# Trace elements in nature – positive and negative sides

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# Trace elements essential to plants

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | | | | | | | | | | | | | | | | He |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| Fr | Ra | Ac | | | | | | | | | | | | | | | |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |

# Essential trace elements in man

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | | | | | | | | | | | | | | | | | He |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| Fr | Ra | Ac | | | | | | | | | | | | | | | |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |

## The elements most commonly discussed as "Toxic metals"

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | | | | | | | | | | | | | | | | He |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| Fr | Ra | Ac | | | | | | | | | | | | | | | |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |

Discussions of trace elements in the environment most frequently deal with anthropogenic pollution and possible effects on natural ecosystems and human health.

Worldwide however **trace element imbalances in the natural environment** may be much more important in human nutrition than anthropogenic pollution.

Issues related to the latter problems are often denoted Geomedicine or Medical geology

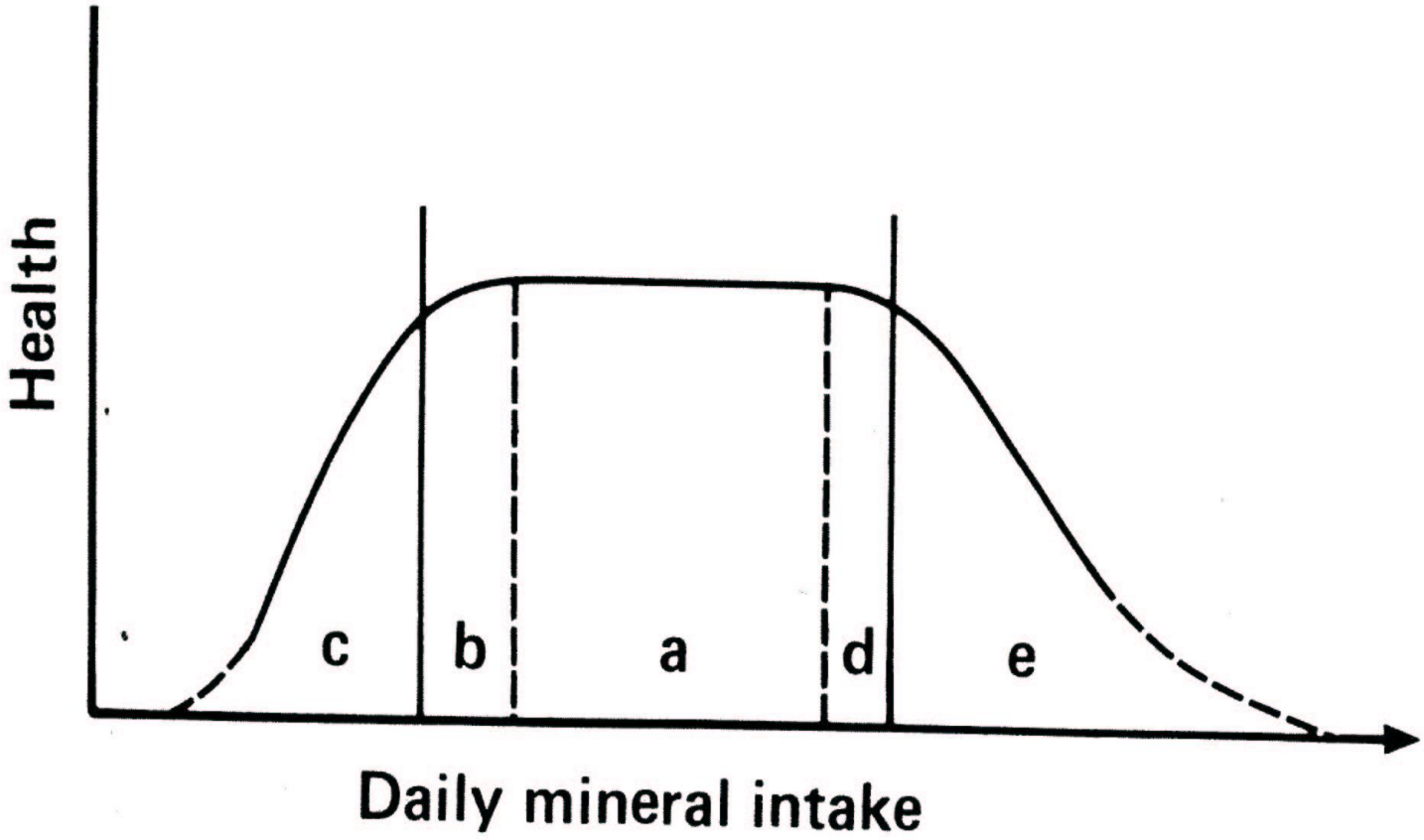



FIGURE 2. The dependence of health on adequate intakes of trace elements. (a) Safe and adequate intake; (b) marginally deficient intake; (c) deficiency; (d) marginal overexposure, may have pharmacological effects; (e) excess.

# Essential trace elements

| Element | Human serum, normal level μg/L | Crustal mean μg/g | Human serum/ crustal mean |
|---|---|---|---|
| Mn | 0.6 | 950 | 0.0006 |
| Cr | 0.2 | 80 | 0.0025 |
| Co | 0.3 | 20 | 0.015 |
| Fe | 1100 | 41000 | 0.027 |
| Mo | 2 | 1.5 | 1.3 |
| Zn | 930 | 75 | 12 |
| Cu | 1100 | 50 | 22 |
| I | 60 | 0.14 | 430 |
| Se | 100 | 0.05 | 2000 |

A. Excess trace elements

- Arsenic poisoning (natural) from drinking water in Bangladesh/India

- Excessive fluoride intake in many areas of the world, leading to dental fluorosis

B. Trace element deficiency

- **Iodine** deficiency disorders, affecting more than 25% of the world population

- **Zinc** deficiency problems: One third of the world population affected

- **Selenium** deficiency problems
  a. General Se deficiency in many countries
  b. Endemic Se deficiency, e.g. Keshan disease in China

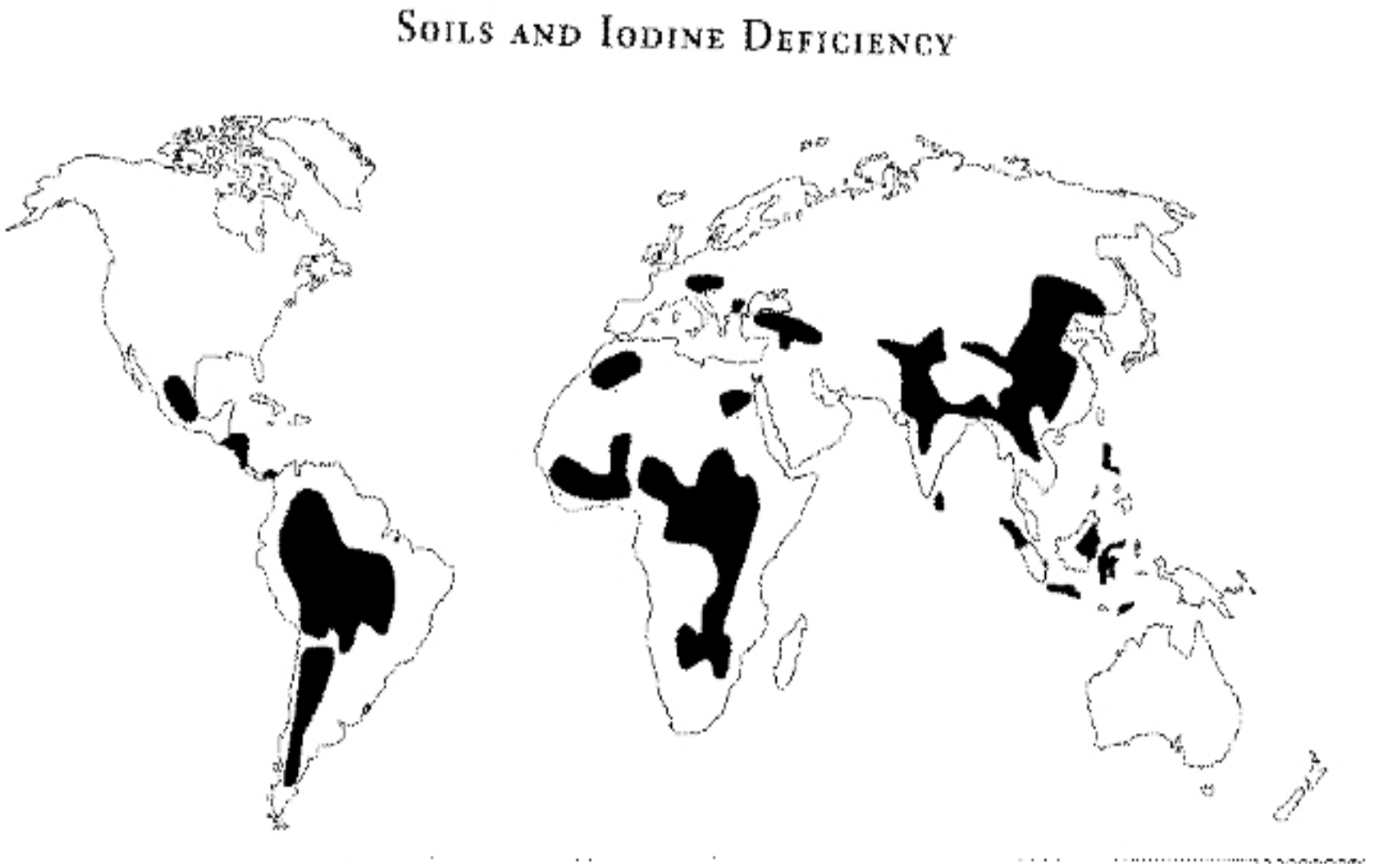
# Iodine Deficiency Disorders (IDD):

C. Dissanayake, Science 339, 5 August 2005:

”Insufficient intake of iodine is the world´s most common cause of mental retardation and brain damage*

- with 1.6 billion people at risk
- 50 million children already affected
- 100,000 more adding to their ranks every year”

**Iodine deficiency during pre-natal development and the first year of life can result in **endemic creatinism**, a disease causing stunted growth and general development, along with brain damage*




Global distribution of Iodine Deficiency Disorders

(R. Fuge, in O. Selinus (ed.): Medical Geology)

Atmospheric supply of trace elements in Norway:

Geographical distribution

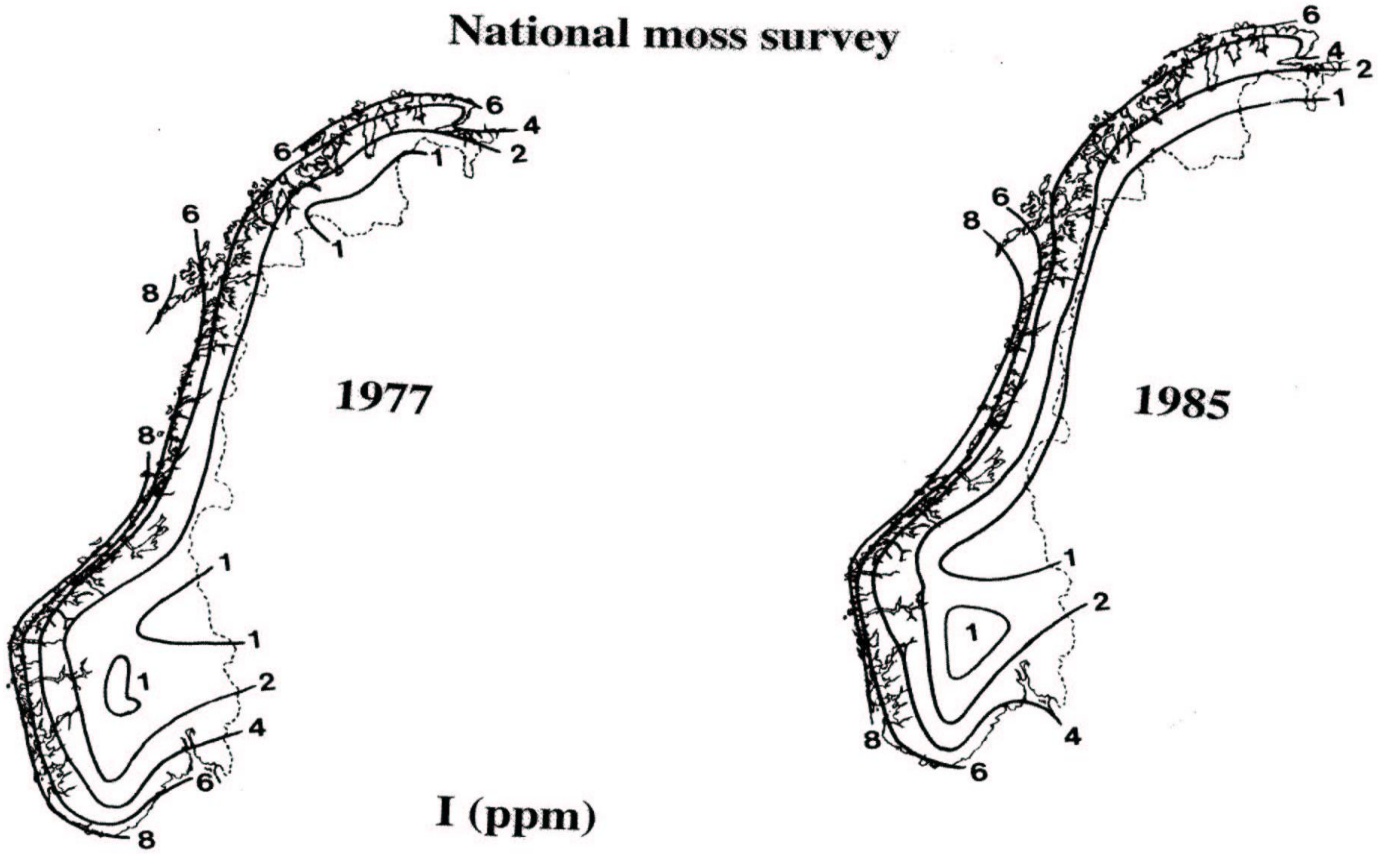
A. Samples of terrestrial moss

B. Surface layer of natural soils

# Moss biomonitor

## *Hylocomium splendens*


Moss annual segments


National moss survey
1977
1985
I (ppm)

