Integrated acidification study and survey on acid rain impacts in China

Soil and soilwater interactions

The Environmental Chemistry group
Department of Chemistry
University of Oslo, Norway
Steppingstones in our Cooperation with China

- **1988**: Cooperation with
  Research center for Eco-Environmental Sciences, CAS

- **1992**: Catchment studies with
  Guizhou Institute of Environmental Science &
  Chongqing Inst. of Environ. Science and Monitoring

- **1995**: Collaboration agreement between
  The Norwegian ministry of environment and SEPA

- **1996**: PIAC funded by
  Norwegian Agency for Development Co-operation (NORAD)
  and the World Bank-ASTEN

- **1996**: PIAC cooperation with SEPA & CREAS

- **1997**: PIAC cooperation with South China Institute of Botany, CAS
PIAC
Planning of an Integrated Acidification study and survey on acid rain impacts in China

Norwegian participants:

In Norway:

- Norwegian Institute of International Affairs
- Norwegian Institute for Air Research
- Norwegian Institute for Forest Research
- The Norwegian foundation for nature and cultural heritage research
- Norwegian Institute for Water Research
- University of Oslo
The PIAC project

- Establish contacts
- Obtain an overview
- Evaluate needs
- Selection of sites
Why Al leaching mechanisms are important to understand

- Al is
  - Mobilised in acidification processes
  - Toxic to plants and aquatic fauna
- To predict future effects of acidification, we must be able to predict future Al-concentrations
  - Under various anthropogenic deposition scenarios
  - In different environments
Overview (After Bergren & Mulder, 1995)

- Al in primary minerals
- Al in secondary mineral phases
- Al adsorbed by SOM and exchangeable
- Adsorbed Al(OH)₃ and Al in secondary minerals
- Al³⁺ (aq)

Slowly reacting solid phases
Rapidly reacting solid phases
1. Gibbsite

Solubility & Ion exchange

\[
\text{Al(OH)}_3 \text{(s)} + 3\text{H}^+ = \text{Al}^{3+} + \text{H}_2\text{O}
\]

May be expressed as:

\[
p\text{Al} = 3p\text{H} + pK
\]

Reported values vary more than a factor 1000

Most reported values for soilwater are less than 3
2. Ion exchange with base cations

E.g. Ca$^{2+}$:

$$2\text{Al}^{3+} + 3\text{CaX} = 3\text{Ca}^{2+} + 2\text{AlX}$$

The Gaines Thomas constant is difficult to estimate.
3. Jurbanite
Solubility/Co-adsorption

\[
\text{Al(OH)SO}_4^{(s)} + H^+ = Al^{3+} + \text{SO}_4^{2-} + H_2O
\]

\[
K_{sp} = \frac{\{Al^{3+}\} \{SO_4^{2-}\}}{\{H^+\}}
\]

May be expressed as:

\[
pAl = pH - pSO_4 + pK_{sp}
\]
Challenge

The relationships between soil water chemical parameters as pH, pSO₄ and pAl exhibit large spatial variation.

The quest is to find:
A simple soil chemical parameter that, together with key water chemical parameters, describes the Al-activity.
4. SOM-AI Complexation

Al complexed to solid Soil Organic Matter

\[
\text{RAI}^{(3-a)+} + a \text{H}^+ \Leftrightarrow \text{RH}_a + \text{Al}^{3+}
\]

\[
K_{\text{RAI}} = \frac{\text{RH}_a \{\text{Al}^{3+}\}}{\text{RAI}^{(3-a)+} \{\text{H}^+\}^a}
\]
4. SOM-Al
Cont.

Rearranging the equation gives:

\[
\{\text{Al}^{3+}\} \frac{\text{RH}_a}{\text{RAI}^{(3-a)^+}} = K_{\text{RAI}} \{\text{H}^+\}^a
\]

Approximation to identifiable parameters gives:

\[
\frac{\text{RH}_a}{\text{RAI}^{(3-a)^+}} \approx \frac{C_{\text{tot}}}{A_{\text{org}}}
\]

\[
Y = \{\text{Al}^{3+}\} \frac{C_{\text{tot}}}{A_{\text{org}}}
\]

\[
pY = pK_{\text{RAI}}^* + xpH
\]
By analysing soil & soilwater samples from different environments we find empirical relationships between pAl, pH and $\text{Al}_{\text{pyro/C}}$.

- Other relevant water parameters: $\text{SO}_4^{2-}$, $\text{Ca}^{2+}$, I
- Other relevant soil parameters: $\text{Al}_{\text{CuCl}_2}$, $\text{Al}_{\text{ox}}$
Field studies

- Precipitation
- Throughfall
- Soil water
- Stream water
- Soils
Ions in precipitation

μeq/L

Norway  Czech Republic  Poland  China

0.6  1.1  1.6  4.4  5.3  8-10  8-10  9.1

Locations

HUMEX  Birkenes  Kosetice  Czerniawka  Ratanica  LCG  TSP  Guangzhou

Ca^{2+}Mg^{2+}  Na^+K^+  NH_4^+  H^+  SO_4^{2-}
Exchangeable cations in soils

China

Poland/Norway

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<th>AIS</th>
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meq/kg
"Critical load ratio"
$\text{Al}/(\text{Ca}+\text{Mg})$

“The deposition below which significant harmful effects do not occur according to present knowledge”
How does real soilwater data fit the Gibbsite model?

In many (most) cases the gibbsite model does not describe the data at pH < 4.5
What does the data tell us?

