Acid Rain

Rolf D. Vogt

Research Center for Eco-Environmental Sciences
Chinese Academy of Sciences

University of Oslo

Tsinghua University
Outline

Impact

Tsinghua University
Atmospheric emissions

- **SO₂**
  - Oxidized to H₂SO₄
  - **Europe: Gothenburg protocol** (歌德堡议定书)
    - 63% reduction of annual SO₂ emission in Europe in 2010 against the emission in 1990
    - >50% decrease since 1987

- **China: Tenth Five-Year Plan** 十五计划
  - 10% reduction of annual SO₂ emission in China in 2005 against the emission in 2000

- **NO, NO₂**
  - Oxidized to HNO₃

- **NH₃**

- **Alkaline dust**
  - E.g. CaCO₃, MgO,

---

**European SO₂ emissions (million tonnes) in the EMEP-area. Mylona (1996) and UN-ECE, 1997.**

**Energy (Mtoe)**

million tons of oil equivalent

**Chinese energy production. BP Statistical review of world energy (June 2002)**

Tsinghua University
$1^\circ \times 1^\circ$ SO$_2$ emission in China

Liu Zi, 2002

Tsinghua University
Deosition in Europe

- Dry
  - \( \text{SO}_2, \text{NO}_2, \text{NH}_3 \)
- and wet
  - \( \text{H}_2\text{SO}_4, \text{HNO}_3, \text{NH}_4^+ \)
- In Europe the highest deposition has been in the "The Black Triangle"
  - Industrial conglomerate (聚集) of Poland, Czech republic and former East Germany
- Also considerable deposition in remote areas due to Long-range transported pollutants

EMEP, 1990
Long range transported S and N

- Tall stacks (烟囱) solve local problems but generate acid rain in remote regions
  - Southernmost Norway has no significant local anthropogenic (人为) emissions
  - Receives long-range transported pollutants from England and continental Europe
    - Due to
      - dominating wind trajectories (轨迹)
      - high precipitation (降水) amount
Deposition in China

- Alkaline dust play an important role in mitigating the effect of acid rain

pH distribution:

Sulfur deposition:
Reference: RAINS-Asia (Downing et al., 1997)

Calcium deposition:
Reference: Larssen and Carmichael, 2000
China’s two control zones

- Tenth Five-Year Plan
  - 20% reduction in the Two-Control-Zone
  - Significant decrease in acidity and frequency of acid rain

![Map showing two control zones in China](image)

![Bar chart showing city, area, population, and GDP](image)

Tsinghua University
Differences China - Europe

- Different deposition
- Older soils
- Different climate
- Steep topography （地形）
- Different biota

Existing knowledge need to be adopted to Chinese conditions
- Need an integrated monitoring programme
Integrated Monitoring Program on Acidification of Chinese Terrestrial Systems
Chinese participants in IMPACTS

- Chinese Research Academy of Environmental Sciences (中国环科院)
- The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences (中科院生态环境中心)
- Chinese Academy of Forestry (中国林科院)
- Center for Environmental Sciences, Peking University (北大环境中心)
- Department of Environmental Science and Engineering, Tsinghua University (清华环境系)
- Institute of Environmental Economics, Remin University (人大环经系)
- Guangzhou Research Institute of Environmental Protection (广州环保所)
- Guizhou Institute of Environmental Protection Research (贵州环保所)
- Chongqing Institute of Environmental Science and Monitoring (重庆环保所)
- Hunan Research Institute of Environmental Protection Science (湖南环保所)
The sites

LCG, Guizhou

TSP, ChongQing

CJT, Hunan

LXH, GuangDong

Tsinghua University
Ions in precipitation and S-deposition
Comparison between Europe and China

Dry and wet deposition
Local – Long-range transported
CaSO₄ – H₂SO₄

Important factors:
- Concentration
- Composition
- Total loading (负荷)

Min Shao, 2002
Chemical effect on soil and water

- $\text{H}_2\text{SO}_4$, $\text{HNO}_3$, $(\text{NH}_4)_2\text{SO}_4$
  - $\text{SO}_4^{2-}$ - Mobile anion, leached through the soil
  - $\text{H}^+$ - exchanged with metal cations
    - Neutral and alkaline soil: Ca, Mg
    - Acid soils: Al, $\text{H}^+$ (pH < 5, BS < 20%)
- $\text{NO}_3^-$, $\text{NH}_4^+$ - several pathways
  - Assimilation (同化)
  - Nitrification (硝化)

