61
Mg^{2+}	1	5	50
Na^+	2	20	22
K^+	1	1	78
Ca^{2+}	1	8	31
NH_4^+	2	19	50
pH	4.96	4.72	3.52

Acidic Rainfall



- Lowest recorded pH ~ 2.1
- pH < 3-4 not uncommon
- Past two decades [SO_4^{2-}] decreasing, but [NO_3^-] increasing



Emissions
Deposition
Effects
NH_4
Hg
NO_3
SO_2
NO_x
Particulates
NH_3
H
SO_4
Al
Al NH_4 Ca
NO_3 H SO_4
Image courtesy of Hubbard Brook Foundation

Why does acid rain matter?

Affects both

Natural

&

Built

environments

Acid Rain Affects

SO_2 – respiratory, heart and lung disease
Contributes PM

Human health

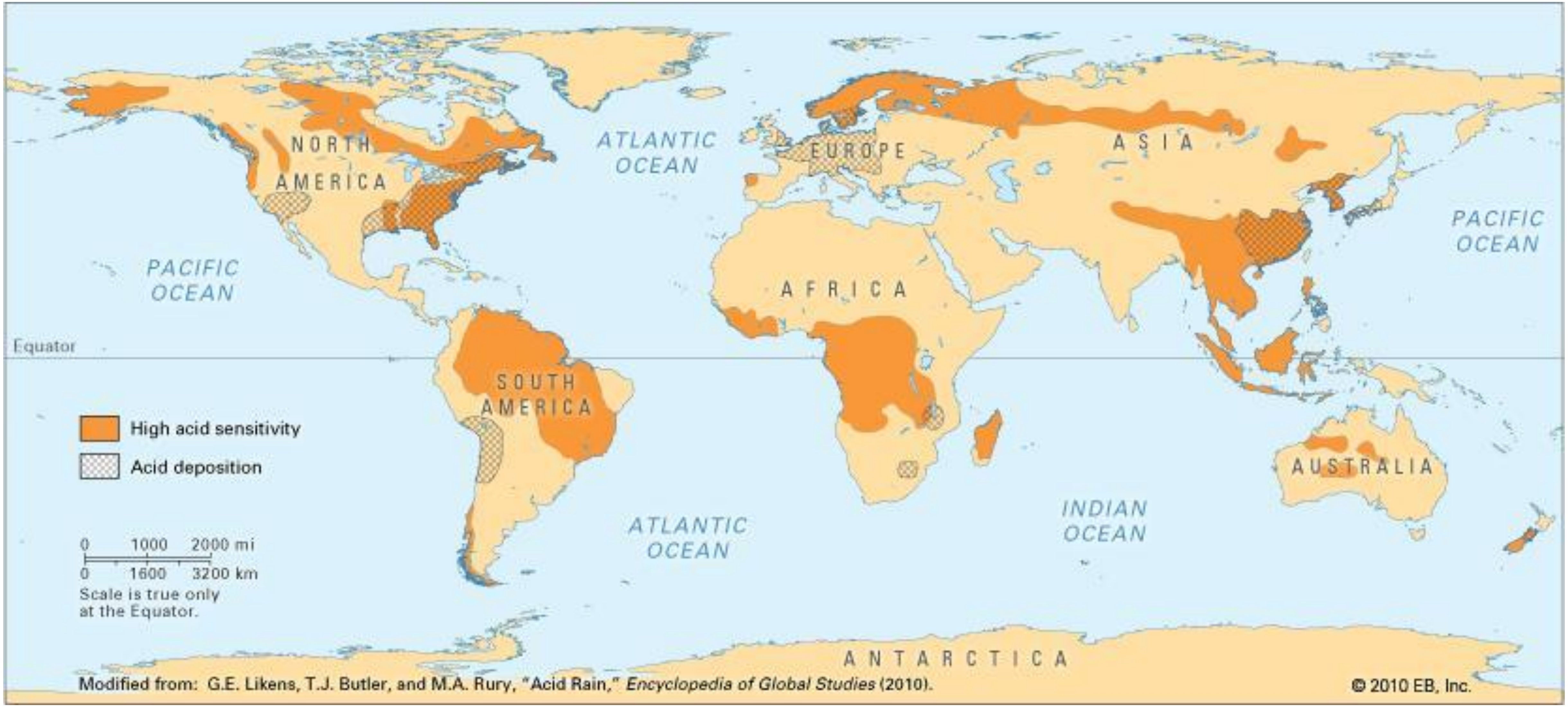
Aquatic Life

Terrestrial Life

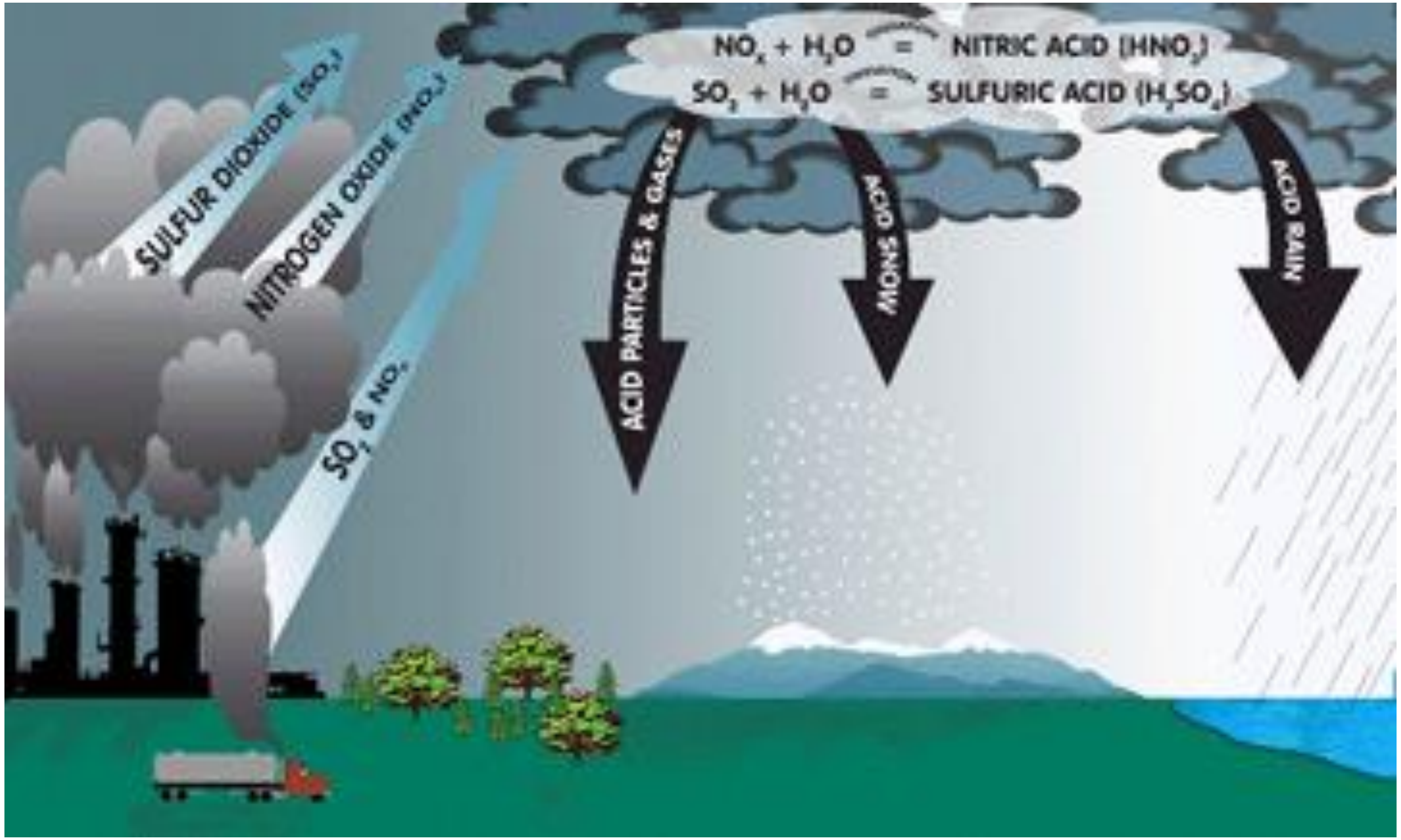
Water Chemistry – increased metal/nutrient concentrations

