

Lecture 24. Acid rain.

Part3. Controlling acid rain.

Objectives:

1. Current acid rain data and trends.
2. Acid rain control.

Readings: Turco: p. 284- 287;

1. Current acid rain data and trends.

Monitoring of wet deposition acidity is performed in Europe, Canada and United States.

Europe: data are available from the European Air Chemistry Network (EACN) in NW Europe, several national programs, and individual studies.

Trends:

Sulfur emissions in Europe have been reduced by 40 % during the period 1980-1994. For instance, in Norway, SO₂ emissions were reduced by 75% from 1980 to 1995. These reductions are due to increasing duties on sulfur in oils and a reduction of sulfur in light heating oils and diesel.

Canada: data are available from five sites in the Atlantic provinces as part of the nation-wide Canadian Air and Precipitation Monitoring Network (CAPMoN). These sites are downwind of the major sources of acidifying pollutants in North America.

Trends:

U.S. and Canadian sulfur dioxide emissions are declining. They dropped by 16.5% from 1980 to 1992. Statistically significant decreases of 28 to 40% in precipitation sulfate (corrected for sea salt) are now detectable at the four CAPMoN sites. A decrease of 25% has occurred at the site in Labrador. It should be noted that no significant trends in hydrogen ion concentration were detected.

NOTE: It has been estimated that about 50% of the sulfate deposited in Canada is derived from sources in the U.S.

USA: data are available from 58 National Atmospheric Deposition Program/National Trends Network (NADP/NTN) sites.

Trends: from 1980 through 1992: widespread declines in SO_4^{2-} concentrations accompanied by significant decreases in all of the base cations, most noticeably calcium (Ca^{2+}) and magnesium (Mg^{2+}). As a result, only 17 of the 42 sites with significant decreasing SO_4^{2-} trends had concurrent significant decreasing H^+ trends.

The National Acid Precipitation Assessment Program (NAPAP) has two mandates from the U.S. Congress:

1. to track compliance of emission sources with Title IV of the Clean Air Act Amendments (CAAA) of 1990, and
2. to assess its costs, benefits, and effectiveness in reducing environmental impacts.

2. Acid rain control.

Acid rain is a complex political, economical and scientific problem.

In developing control strategies one seeks to establish relationships between emissions and deposition, so-called **source-receptor relationships**.

- Derivations of source-receptor relationships include experimental and modeling approaches. Both approaches have serious limitations.

Some problems:

- ◆ North America is about 2500 by 2500 km gridded in cells of 250 by 250 km gives 100 cells, each of which is in principle both a source and a receptor of acidity. The source-receptor relation is the contribution of each source to acid deposition at each receptor. Therefore one needs to quantify 10,000 source-receptor elements.

Limitation of field experiments:

Suggested experiments: release of passive tracer (such as transition metal ions) or stable isotopes.

Limitations: passive tracers cannot mimic the acid deposition; use of stable isotopes requires large quantities of the isotopes, because similar isotopes emitted already by the various sources.

Limitation of mathematical models:

Despite significant progress during last decade, limitations of models leave uncertainties of a factor of 2 or more in the most substantial property of source to receptor relationships (for instance, mean transport distance).