- $\text{CaSO}_4$
  - $\text{Ca}^{2+}$ - exchange with other cations
    - Neutral and alkaline soil: Mg, Ca
    - Acid soils: Al, $\text{H}^+$
Mobile anions

Move easily through the soil

- Cl⁻
- SO₄²⁻

  - pH < pH_{pzc}
  - Oxides adsorb sulphate

P NO₃⁻

  - taken up (吸收) by vegetation until saturated

P Organic anions

  - Usually less mobile, but contribute to the relocation within natural acid soil
Mobile anions

Move easily through the soil

- Cl⁻
- SO₄²⁻
  - pH < pHₚᵢₙₙ
  - Oxides adsorb sulphate

P NO₃⁻
  - taken up (吸收) by vegetation until saturated

P Organic anions
  - Usually less mobile, but contribute to the relocation within natural acid soil
N-effects

Composition of wet deposition in TSP

\[ H^+_{\text{prod}} = (\text{NH}_4^+_{\text{in}} - \text{NH}_4^+_{\text{out}}) + (\text{NO}_3^-_{\text{out}} - \text{NO}_3^-_{\text{in}}) \]

Tsinghua University
Soil acidification

2 definitions of soil acidification:
- Reduction in %BS
  - Low CEC and %BS > 20 most sensitive
- Reduction in soil pH
  - Low CEC and %BS < 20 most sensitive

Reservoirs and fluxes of cations:

Causes for soil acidification
- Biological uptake
- Elution 洗脱 with anions
  - Natural with HCO$_3^-$, A$^-$ and Cl$^-$
  - Anthropogenically with SO$_4^{2-}$ and NO$_3^-$
Buffer systems

- Weathering (风化) consumes $H^+$ and release Base Cations (BC)
  \[ 2KAlSi_3O_8 + 2H^+ + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + 4H_2SiO_4_{aq} \]
  - Weathering speed has consequence for the buffer capacity
  - Different pH ranges have different buffer (缓冲) systems:

```
Buffer systems

- Al is mobilized
- Si-Al minerals
- Calcite or other carbonates
  
  Cation exchange
  
  Al minerals dissolve and Al-species buffer the solution
  
  Al-minerals dissolve

- Fe-minerals dissolve
  
  Organic acids
```

Soil pH

```
2,5 3,0 3,5 4,0 4,5 5,0 5,5 6,0 6,5 7,0 7,5 8,0
```
Chinese acid sensitive soils

Soil pH (BaCl₂) for various soil horizons:

- TSP
- LCG
- CJT
- LXH
- LGS

Guo et al., 2002
Effect of alkaline dust

- E.g. CaCO₃, MgO
- Antagonistic (对抗的) effect on acid rain
  - Base cations reduce BS loss
  - Carbonate (碳酸盐) and oxides neutralize acidity
  - Lime (石灰) potential, $K_L$
    - $K_L = \text{pH} - \frac{1}{2} \text{p} \{\text{Ca}^{2+}\} + \{\text{Mg}^{2+}\}$
    - i.e. the combined effect of $H^+$ and Ca+Mg in deposition
      - High value = Low $\{H^+\}$ and high $\{\text{Ca}^{2+}\} + \{\text{Mg}^{2+}\}$
Al Saturation

**AIS and BS in Chinese soil profiles**

![Graph showing Al Saturation in different soil horizons: TSP, LCG, CJT, LGS. The graph compares BS (brown) and AIS (red) percentages across various soil horizons (O, A, AB, B1, B2, B3).](image-url)
Composition of soil Ion exchanger
Comparison China, Poland and Norway

- B-Horizon exchanger mainly consists of Al
- Similar composition and capacity to buffer acidification by ion exchange

**Graph:**
- **China**
- **Poland/Norway**

**Legend:**
- BS
- HS
- AIS

**Data Table:**

<table>
<thead>
<tr>
<th>Location</th>
<th>BS</th>
<th>HS</th>
<th>AIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leigong</td>
<td>13</td>
<td>11</td>
<td>83</td>
</tr>
<tr>
<td>Chonghua</td>
<td>34</td>
<td>31</td>
<td>44</td>
</tr>
<tr>
<td>Guiyang</td>
<td>53</td>
<td>47</td>
<td>26</td>
</tr>
<tr>
<td>Nanshan</td>
<td>26</td>
<td>37</td>
<td>39</td>
</tr>
<tr>
<td>Nanshan</td>
<td>34</td>
<td>31</td>
<td>44</td>
</tr>
<tr>
<td>Leigong</td>
<td>7</td>
<td>58</td>
<td>30</td>
</tr>
<tr>
<td>HeShan</td>
<td>16</td>
<td>43</td>
<td>26</td>
</tr>
<tr>
<td>Nanshan</td>
<td>74</td>
<td>26</td>
<td>74</td>
</tr>
</tbody>
</table>
Soil water acidification