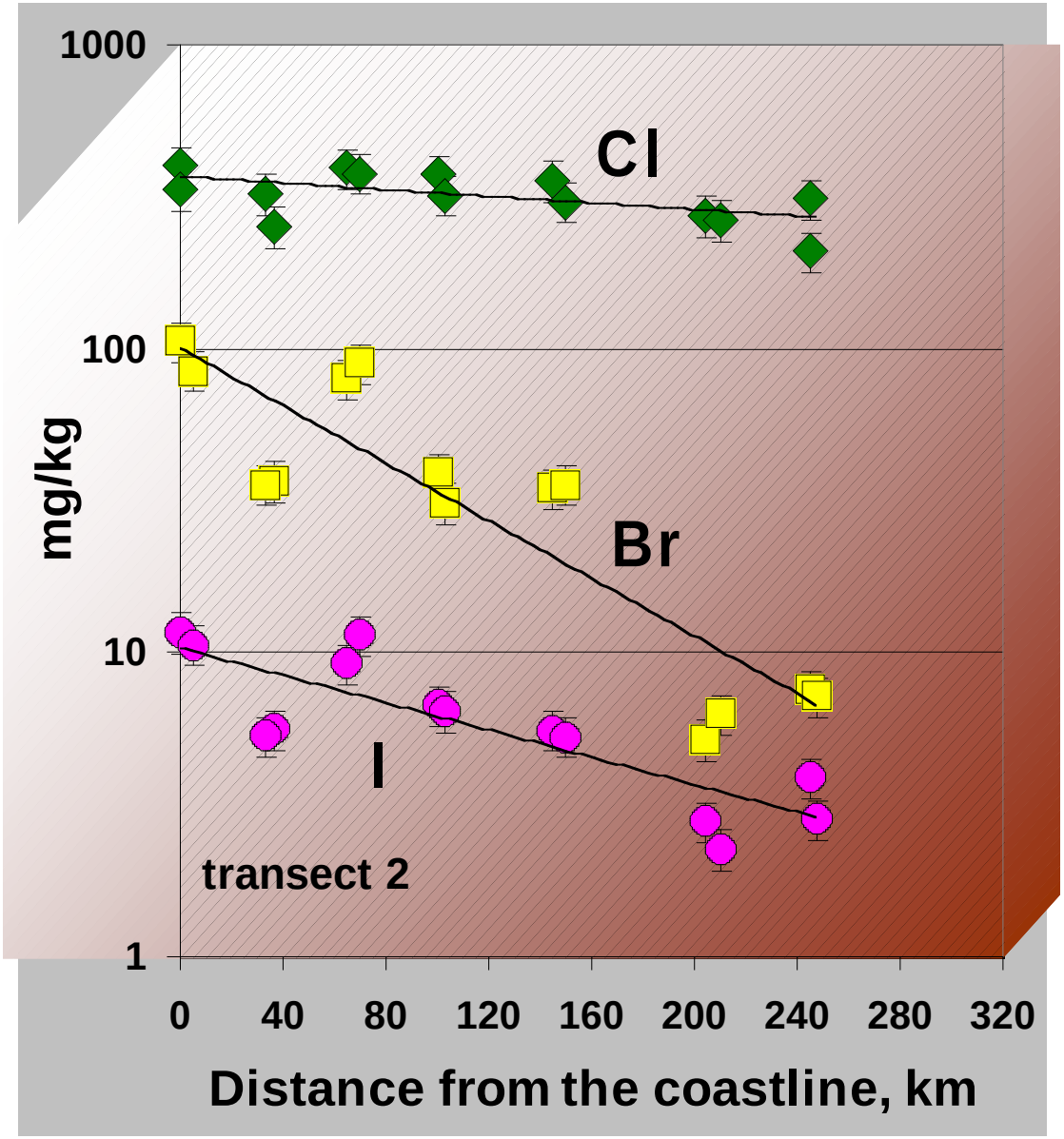
# Most natural soils in Norway are podzols:

# Cl, Br, and I in natural surface soils

*J. Låg and E. Steinnes, Geoderma 16 (1976) 317-325*

Regional differences in iodine concentrations (ppm):

| | |
|---|---|
| <u>Central Norway</u> | |
| Coastal areas: | 15.4 |
| Areas 150 km inland: | 5.8 |
| <u>Southeast Norway</u> | |
| Areas near Oslo fjord: | 7.2 |
| Upper valleys: | 3.0 |




**Halogens in surface soil in northern Norway**
**(Frontasyeva and Steinnes, 2005)**

Halogen concentrations in the ocean: Cl/I = 300 000

Cl - 19400 mg/L
Br - 300 mg/L
I - 0.06 mg/L

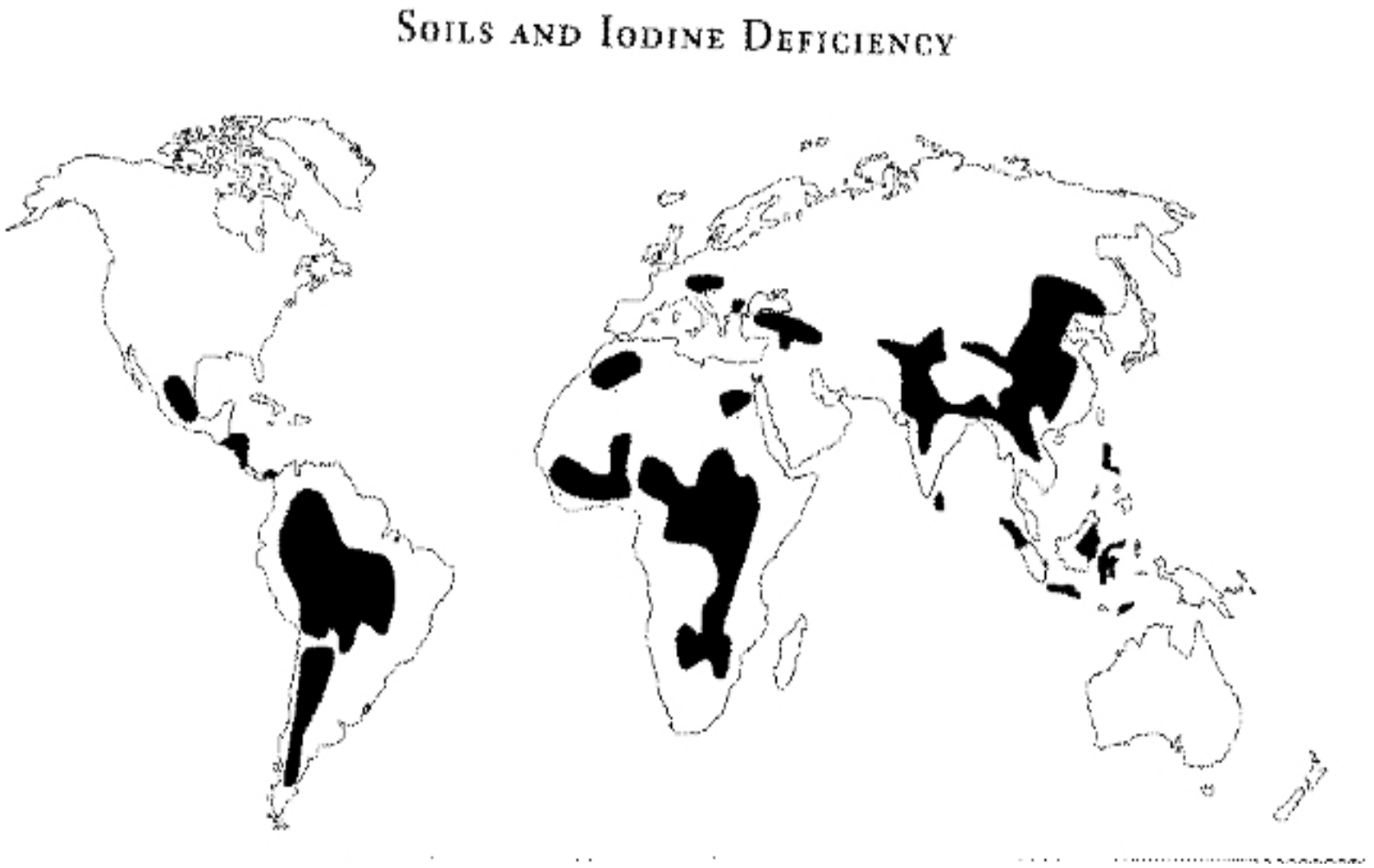
Why is iodine so enriched in surface soil relative to the other halogens?

Iodine is strongly concentrated in marine organisms such as algae

During their metabolic processes the organisms release iodine in the form of methyl iodide ($CH_3I$)

Methyl iodide is volatile and insoluble in water, and therefore released to the atmosphere

Iodine thus becomes strongly enriched on marine aerosols, carrying halogens onto land surfaces



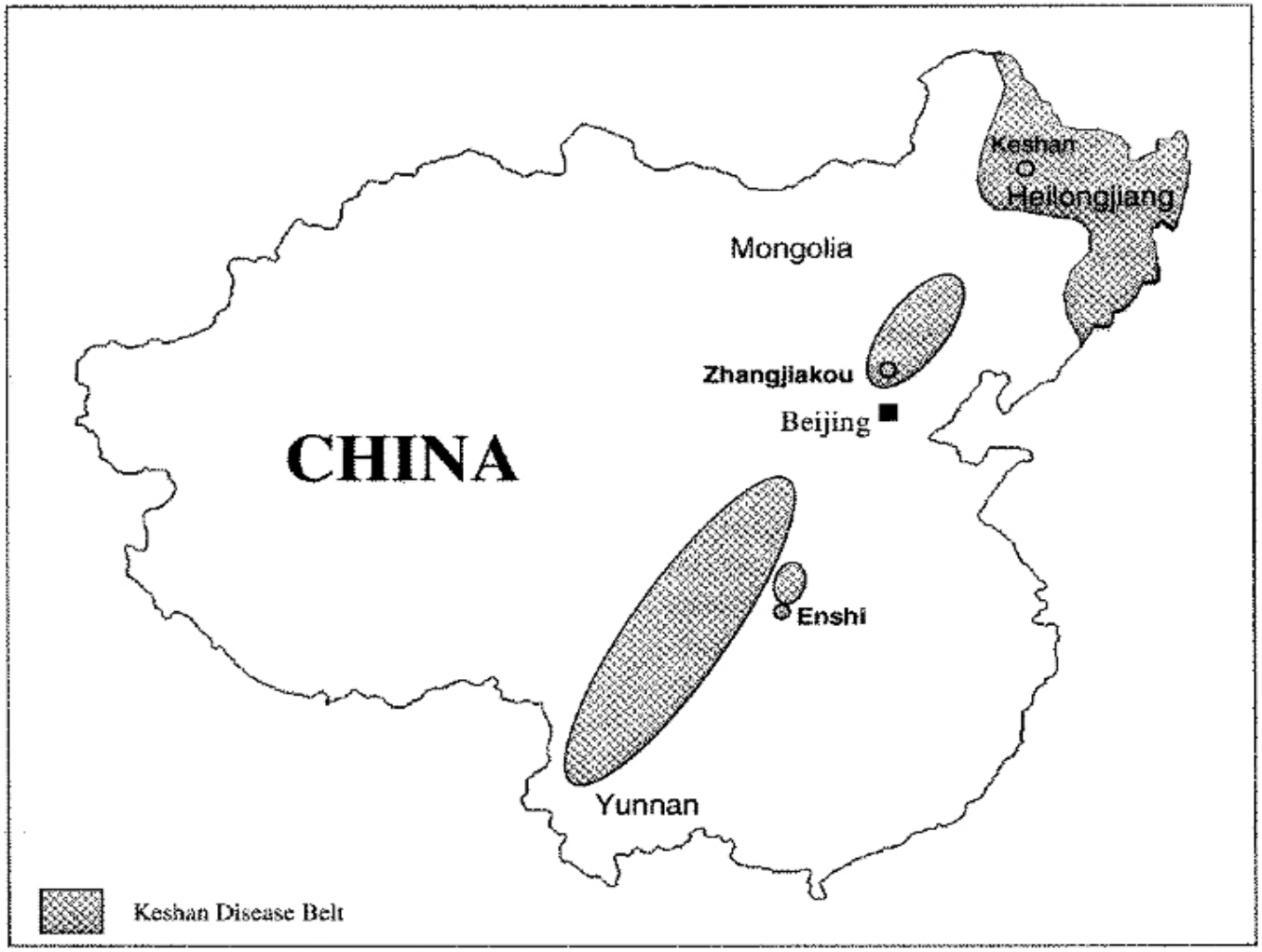

Global distribution of Iodine Deficiency Disorders

(R. Fuge, in O. Selinus (ed.): Medical Geology)