Soil Chemistry – decreased metal/nutrient concentrations

Global distributions of Acid deposition and Acid Sensitivity

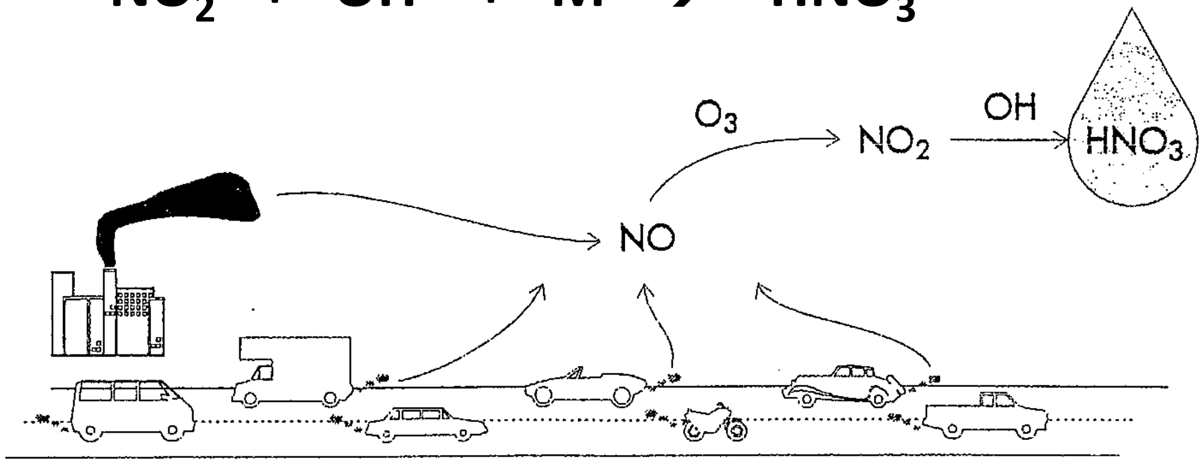


3. Mechanisms of HNO_3 and H_2SO_4 production



Atmospheric production and removal of nitric acid

$NO + O_3 \rightarrow NO_2 + O_2$
(daytime)
$NO_2 + OH + M \rightarrow HNO_3$



Combustion sources, especially non-point sources, are the principal cause of acid precipitation from nitrogen oxides.

Wet deposition in form of **HNO_3**(aq)

If **NH_3**(g) is present,
$\rightarrow$**NH_4NO_3**(aq)

In dry conditions, **NH_4NO_3**(s)
$\rightarrow$CCN and/or dry deposition

Nitrogen oxides in the atmosphere

Sources:

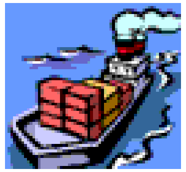
$NO_x \equiv NO + NO_2$

Natural:

- lightning
- bacteria in soil
- biomass burning

Anthropogenic (man-made):

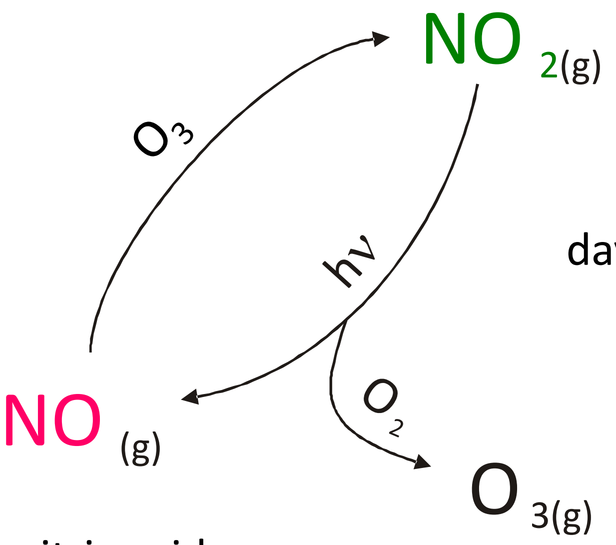
- combustion engines



$NO \leftrightarrow NO_2$ interconversion is:

- a chemical null cycle.
- rapid ⇨ NO and NO_2 are in steady state.