- Al mobilization significant when pH<5 or %BS<20
- Many mechanisms control Al^{3+}
Natural organic vs. anthropogenic mineral acidity

- **Humus:**
  End product of chemical and biological decay
- **Poorly defined:**
  - Many functional groups (官能团):
    - Fenol
    - Carboxyl
    - Amine
    - Alcohol
    - Sulfhydryl

Tsinghua University
Inorganic aluminium (Ali) in soil solution of Acid Chinese soils

Guo et al., 2002
Ions in acid soil water
Comparison China, Poland, Norway

- Comparable [Ali] as in Poland, but higher [Base Cations]
The calculations become complex where a metal cation have the opportunity to bind to more than one type of ligands. In natural water systems:
- Basic: CO$_3^{2-}$, OH$^-$, Cl$^-$
- Acid: F$^-$, SO$_4^{2-}$, Org$^-$, Cl$^-$

Multiple iterations of the calculations are necessary. For such calculations we apply computer programs as MINEQL and ALCHEMI.
Why chemical speciation is important?

- The bioavailability of metals and their physiological and toxicological effects depend on the actual species present
  - Examples:
    - Al\(^{3+}\) and Al(OH)\(_n\)^{3-n} effect biota in different ways
    - Organic bound Al is not toxic to fish

- Mobility depend on speciation
  - Examples:
    - Al is more mobile if complexes to fluoride (氟化物) or sulphate
Critical load

- Definition
  - “The deposition below which significant harmful effects do not occur according to present knowledge”

- Direct and indirect effects on vegetation
  - Direct: SO₂ & O₃ damage
  - Indirect: \( R_{CL} = \frac{Al}{(Ca+Mg)} \)
    - \( R_{CL} = 1 ? \)
Molar critical load ratio $R_{CL} \text{ Al}/(\text{Ca+Mg})$
Critical load of Sulfur deposition in China

- Based on S-deposition,
- Deposition of alkaline dust
- Soil sensitivity

Lei Duan, 2002

Liu Zi, 2002
Understand $\text{Al}^{3+}$ mobilization mechanisms

- **Gibbsite $\text{Al(OH)}_3$ (三水铝石) & Ion exchange**
  - $\text{Al(OH)}_3 (\text{S}) + 3\text{H}^+ = \text{Al}^{3+} + \text{H}_2\text{O}$
  - $p\text{Al} = 3p\text{H} + pK_{sp}$

- **Organic complexation, SOM-Al**
  - $\text{SOM-Al}^{m+} + n\text{H}^+ = \text{SOM-H}_n^{(m+n-3)+} + \text{Al}^{3+}$
  - $p\text{Al} = np\text{H}-\log(K_2[\text{SOM-Al}^{m+}]/[\text{SOM-H}_n^{(m+n-3)+}])$
Crisis = Danger + Possibilities

谢谢大家！

rolf_vogt@mail.rcees.ac.cn

Tsinghua University
SO$_2$, NOx and TSP in Chinese cities
Episode studies -

- Hydrological episodes (rain events)
- Large changes in streamwater chemistry
  - due to changes in dominating water flowpaths
Salt effect -

- Desorption of polyvalent ions increase as ionic strength increase
- Since
  \[
  \frac{3 \cdot \{Al^{3+}\}^2}{2 \cdot \{Ca^{2+}\}^3} = \text{Constant}
  \]

- $10 \cdot$ increase in $\{Ca^{2+}\}$ will lead to an $\sim 30 \cdot$ increase in $\{Al^{3+}\}$
  - An increase in ionic strength will in addition lead to a greater activity reduction the higher the valence
  - pH will also decrease

Tsinghua University
Recovery or amelioration -

- Due to reduced S-deposition and possibly increased precipitation
- Negative salt effect
Mountains are vulnerable

- Why are soils in mountain regions more sensitive to acidification than in the lowlands?
- Due to:
  - Thin soils
  - Less weatherable parent rock
  - More precipitation
Value of the mountain

- Large biodiversity
  - Gene bank
- Recreational
- Few forests in China
- Low commercial value today

Liu Haiying et al., 2002