# Selenium deficiency:

## Distribution of the incidence of Keshan Disease in China

(After J. Tan (1989)



Selenium concentrations in human blood from around the world

| Country | Se (mg/L) | Year |
|---|---|---|
| Normal level | 0.2 | |
| Canada (Ontario) | 0.18 | 1967 |
| U.S.A. | 0.16-0.26 | 1968 |
| Guatemala | 0.23 | 1967 |
| Venezuela (high soil Se) | 0.35-0.81 | 1970 |
| China (high soil Se, disease) | 1.3-7.5 | 1983 |
| China (high soil Se, no disease) | 0.44 | 1983 |
| China (low soil Se, disease) | 0.021 | 1983 |
| China (low soil Se, no disease) | 0.027 | 1983 |
| New Zealand | 0.059-0.083 | 1979 |
| Finland | 0.056-0.083 | 1977 |

## ”Large-scale selenium experiment” in Finland

Background:

High incidence of cardiovascular disease in the Finnish population around 1970

Observations:

- Finnish agricultural crops were distinctly poorer in Se than comparable products in other European countries
- Epidemiological studies indicated that low Se intake correlated positively with increased risk of cardiovascular disease

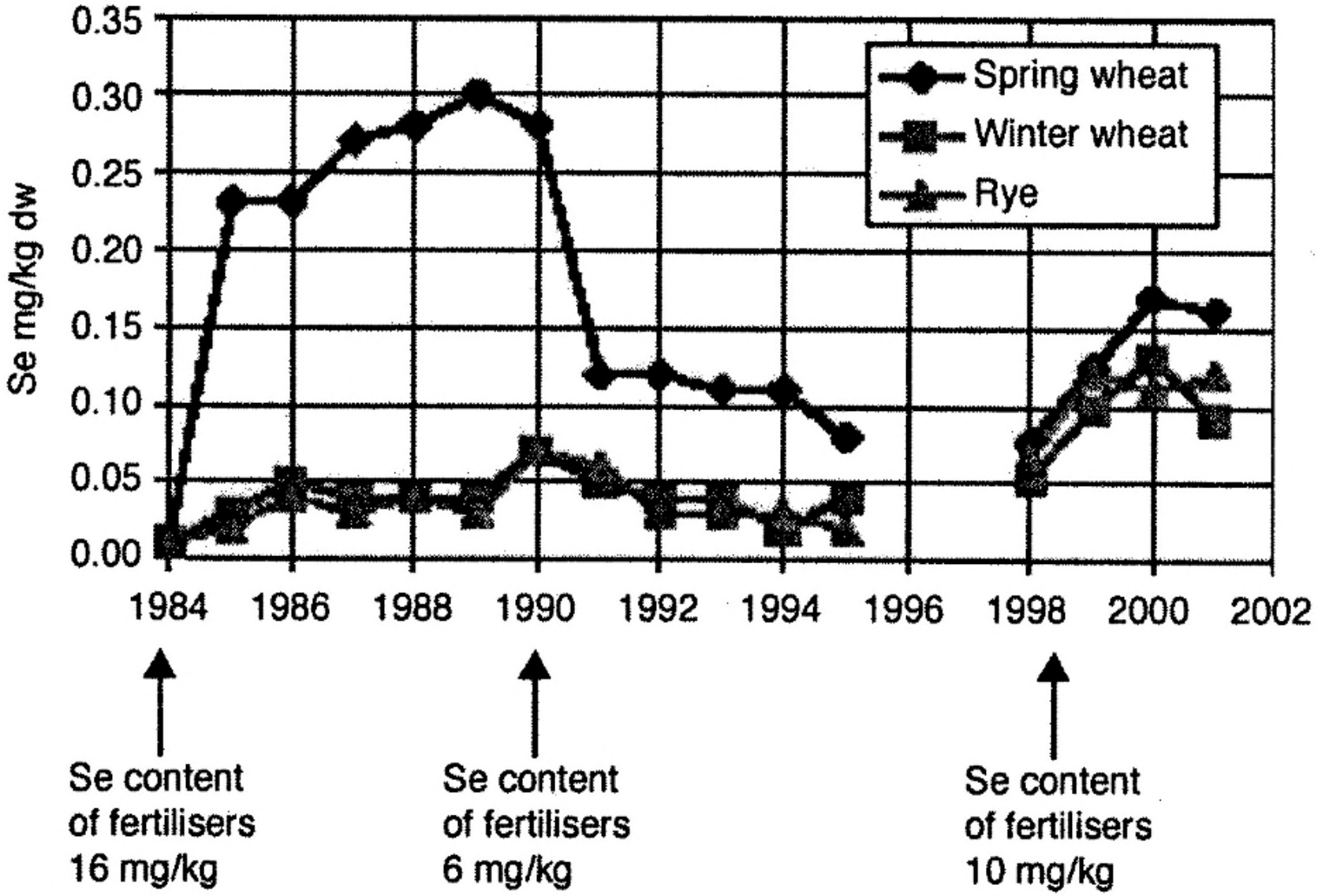
Action:

Addition of selenium to all multinutrient fertilizers

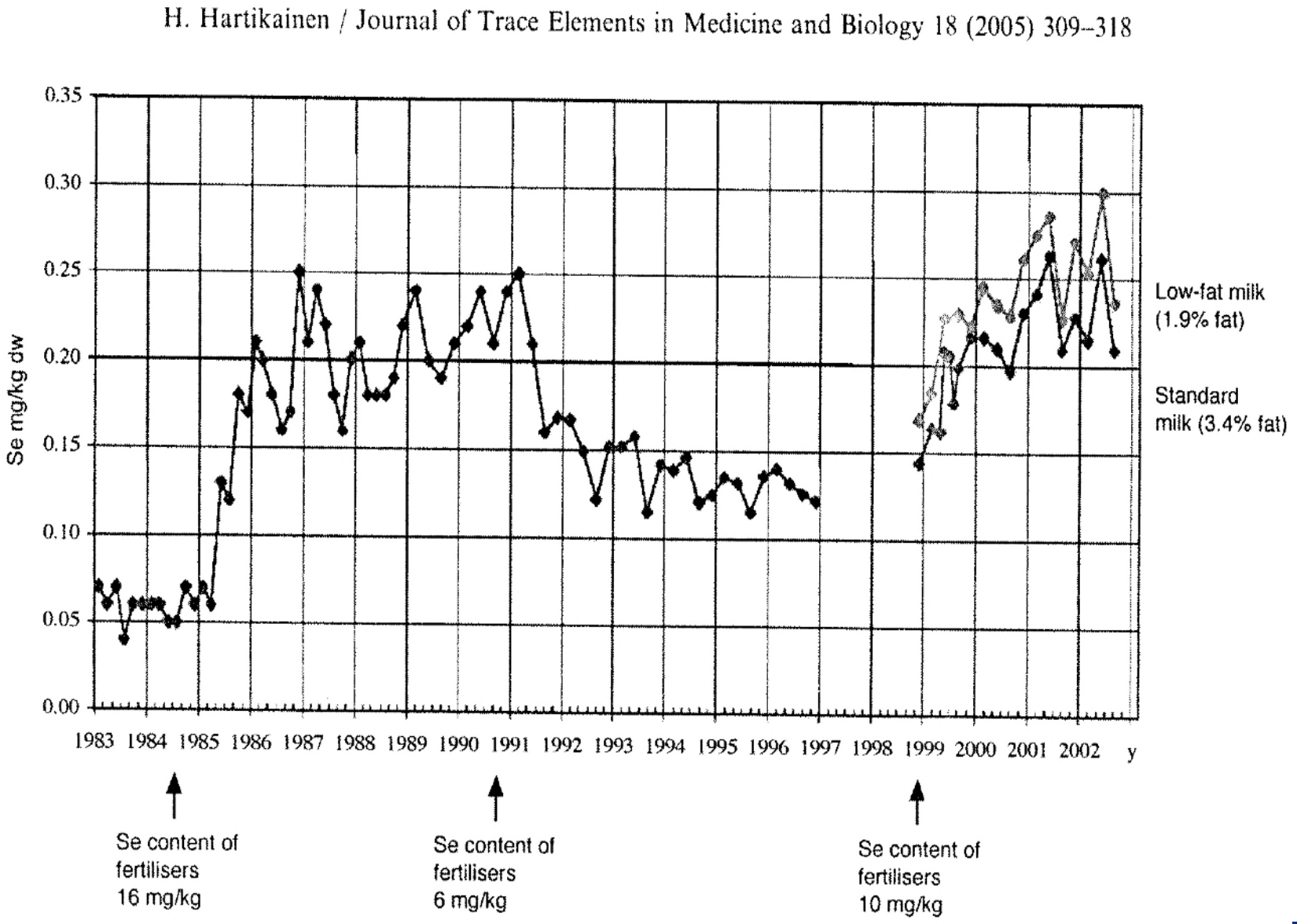
(came into use in 1985)

## Se content in cereals grown in Finland

(H. Hartikainen, J. Trace Elements in Medicine and Biology 18 (2005) 309-318)



