PRESENT AND FUTURE RISKS
OF EXCESS HEAVY METAL INPUT
TO TERRESTRIAL ECOSYSTEMS
IN THE KOLA PENINSULA

Sergey Koptsik
Physics Faculty
Lomonosov Moscow State University
Moscow, Russia
Acknowledgements

Sudbury 2007 Organizing Committee

Galina Koptsik
Soil Science Faculty, MSU, Moscow, Russia

Wim de Vries
Alterra, Wageningen, the Netherlands

Bert Jan Groenenberg
Alterra, Wageningen, the Netherlands

Stephen Lofts
CEH, Lancaster Environment Centre, UK

Jan Cees Voogd
Alterra, Wageningen, the Netherlands
General problem

- **Europe:** 19.5 million ha of industrial and urbanized lands and 550 million ha of agricultural lands become degraded, 1.5 million of polluted sites were recognized (FAO).

- **Russia:** more than 15% of inspected cities and towns, 70 million ha of agricultural lands are polluted with heavy metals (State Report..., 2001).
Specifying situation

$\text{SO}_2$ up to 10
Ni, Cu, Co $10^3$
Al, Fe, Sr $10^2$
V, Cr, Mo, As 10
Cd, Pb, Mg, Ba
Ca, Na, K, Zn, Mn up to 10
Tasks

- Assessment of heavy metal critical contents and loads for terrestrial ecosystems of the Kola Peninsula

- Analysis of present and potential risks of excess heavy metal input to terrestrial ecosystems of the Kola Peninsula

- Comparison of exceedance maps with expectations and suggestions for future research
Methodology
Methodology: Critical loads concept for heavy metals

- Developed within the frames of Convention on Long-range Transboundary Air Pollution (CLRTAP) of the UNECE

- Based on assessment of impact on ecosystems

- Developed and approved mostly for Cd and Pb (and Hg)
Methodology: Present and future risks

- **Current risks**: comparison of real/observed metal contents with critical contents (momentary aspects).

- **Potential risks**: comparison of real and/or expected loads with critical loads (long-term aspects; comparison of real/expected metal fluxes).
Potential risks:
Stationary balance of metal fluxes

\[ CL(M) = M_{gu} + M_{le(crit)} \]

- **Load**: Dissolved metals
- **Uptake**: Free ions → Bound to complexes with DOM

\[ M_{le(crit)} = Q_{le} \times [M]_{tot, ss(crit)} \]

- \( Q_{le} \): flux drainage water
- \([M]_{tot, ss(crit)}\): total metal critical concentration in solution

**CL(M)** – critical load of metal; \( M_{gu} \) – metal net uptake in harvestable parts of vegetation; \( M_{le(crit)} \) – critical metal leaching flux.
Methodology:
Critical limit for ecosystem functioning

- **Direct ecotoxicological effects**: impacts on soil micro-organisms, plants and invertebrates
- Ecotoxicological effects related to *free metal ion* soil solution concentrations depending on pH
- Derived from NOEC data using *transfer functions* for solid-solution partitioning
Methodology: free metal ion as critical limit

Aspects critical limit of free ion concentration:

- This form is available for interactions with organisms
- Assumed to give smallest variance in endpoint concentrations.
- Toxicity to freshwater organisms also depends on other cations (e.g. H⁺)
- A greater variance among different soils than reactive soil metal.
- Strong relationships with pH
Functions for critical concentrations

- In soil solution: $f(\text{pH})$
- In soils: $f(\text{pH}, \log(\%\text{SOM}))$
Functions for critical metal concentrations and contents

- in soil solution:
  \[ \log[Ni]_{free(crit)} = -0.64 \text{ pH}_{ss} - 2.59 \]
  \[ \log[Cu]_{free(crit)} = -1.23 \text{ pH}_{ss} - 2.05, \text{ [mg·m}^{-3}] \]