NO_2 = nitrogen dioxide (brown gas)



daytime

NO = nitric oxide (colorless gas)

Carbonyl sulfide (COS) in the stratosphere

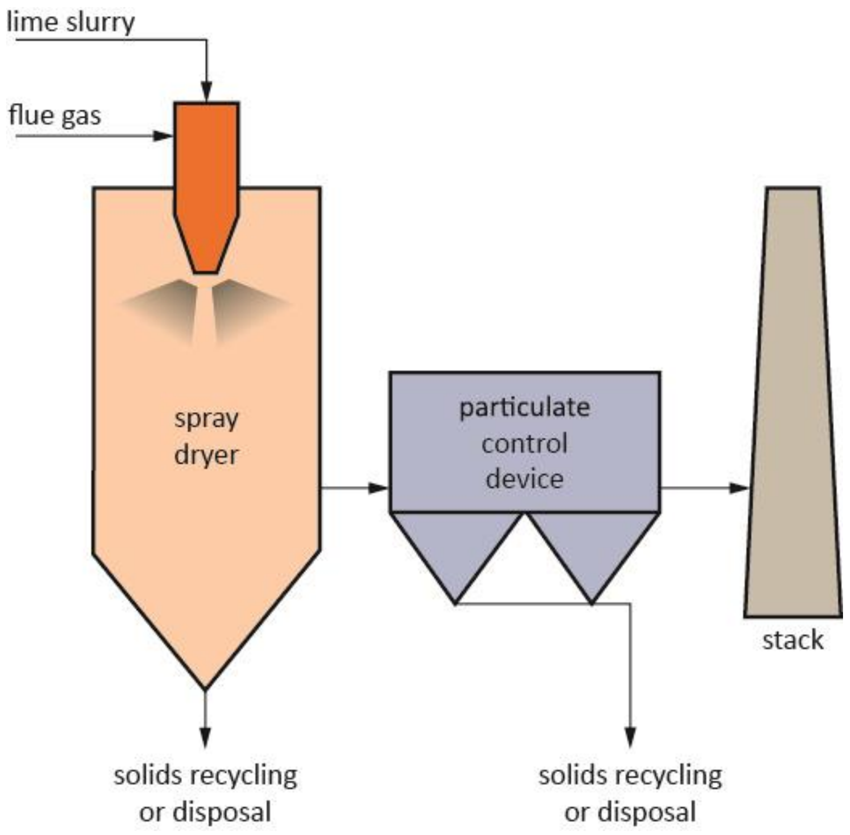
Photochemical oxidation leads to SO_2 → SO_4^{2-} (sulfate aerosols)