# Selenium in milk in Finland 1983-2002



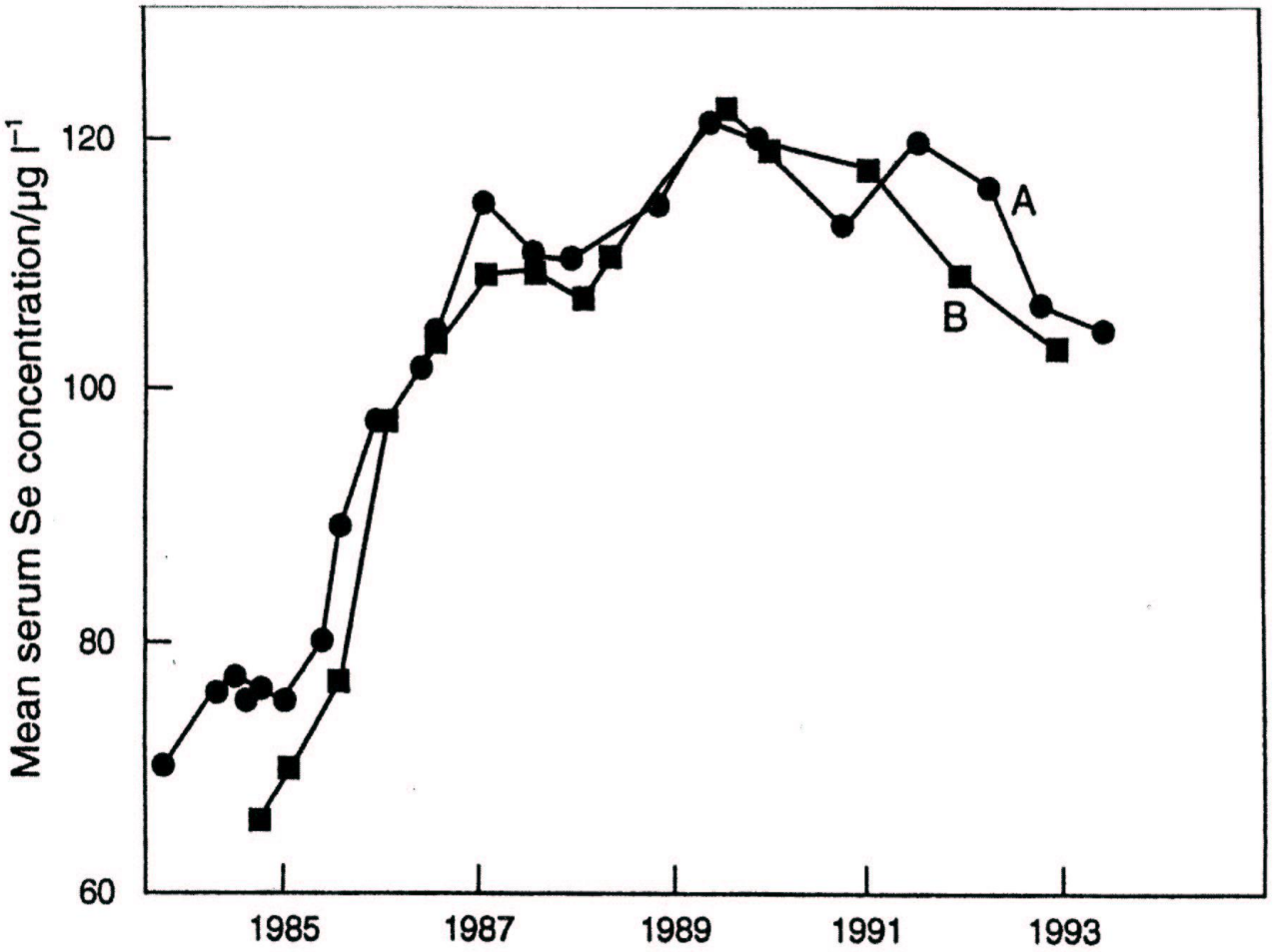
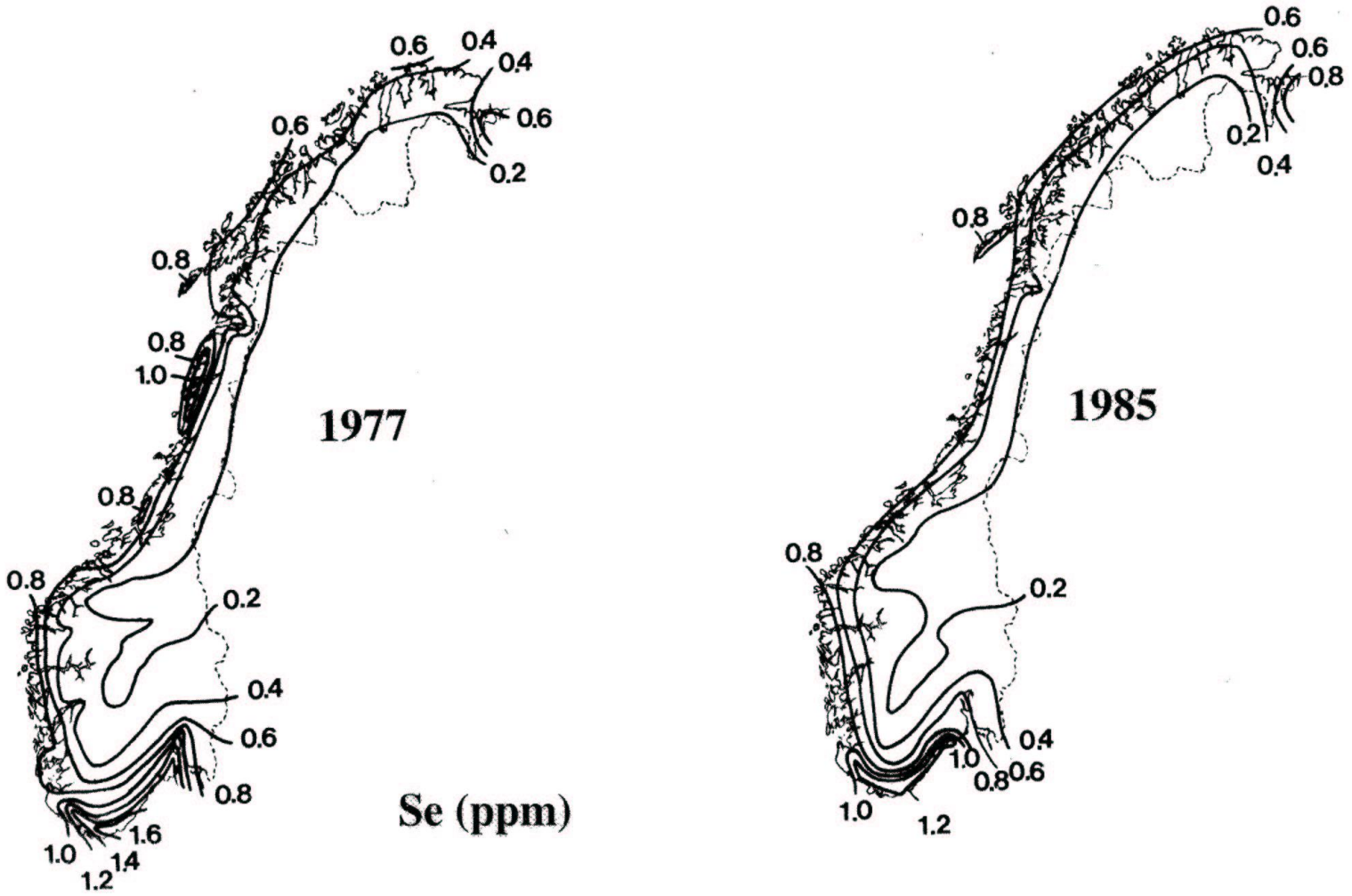
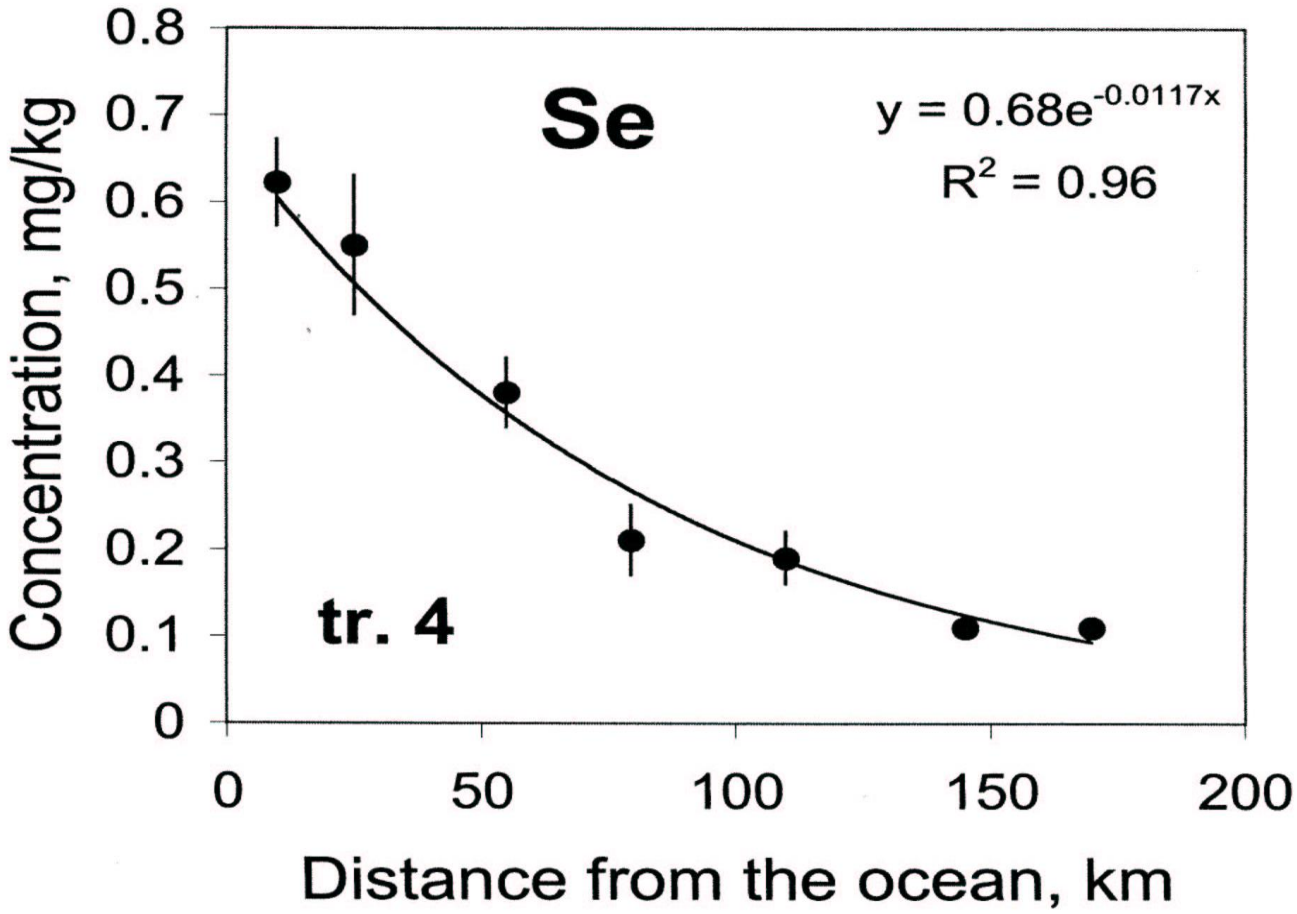



**Fig. 2** Mean serum Se concentrations of A; healthy urban (Helsinki) and B, rural (Leppävirta) people in Finland between 1985 and 1993. Se supplementation was started in 1985, and the amount was reduced in 1991.

# National moss survey






**Atmospheric deposition of selenium in western Norway as a function of distance from the ocean, as reflected by moss analysis**

# Most natural soils in Norway are podzols:

*J. Låg and E. Steinnes, Ambio 3 (1974) 237-238:*

Selenium concentrations in natural surface soils are more than 5 times higher in coastal regions of Norway than in some areas protected from marine influence by mountain ranges (0.82 vs 0.15 ppm)

This indicates that the marine ecosystem is a source of Se in the soil.

Selenium concentration in ocean water is only 0.1 µg $L^{-1}$!

- but Se is strongly concentrated from the water by marine organisms

- and liberated in the form of $(CH_3)_2Se$ and other volatile and water-insoluble selenium compounds

# NILU bulk deposition sampler

(Norwegian institute for air research)

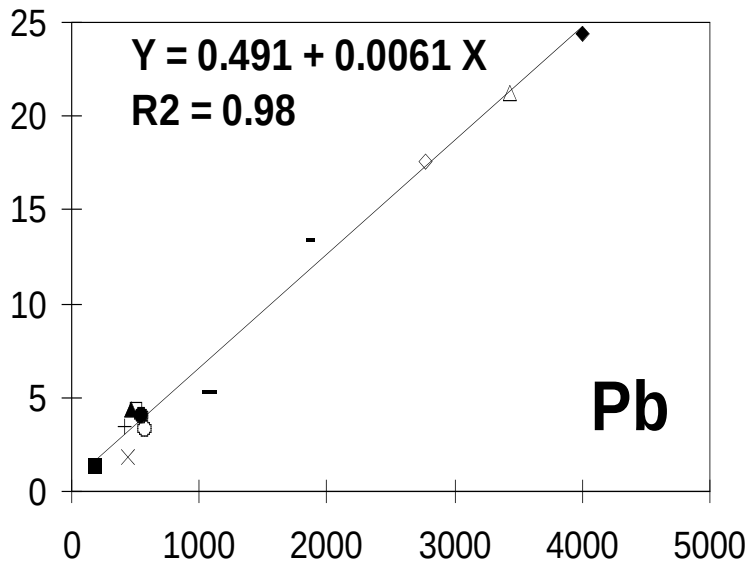
# Moss biomonitor

## *Hylocomium splendens*

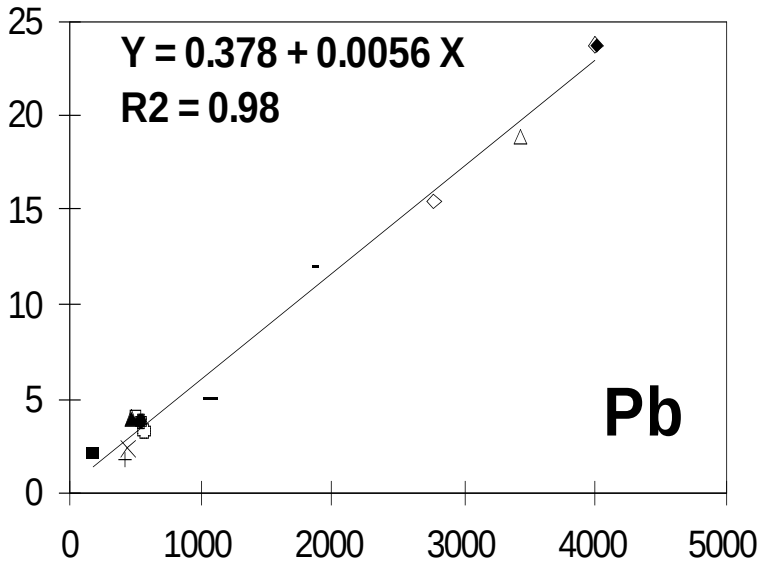

Moss annual segments

Concentrations of Pb in *Hylocomium splendens* and *Pleurozium schreberi* (µg $g^{-1}$) versus atmospheric bulk deposition (µg $m^{-2}$)

H. Sp.




Pl. Sch.