- in soils:
  \[ \log[Ni]_{re(crit)} = -0.19 \text{ pH} + 1.04 \log(\%\text{SOM}) - 3.18 \]
  \[ \log[Cu]_{re(crit)} = 0.02 \text{ pH} + 0.68 \log(\%\text{SOM}) - 4.54, \text{ [mg·kg}^{-1}] \]
  (Lofts et al., 2004)
Methodology:
Metal free ion concentration →
total metal concentration in solution

- Model WHAM VI
- DOC
- pH
- Base cations
- Al, Fe – empirical dependencies on pH
Input data

- Vegetation map (Ecological Atlas of Murmansk Region, 1999)
- Soil map (Fridland, 1988)
- Database of soil properties

- Organic matter and pH in soils
- DOC – dissolved organic carbon
- Heavy metals in soils (Reimann et al., 1998; our experimental data)
- Metal uptake in harvestable parts of vegetation
- Water discharge
- Metal depositions (in the vicinity of smelters)

→ 43 soil-vegetation combinations
Testing applicability of transfer functions

- \( \log_{\text{Ni}}_{\text{HNO}_3} = 0.74\log_{\text{Ni}}_{\text{AR}} + 0.61\log_{\text{OM}} + 0.09\log_{\text{Clay}} - 1.0 \)
- \( \log_{\text{Cu}}_{\text{HNO}_3} = 1.15\log_{\text{Cu}}_{\text{AR}} + 0.023\log_{\text{OM}} - 0.17\log_{\text{Clay}} - 0.33 \)

"Global": (Römkens et al., 2004; De Vries et al., 2005)

Regional:
- \( \log_{\text{Ni}}_{\text{HNO}_3} = 0.95\log_{\text{Ni}}_{\text{AR}} + 0.31\log_{\text{OM}} - 0.84 \)
- \( \log_{\text{Cu}}_{\text{HNO}_3} = 0.92\log_{\text{Cu}}_{\text{AR}} + 0.35\log_{\text{OM}} - 0.62 \)
Functions for dissolved organic carbon (DOC)

Original:

\[
\log(\text{DOC}) = 2.15 + 0.35\log(\text{OM}) - 0.27pH + 1.52\log(s/s)
\]

“Global”: \[
\log(\text{DOC}) = 2.66 + 0.70\log(\text{OM}) - 0.15pH + 1.52\log(s/s)
\]
Correction of water drainage flux for vegetation type

\[ Q_{le} = P - E_i - \ldots \]

\( P \) – precipitation

\( E_i \) – intercept by vegetation

Direct intercept of precipitation is assumed to depend on vegetation type

\[ E_i = f_k P^{n_k} \]

\( f_k, n_k \) – empirical constants

De Vries, 1991
Present risks
Critical contents for Cu and their exedances

Sensitive soils:

(O) tundra podburs under tundra vegetation and under forest tundra birch open woodlands and shrublands, and podzols under forest tundra and forests.
Critical contents for Cu and their exedances, B horizon

Sensitive soils:
(B) tundra podburs under tundra and forest tundra vegetation, peaty and peat gleyic podzols, iron-illuvial podzols
For both Ni and Cu, the most sensitive soil surface organic horizons are widespread across the northern tundra and forest tundra, although Ni critical limits are also low in Khibiny, Lovozero, Chuna-tundra and Monche-tundra upland areas.
Critical contents and their exceedance

- High variability of critical metal contents.
- Critical Ni contents > critical Cu contents.
- Critical metal contents in organic horizons are almost an order of magnitude higher then in mineral horizons.
- Current contents of Cu and Ni in soils in the vicinity of smelters exceed their critical levels. The degree of exceedance in organic layers is higher, while the area of exceedance is lower comparing with mineral horizons.
- Current contents of Cd and Pb are not exceeded.
Future risks
Metal uptake by plants

- Metal concentration in plants
- Biomass and productivity
- Uptake = productivity * concentration

$$0.005-0.023 \text{ g Ni·ha}^{-1}·\text{y}^{-1}, \ 0.008-0.069 \text{ g Cu·ha}^{-1}·\text{y}^{-1}$$
Sensitive soils:

(O) tundra podburs under tundra vegetation and under birch open woodlands and shrublands, podburs under mountain coniferous forests, some podzols (north, east)
Critical loads for Cu, B-horizon

Sensitive soils:
(B) Peaty and peat gleyic podzols
Critical loads for Ni, O-horizon

Sensitive soils:

(O) Plain and mountain tundra vegetation and forest tundra birch open woodlands and shrublands on tundra podburs, scarce mountain spruce and pine forests on podburs and some podzols (north, east)
Critical concentrations

Critical concentrations for copper (Cu) in water are shown in this graph. The x-axis represents pH levels ranging from 3.0 to 6.0, while the y-axis shows the critical concentration of Cu in μg/L, ranging from 0 to 60. The graph plots the critical concentrations (Mcrit Cu) against pH, with data points indicating a decreasing trend as pH increases.
The leaching metal fluxes determine critical loads for soils of the Kola Peninsula.

Contribution of metal uptake is much smaller.

Organic horizons are characterized by higher critical loads for metals comparing with mineral horizons, specifically for Cu and Pb.

Critical loads for metals are notably exceeded in vicinity of the smelters, specifically for Cu (>10 times in organic horizons and >100 times in mineral horizons).
Conclusions

- Both, the current and potential threat of heavy metal impact on soil and ecosystem functioning is high.
- Critical metal contents and loads notably depend on basic soil properties.
- The negative impact of metals is observed in the vicinity of smelters only.
Problems
to be solved
However …

- **Heavy metals:** the degree of exceedance is high, the exceedance area seems to be less than zone of visible vegetation damage.

- **Sulfur:** the degree of exceedance is relatively low, the exceedance area is larger than zone of visible vegetation damage.

- The mutual impact of heavy metals and sulfur as well as severe climatic conditions aggravate ecological situation in the region.
**Problems**

- Despite comprehensive investigations quantitative estimation of possible changes in forest ecosystems in this area is still far from completion.

- There are no predictions of combined effects of sulfur deposition and heavy metals in the area.

- The quantitative assessment of combined effects though suggested by pioneer investigations is not applied at regional and European scales and is typically not considered by environmental managers.

- Variability. Air pollution is not the only (the major ?) factor… The necessity to account for natural factors (climate, nutrients,...)
Methods: linear approach

Process oriented modelling

\[ IMPACT = f(S_{SS}, N_{SS}, HM_{SS}, ClStr, ...) \]

\[ IMPACT = \frac{\partial f}{\partial S_{SS}} S_{SS} + \frac{\partial f}{\partial N_{SS}} N_{SS} + \frac{\partial f}{\partial HM_{SS}} HM_{SS} + \frac{\partial f}{\partial ClStr} ClStr + ... \]

\[ growth = \frac{1}{1 + \exp(-0.005 \cdot \sum T_{>5} + 5)} \] 

(Kauppi & Posch, 1988)

\[ ClStr = \frac{1}{growth} - 1, \quad 0 < ClStr; \quad ClStr_{crit} = 1 \]

\[ S_{crit_{Mid-Europe}} \cdot \frac{\partial f}{\partial S} \cdot S_{crit_{Mid-Europe}} = \frac{\partial f}{\partial S} \cdot S_{crit_{Kola}} + \frac{\partial f}{\partial ClStr} \cdot 0.4 = 1 \]

\[ \frac{\partial f}{\partial S} = \frac{1}{S_{crit_{Mid-Europe}}}, \quad \frac{\partial f}{\partial ClStr} = 1 \]

\[ S_{crit_{Kola}} = 0.6 S_{crit_{Mid-Europe}}, \quad HM_{crit_{Kola}} = 0.6 HM_{crit_{Mid-Europe}} \]
Methods: PAF - SSD

- Application of concept based on notions of species sensitivity distribution and potentially affected fraction

- Independence of factors:
  \[ PAF_{A+B+\ldots} = 1 - (1-PAF_A)*(1-PAF_B)*\ldots \]
Thank you for attention!

The work was supported by NWO, Russian Foundation for Basic Research and EC FP6