- **Gibbsite:**
  \[ \text{pAl} = \text{pK}_{sp} + 3\text{pH} \]

- **Empirical fitting:**
  \[ \text{pAl} = \text{pK}_0 + a\text{pH} \]

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<thead>
<tr>
<th>Locality</th>
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<td>All</td>
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<td>46</td>
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</table>

- \( \text{pK}_{sp} = -8.11 \) (synthetic)
- \( -10.8 \) (amorph)

- Reuss et al., 1990: \( r^2 = 0.75 \)
  \[ \text{pAl} = -2.29 + 1.65\text{pH} \]
Does the Jurbanite model describe the field data better than the Gibbsite model?

\[ pK = p\text{Al} + p\text{SO}_4 - \text{pH} \quad \text{(Jurbanite)} \]

\[ pK = p\text{Al} - 3\text{pH} \quad \text{(Gibbsite)} \]
What does the data tell us?

Jurbanite:
\[
p_{\text{Al}} = pH - p_{\text{SO}_4} + p_{K_{\text{sp}}}
\]

Empirical:
\[
p_{\text{Al}} = apH + bp_{\text{SO}_4} + pK
\]

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</table>

\(p_{K_{\text{sp}}}: 3.8\) (Nordstom, 1982)
How does real data fit the SOM-Al model?
What does the data tell us?

**SOM-Al model**

\[ p_Y = p \left( \{ Al^{3+} \} \frac{C_{tot}}{Al_{org}} \right) = pK^{*}_{RAI} + a pH \]

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</table>

*Wesselink et al., 1995: \( r^2 = 0.82 \)

\[ p_Y = -1.84 + 1.14 pH \]
Model development

- **pAl** is empirically correlated to:
  - pH, pSO$_4$ & p(Al$_{org}$/C$_{tot}$)

- We hypothesise that Al-mobilisation is controlled by a combined SOM-Al mechanism and sulfate desorption

  \[ RAI^{n+} (n^{1/2}SO_4^{2-}) + (3-n)H^+ = RH_{3-n} + Al^{3+} + (n^{1/2})SO_4^{2-} \]

  \[ pAl = pK_{SOM-Al} + (3-n)pH - (n^{1/2})pSO_4 + p(Al_{org}/C_{Tot}) \]

- Fitted empirical to all data:
  \[ pAl = -3.52 + 1.6 pH - 0.03 pSO4 + 0.8p(C_{Tot}/Al_{pyro}) \]
Model testing

\[ p\Delta = -\log\left(\frac{\sum(10^{-pAl_{\text{measured}}} - 10^{-pAl_{\text{modelled}}})^2)}{N}\right)^{1/2} \]

- **Gibbsite**
  \[ pAl = -2.6 + 1.6pH \]

- **Jurbanite**
  \[ pAl = -4.8 + 1.6pH + 0.7pSO_4 \]

- **SOM-Al model**
  \[ pAl = -3.7 + 1.6pH + p(C_{\text{Tot}}/Al_{\text{org}}) \]

- **New combined model**
  \[ pAl = -3.5 + 1.6pH - 0.03pSO_4 + 0.8p(C_{\text{Tot}}/Al_{\text{org}}) \]

<table>
<thead>
<tr>
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<th>Jurbanite</th>
<th>SOM-Al</th>
<th>New Model</th>
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Conclusions from Al-mobilisation studies

- Different mechanisms control the Al-mobilisation depending on e.g. pH range and sulfate concentrations
  - Complexation of Al to soil organic matter (SOM-Al) may describe Al-activity in most Chinese soil waters
- In regions of high S-deposition Al mobilisation is best described by an combined pH dependent Al dissolution and sulfate desorption ("Jurbanite model")
- A combination of SOM-Al dissolution and mobile anion mobilisation appears promising
Conclusions from field studies

- Very high deposition of sulfur at some sites
- Water acidification only in small 1. order streams
- Soil & soilwater acidification is likely in large areas
- Large spatial variation in soil chemistry
- High conc. of Al in soil water, but also high Ca^{2+} conc.
- Development in S and Ca^{2+} deposition critical
Laboratory experiments

Soil columns:

Batch experiment:

1

Soil A

2

Soil B
Conclusions from laboratory experiments

- Simple batch experiments yield same results as more comprehensive soil column leaching experiments.
- Sulfate adsorption on Yellow- and Red soil is low.
- Al mobilisation correlates best to soil pH and Al$_{\text{org}}$.
- The base cation weathering is low.
- Future soil water acidification depends strongly on changes in base cation deposition in addition to S-deposition.
Model work

- Simple equations for:
  - Cation exchange
  - Gibbsite solubility
  - Sulfate adsorption
  - Weathering
  - Charge balance
- Model calibration
- Hindcast
- Model running
- Simulation & Forecast
Magic simulations

![Graph showing changes in RCL and BS% over years]

- **No change**
- +30%: Ca, Mg, SO4
- -80%: Ca, Mg, SO4
- -30%: Ca, Mg
- -30%: SO4
- +30%: SO4


RCL: 0, 0.2, 0.4, 0.6, 0.8

BS %: 5, 10, 15, 20, 25, 30
Conclusions from model studies

- Soil & soilwater acidification may occur in Southern China under long term acid deposition
- Present deposition loading gives minor changes
- An increase in sulfate deposition or a decrease in base cation deposition give rise to accelerated soil and soilwater acidification
Conclusions from PIAC

- Precursors for the formation of O₃ and other photooxidants occur at high levels
- **Increased emissions of NOₓ may lead to seriously increased O₃-concentrations**
- Damage to vegetation may be attributable to high levels of SO₂, O₃, lack of P or high Al content in soil water.
- Ecological effects of acidification have been observed on surface water organisms
- Waters low in dissolved salts are found in rural areas with low acid loading at present
- These waters are poorly buffered and therefore very vulnerable to acidification