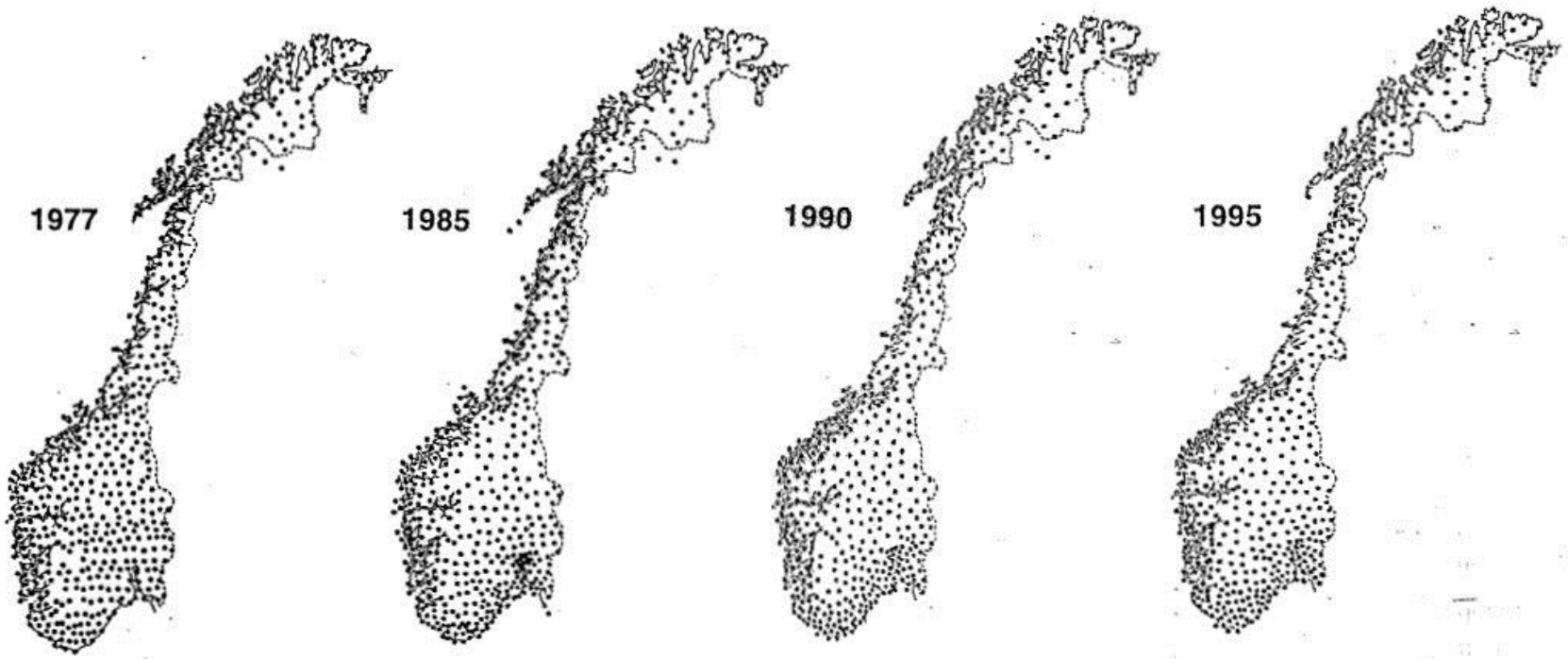


# Metal deposition surveys in Norway:

**Ca. 500 sites**

**Hylocomium splendens**

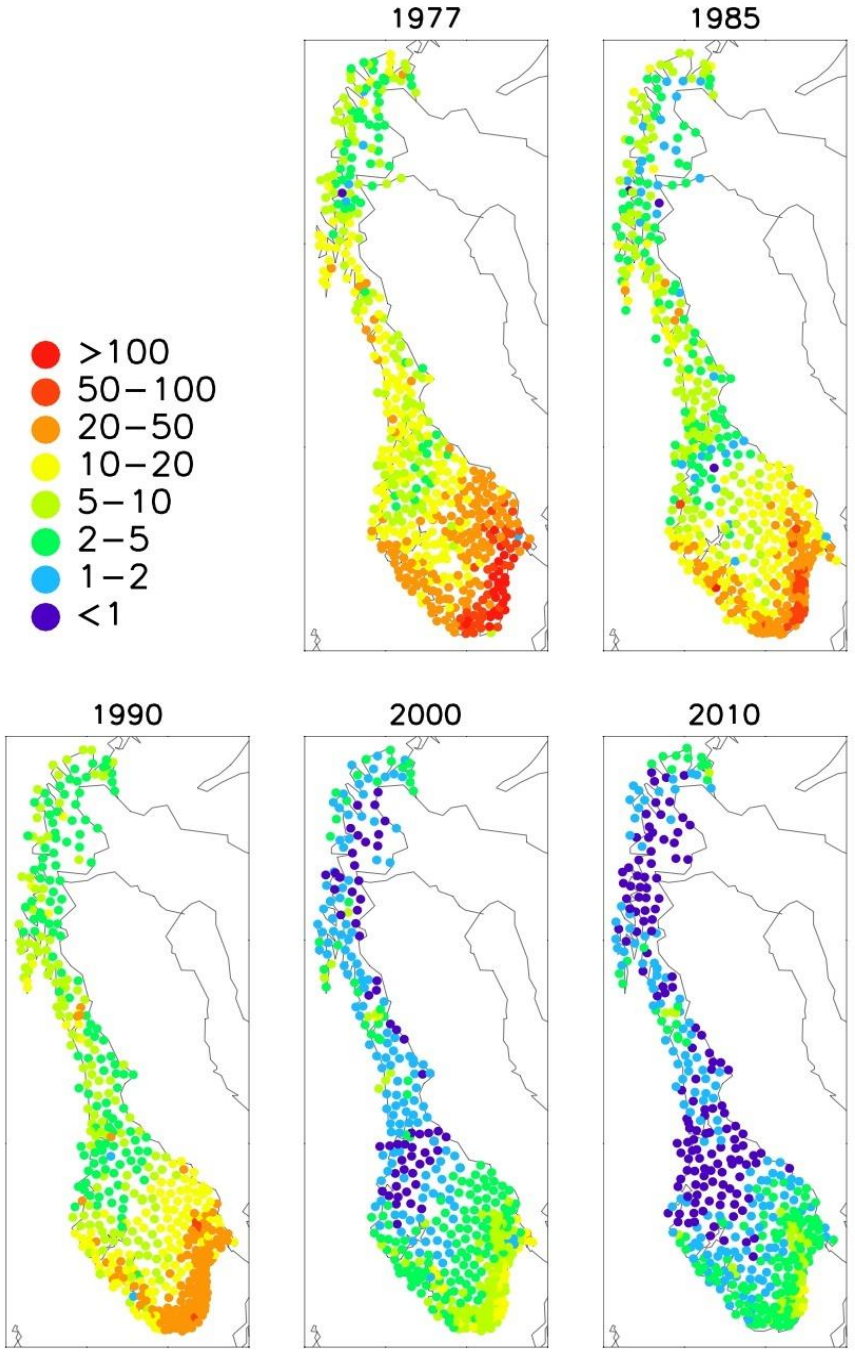
**1977, 1985, 1990, 1995, 2000, 2005, 2010**




**Heavy metal deposition surveys in Norway based on moss analysis: Sampling network**

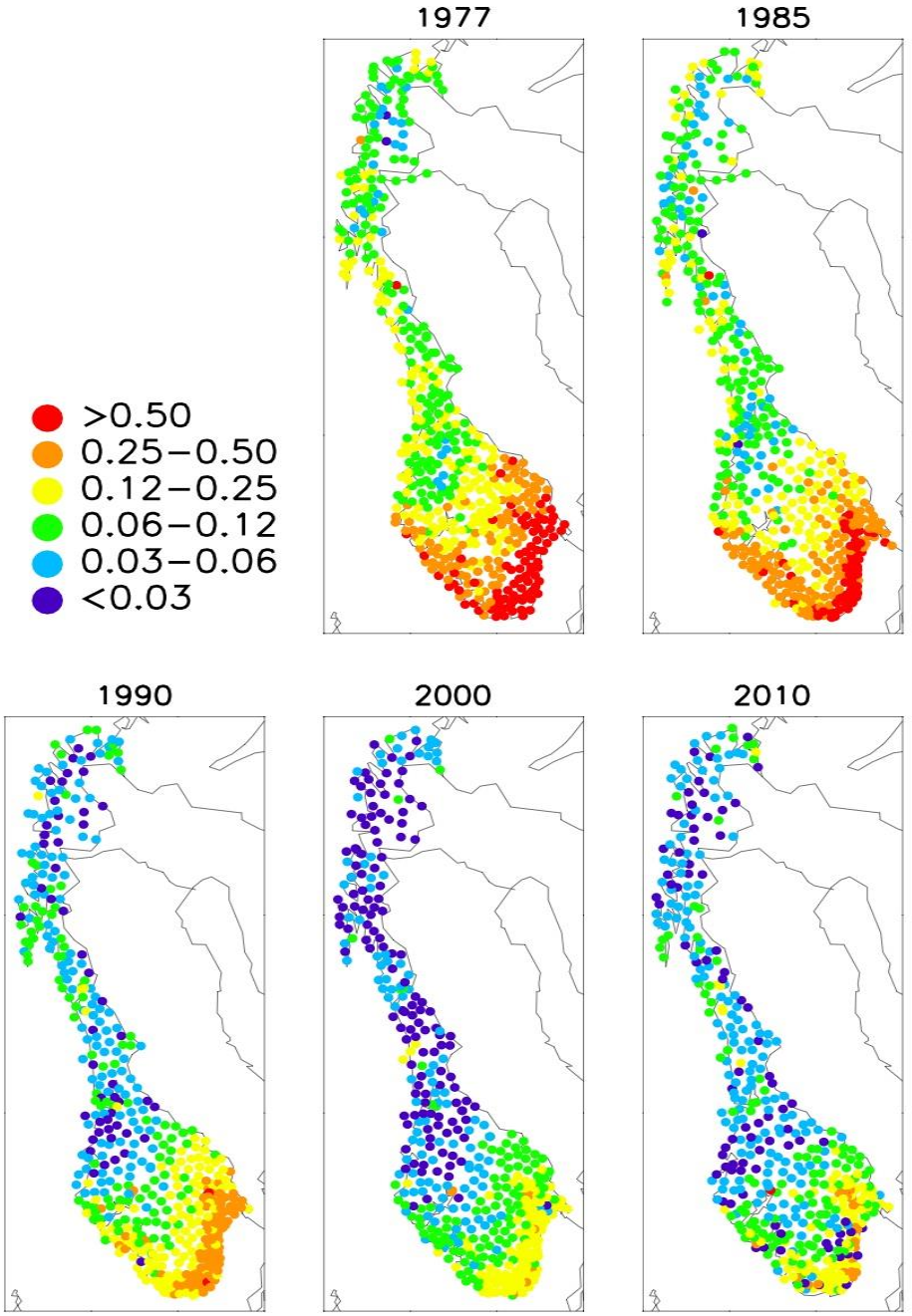
**Pb** in moss in Norway ($\mu g^{-1}$):