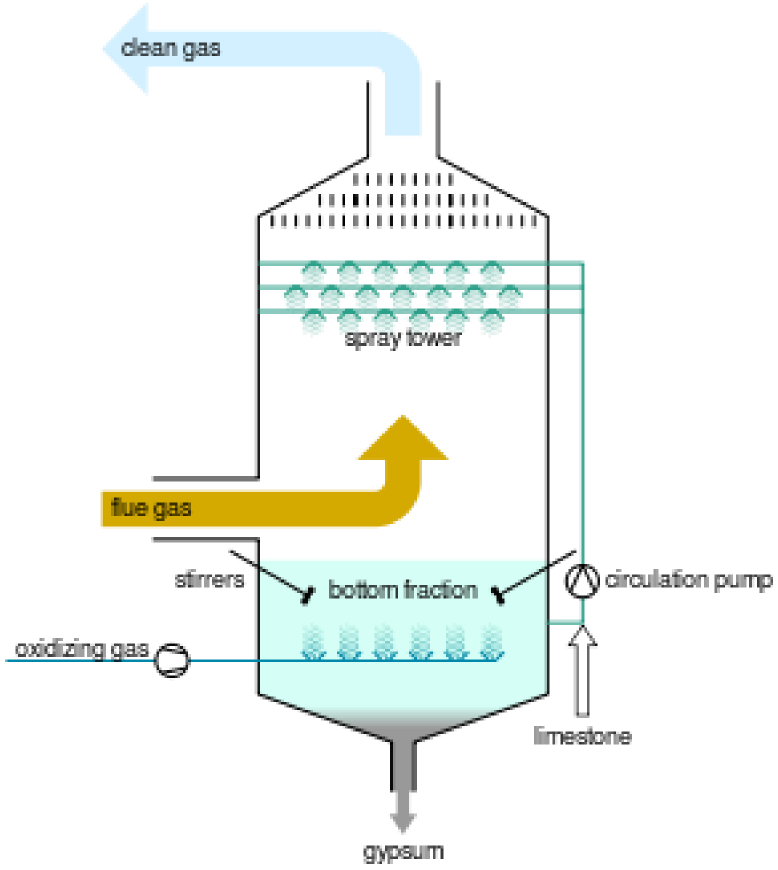
Stratospheric aerosols (global cooling effect)