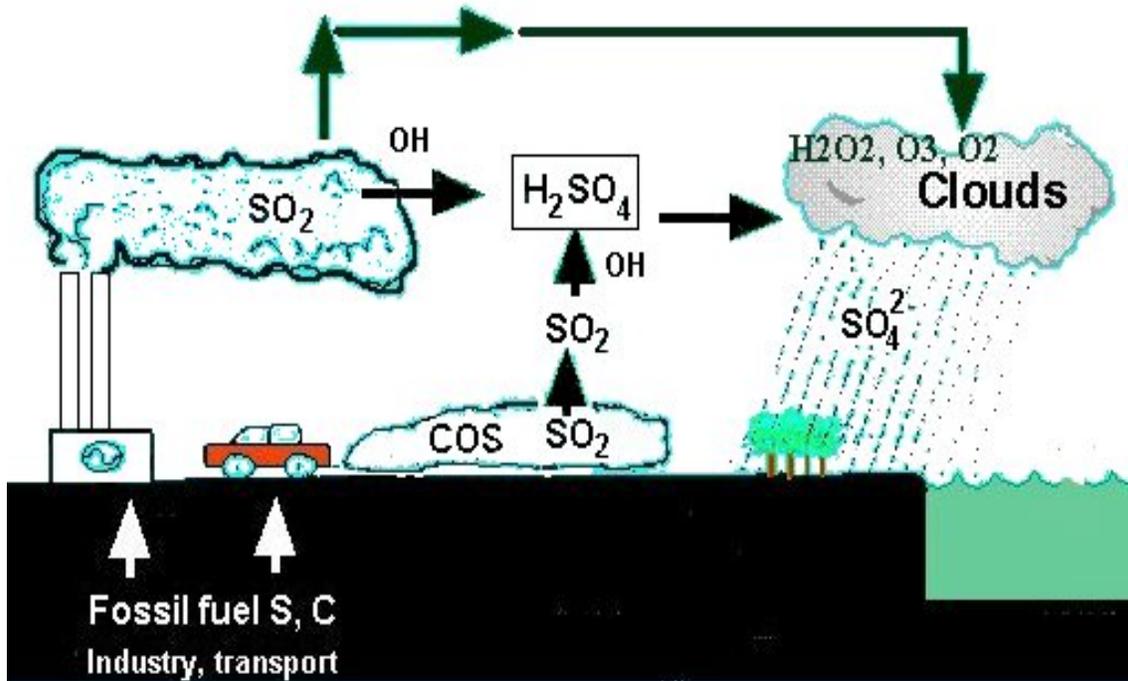
NOTE: introduction to chemical transport models given in Lectures 29-30.

More problems:

- ◆ Nonlinear response of the system to changes in the emissions.

If the emissions were reduced by 50%, would acid deposition (wet and dry) decrease by 50%? If 'yes', it implies that deposition varies linearly with changes in the emissions.

Let's explore this relationship for a case of SO₂ emission.



Processes that involved in SO₂ conversion:

- 1) Emission of SO₂ ;
- 2) Transport of SO₂ ;
- 3) Gas-phase conversion of SO₂ (reaction with OH): Rate = k [OH] [SO₂] ;
- 4) Dry deposition: Rate_d = V_d [SO₂] / H, V_d is the dry deposition velocity of SO₂ and H is the characteristic mixing ratio;

(1)-(4) linear depend on SO₂ concentration

- 5) Aqueous-phase conversion of SO₂ in clouds (reaction with H₂O₂ ; O₃ ; O₂)

However, aqueous phase oxidation of SO₂ in clouds is controlled by the availability of H₂O₂, O₃, or O₂. If concentrations of oxidants were low, not all SO₂ would be converted to sulfate.

- 6) Wet deposition: may be nonlinearly related with SO₂ if cloud droplets would become saturated with SO₂.

(5)-(6) may nonlinear depend on SO₂ concentration

Thus, if gas-phase processes dominated compared to aqueous-phase chemistry, the system will be practically linear. Otherwise it is a nonlinear process.

NOTE: that the system can depend practically linearly or deviate significantly from nonlinearity based on a series of factors: magnitude of SO₂ emissions, H₂O₂ and other oxidant availability, season, and so on. For instance, the most significant deviations from linearity are predicted to occur during the winter (low concentrations of H₂O₂) and close to the source (high concentrations of SO₂).

- Even if pH of rain > 5, it still may be polluted and may be dangerously contaminated: because pH does not measure the amounts of nonacidic toxic materials; because large quantities of anthropogenic acids in rain may be neutralized by alkaline compounds.