Temporal trends 1977-2010



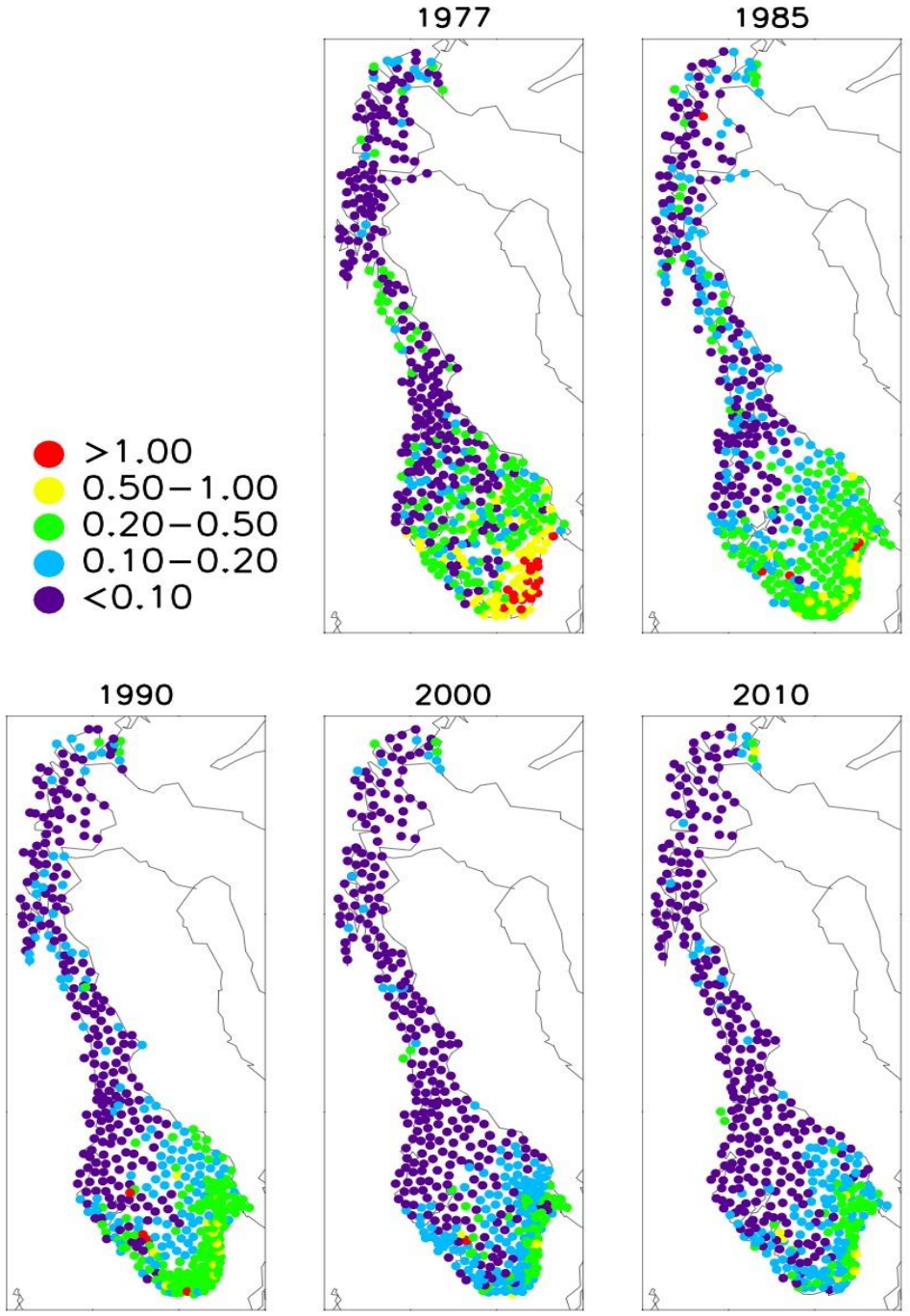
**Sb** in moss in Norway ($\mu g^{-1}$):

Temporal trends 1977-2010



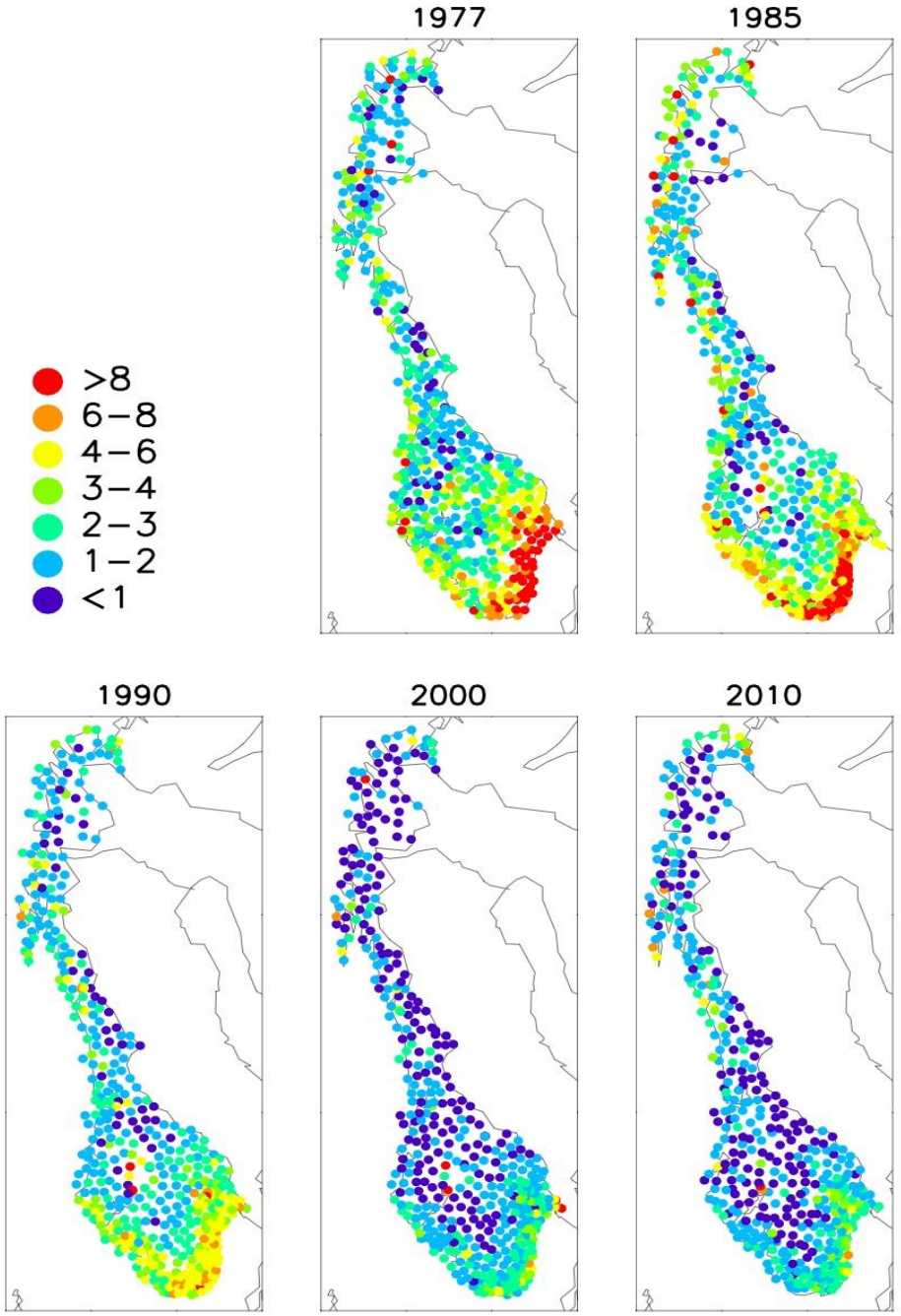
**Cd** in moss in Norway ($\mu g^{-1}$):

Temporal trends 1977-2010



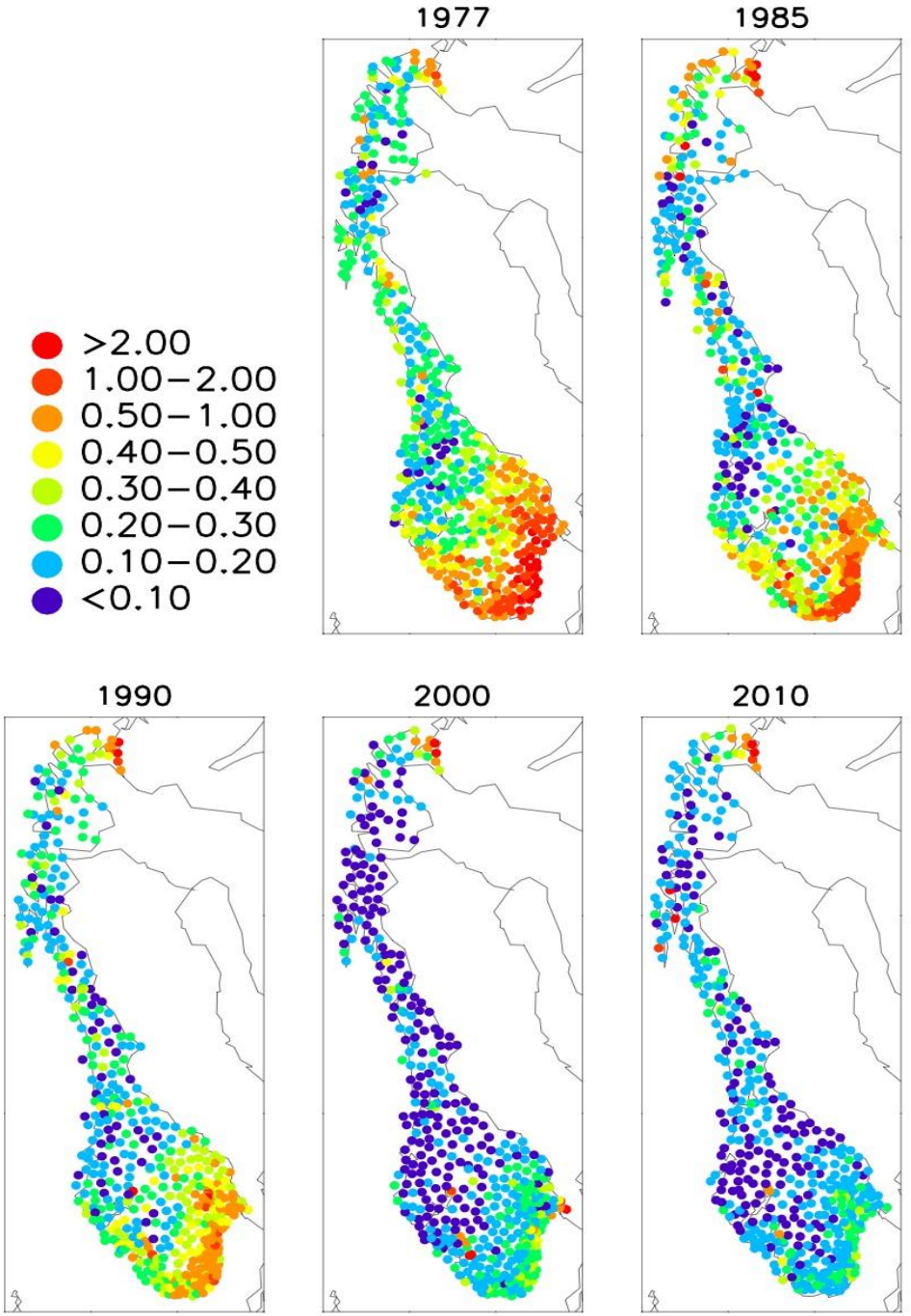
**V** in moss in Norway ($\mu g^{-1}$):

Temporal trends 1977-2010



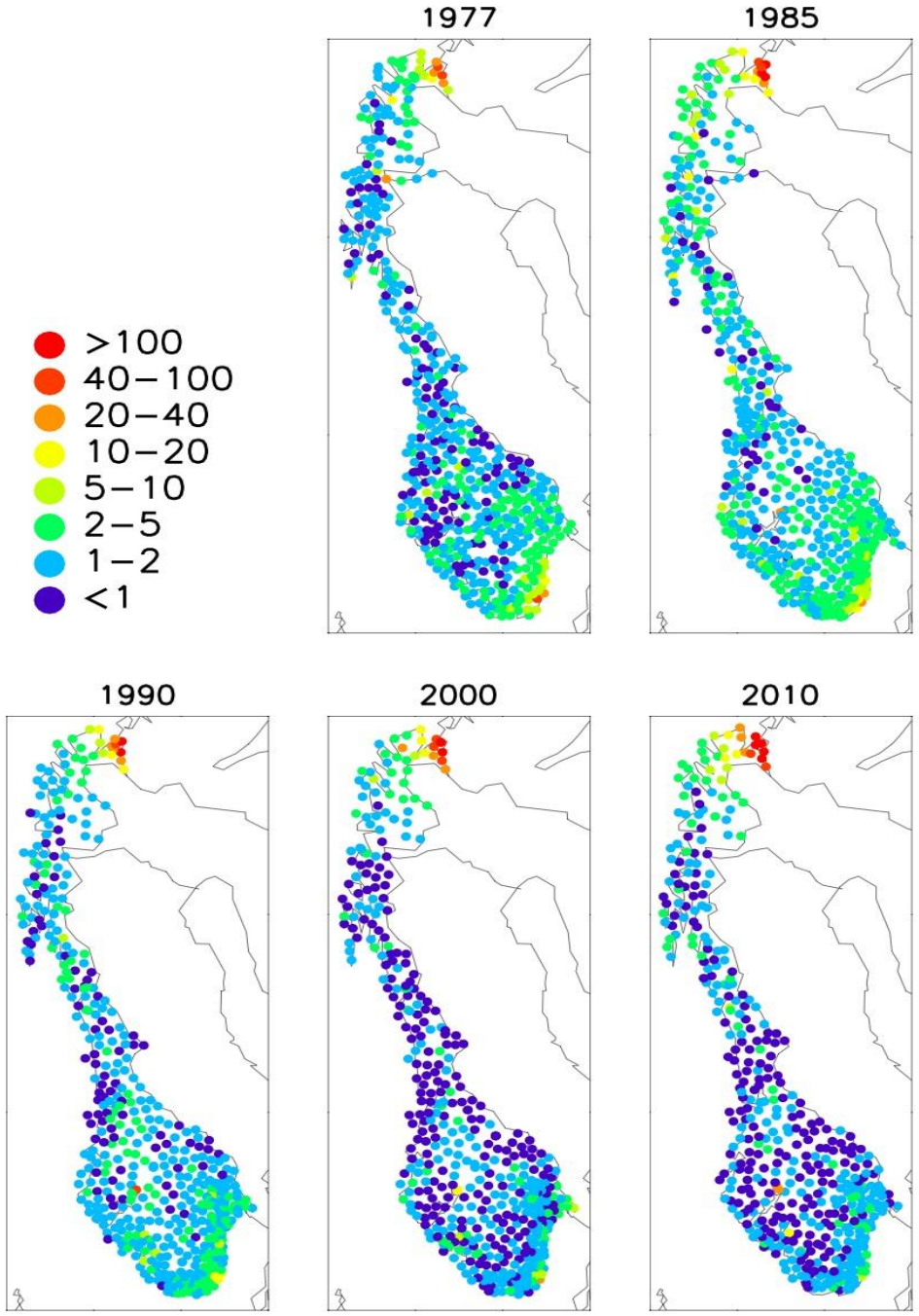
**As** in moss in Norway ($\mu g^{-1}$):