&

Catalytic O_3 loss in polar vortex

4. Emission controls and abatement technology





SONOX for SO_2 and NO removal

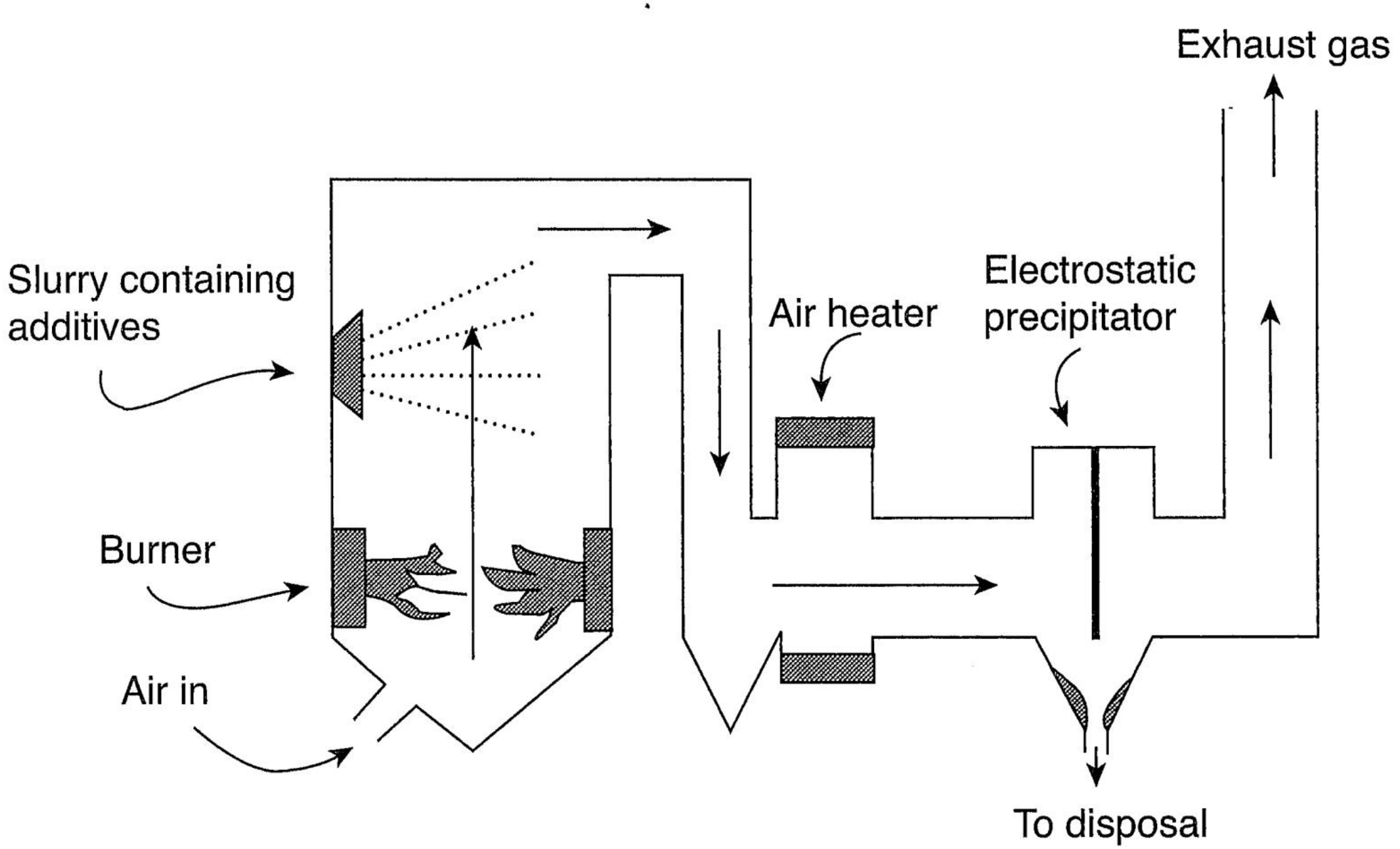
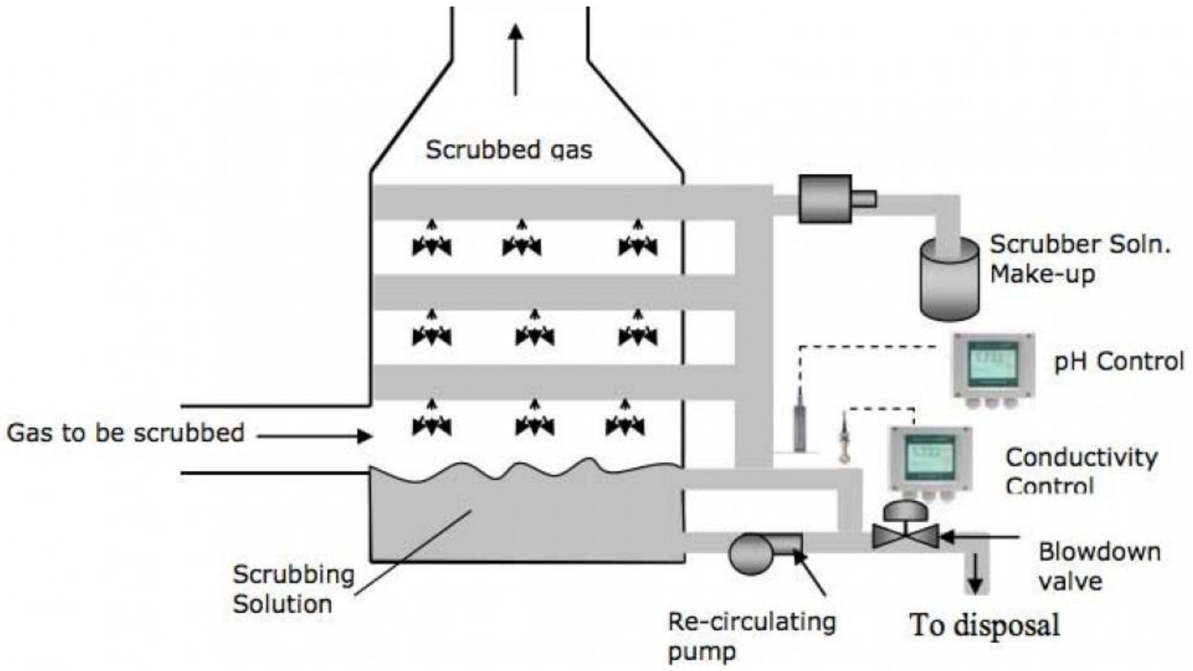


Fig. 5.5 The SONOX process for removal of nitrogen and sulphur oxides from stack gases.


Scrubbed gas
Scrubber Soln.
Make-up
pH Control
Gas to be scrubbed
Conductivity
Control
Blowdown
valve
Scrubbing
Solution
Re-circulating
pump
To disposal

Spray Dryer Absorber (SDA)