Temporal trends 1977-2010



**Ni** in moss in Norway (µg$^{-1}$):

Temporal trends 1977-2010

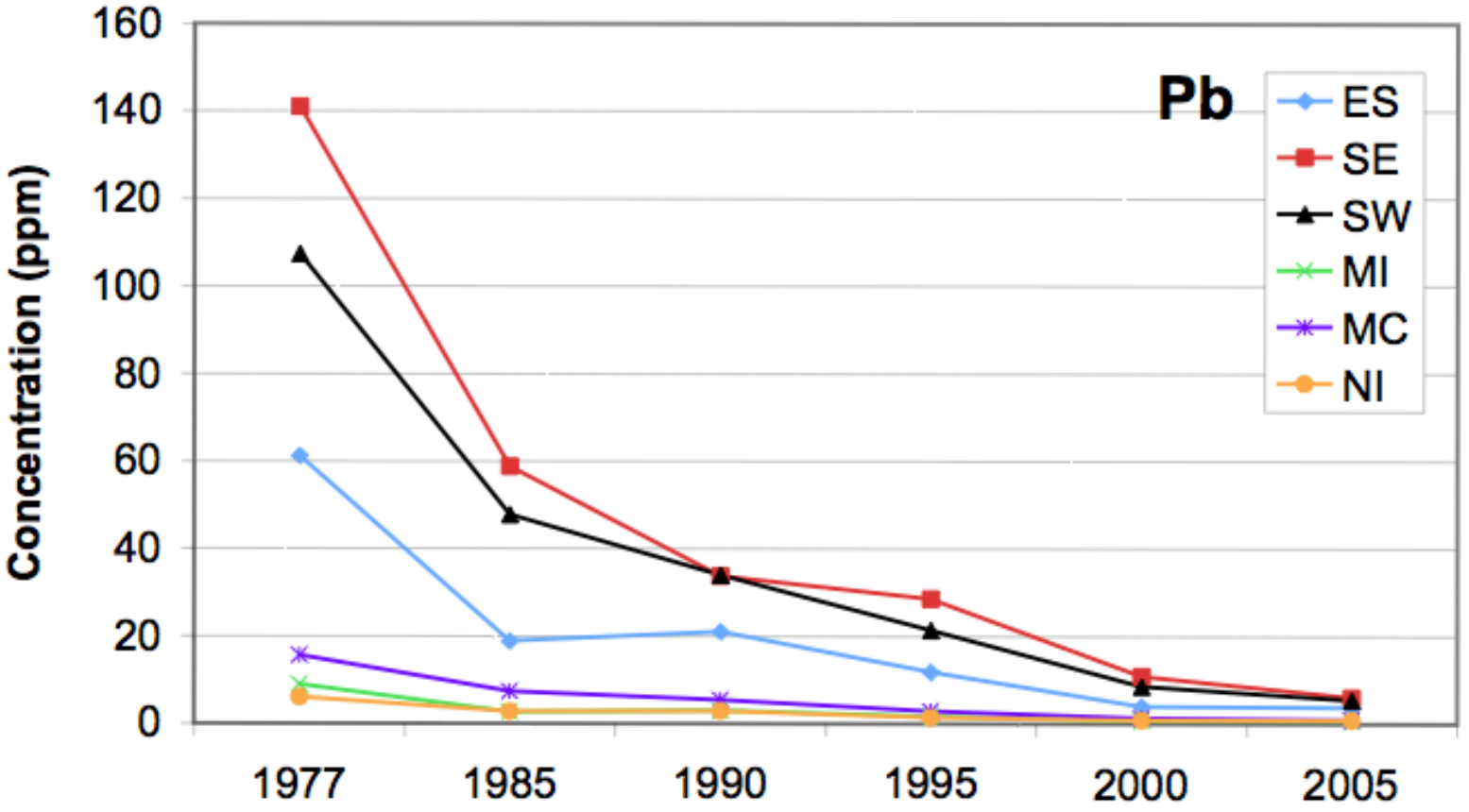


# Time trends of metals in moss in six selected regions of Norway


- Ten sites in each region
- Calculation of median values for each sampling year

- ES: Eastern Norway, south
- **SW: Southernmost Norway, west**
- SE: Southernmost Norway, east
- MI: Middle Norway, inland
- MC: Middle Norway, coast
- NI: Northern Norway, inland

# Temporal trends of lead in moss in different regions of Norway




- ES: Eastern Norway, south
- **SW: Southernmost Norway, west**
- SE: Southernmost Norway, east
- MI: Middle Norway, inland
- MC: Middle Norway, coast
- NI: Northern Norway, inland

Conclusions from the 2010 nationwide moss survey in Norway:

- Most metals of key interest are still declining. The current Pb deposition in the south is only about 5% of the 1977 level.

- Elements previously shown to be derived mainly from long range atmospheric transport are still supplied by this way.

- In the far north-east Russian smelters are supplying high amounts of Ni and Cu to Norwegian territory.

**Characterizing atmospheric deposition of metals around major industries in Norway (2000 - 2005 - 2010)**

Purpose:

Mapping of local deposition of metals from industries, mostly aluminium and iron alloy manufacturing plants situated within or adjacent to densely built-up areas - and comparing with data from previous surveys

Extent:

Sixteen industries distributed among 13 towns

Sampling:

Five sites around each enterprise

Elements:

59 elements determined by ICP-MS

# Most natural soils in Norway are podzols:

# Heavy metal concentrations in natural surface soil: 1977 sampling (μg/g)



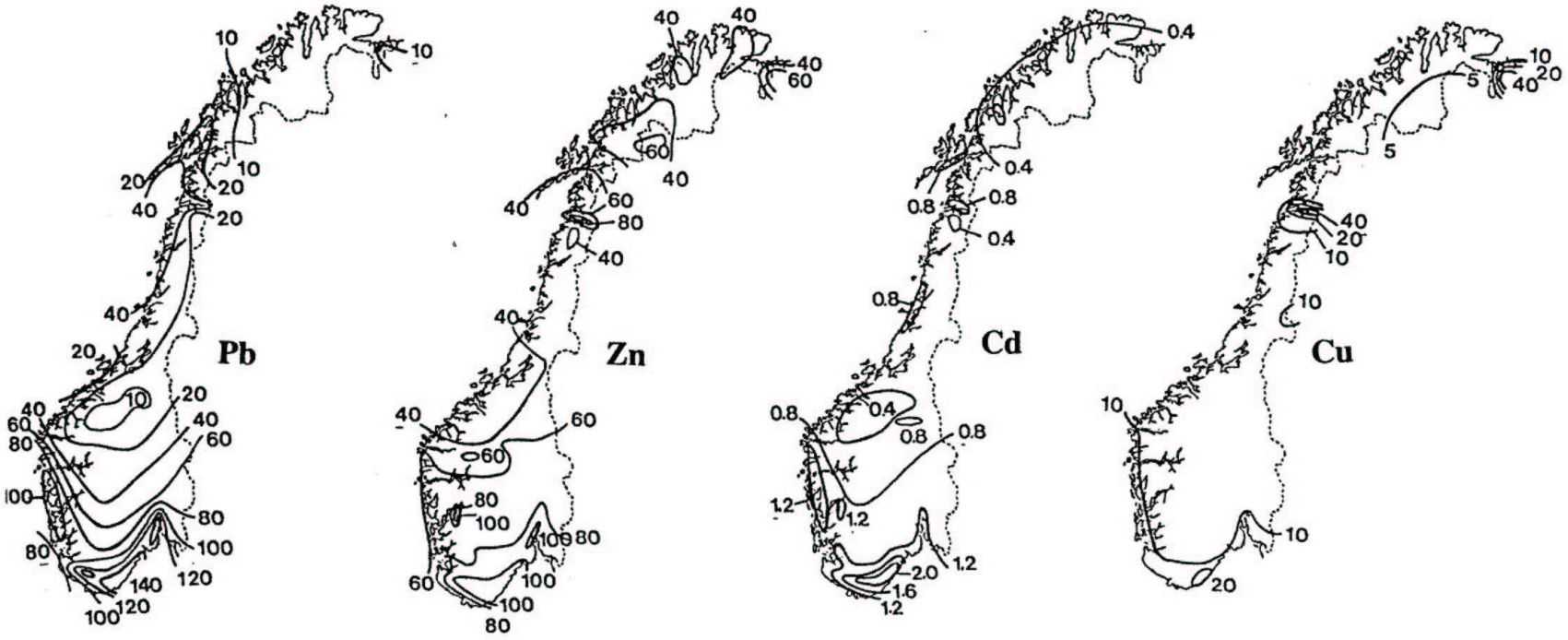
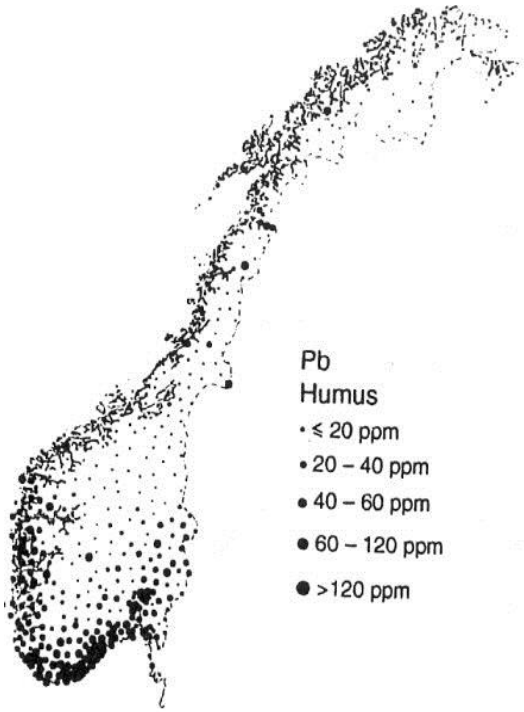
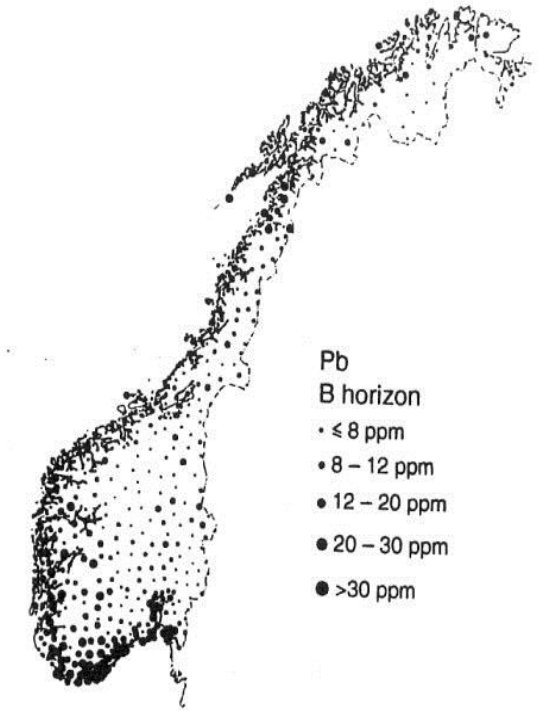
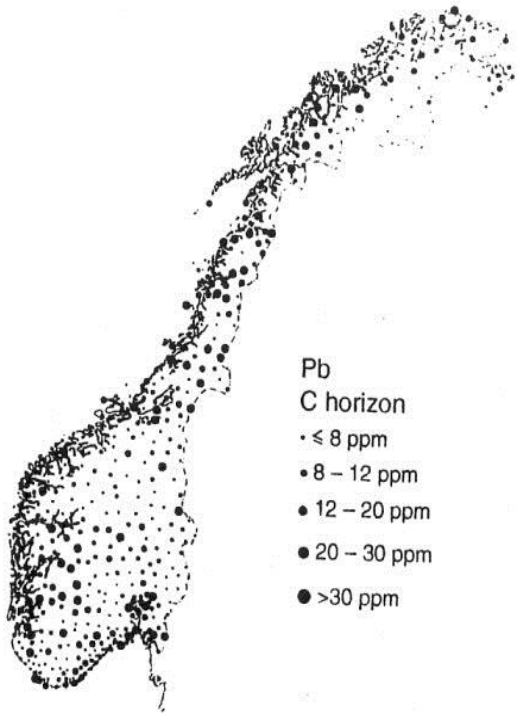



Fig. 4. Concentrations of copper, zinc, cadmium and lead in the humus layer of natural soils in Norway (ppm).

# Pb in natural soil in Norway 1985

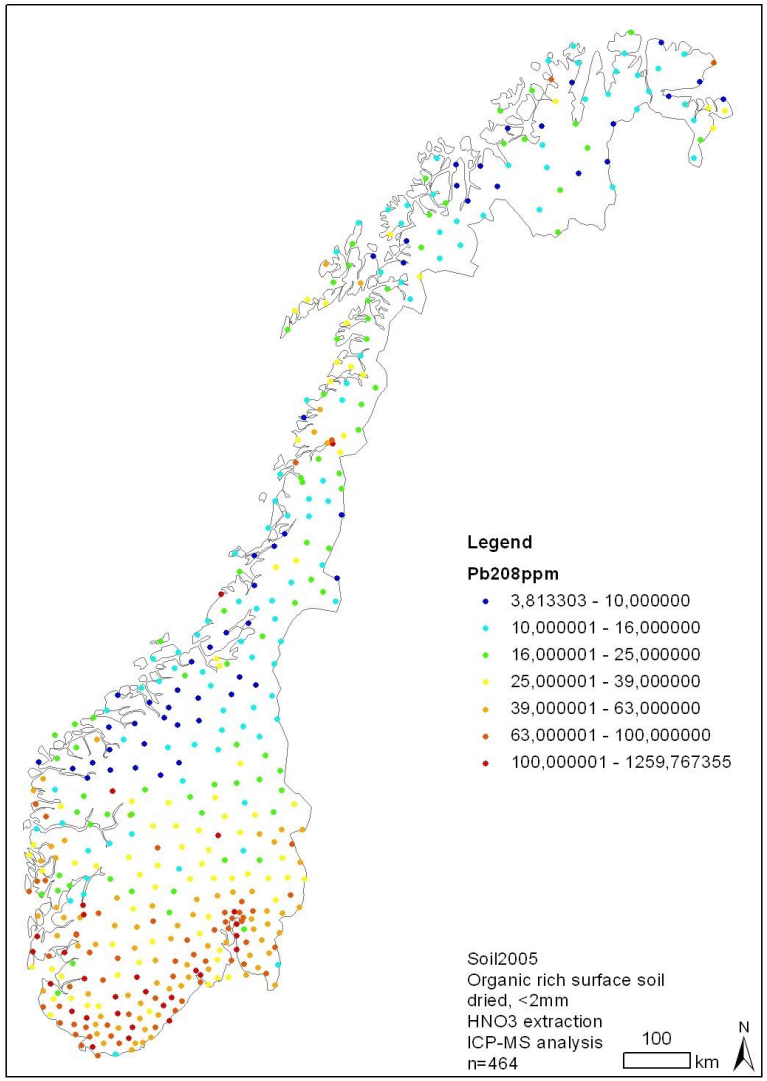


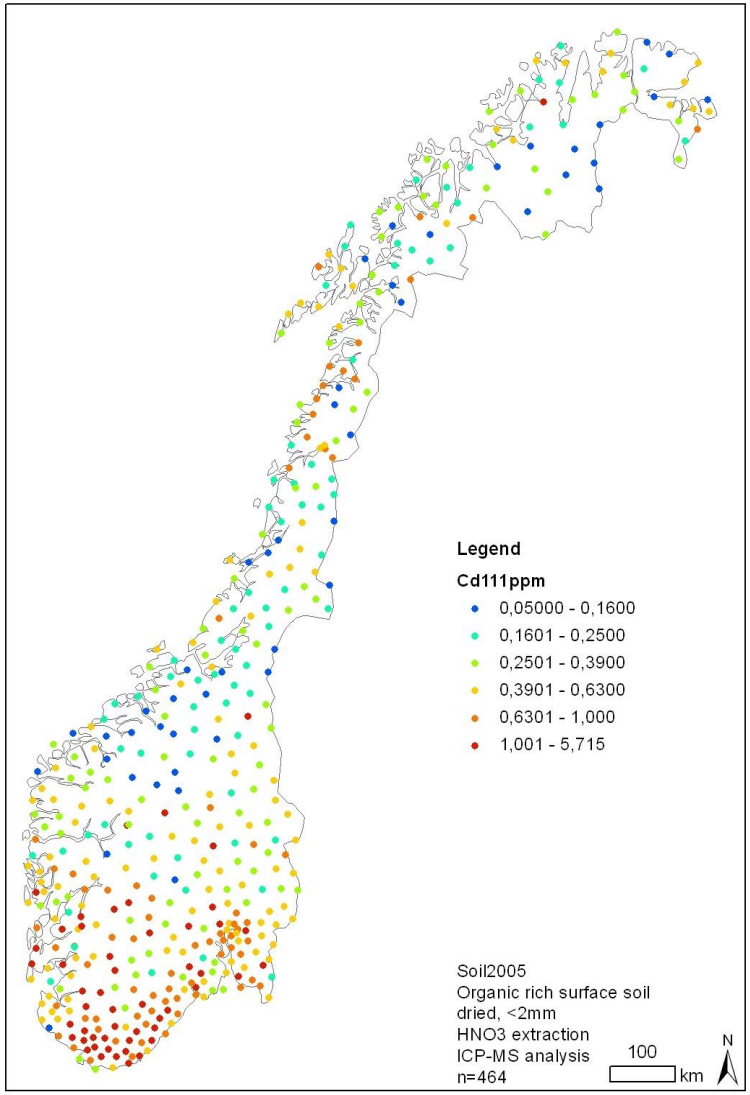



# Concentrations of metals in natural surface soils 2005

**Pb**

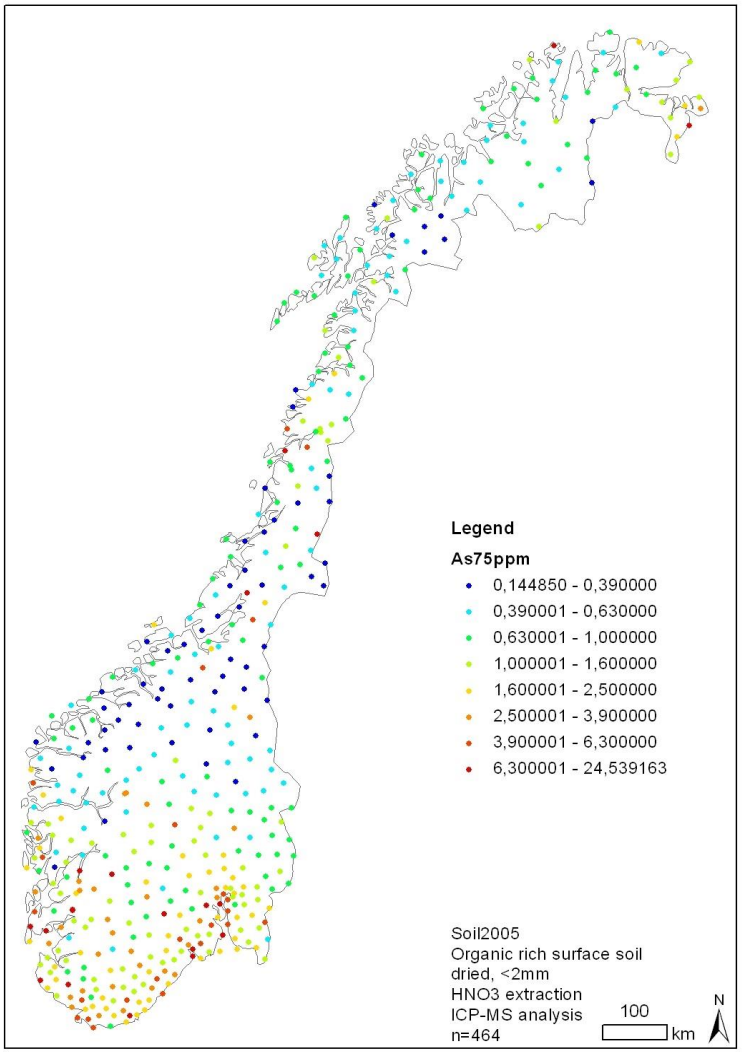



**Cd**

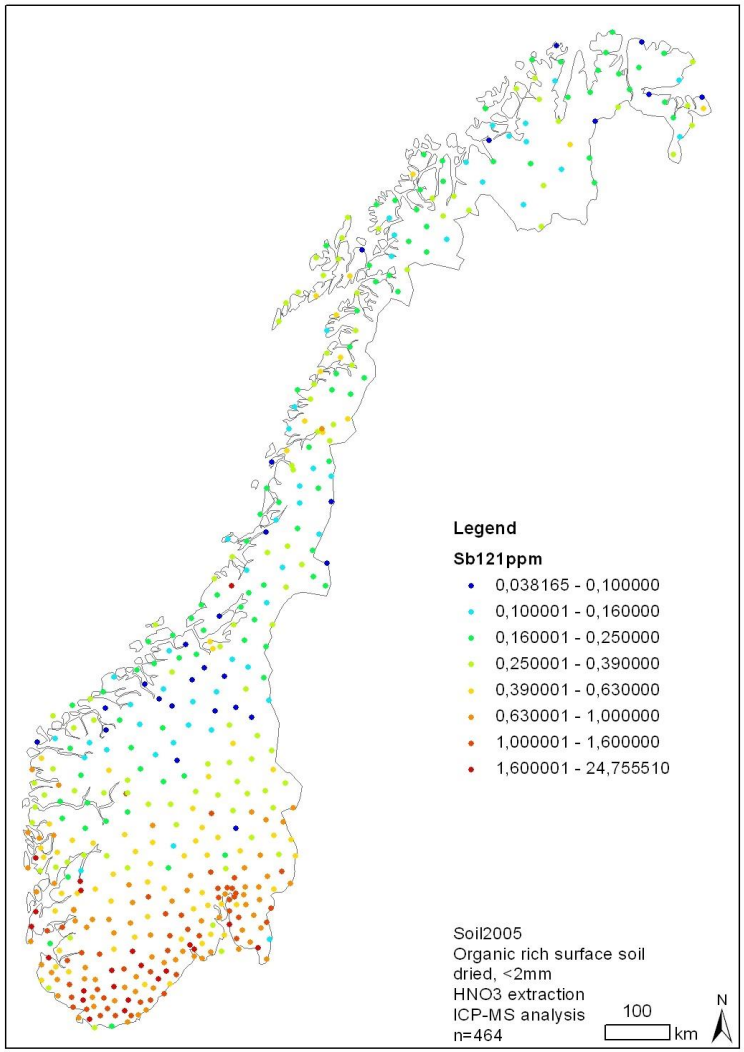


# Concentrations of metals in natural surface soils 2005

## As

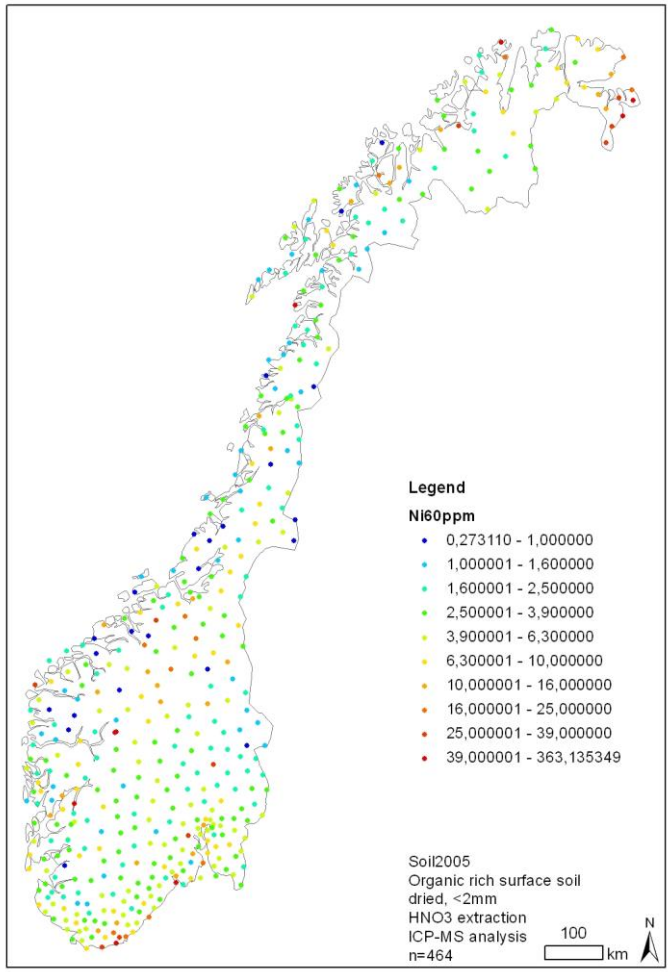



## Sb

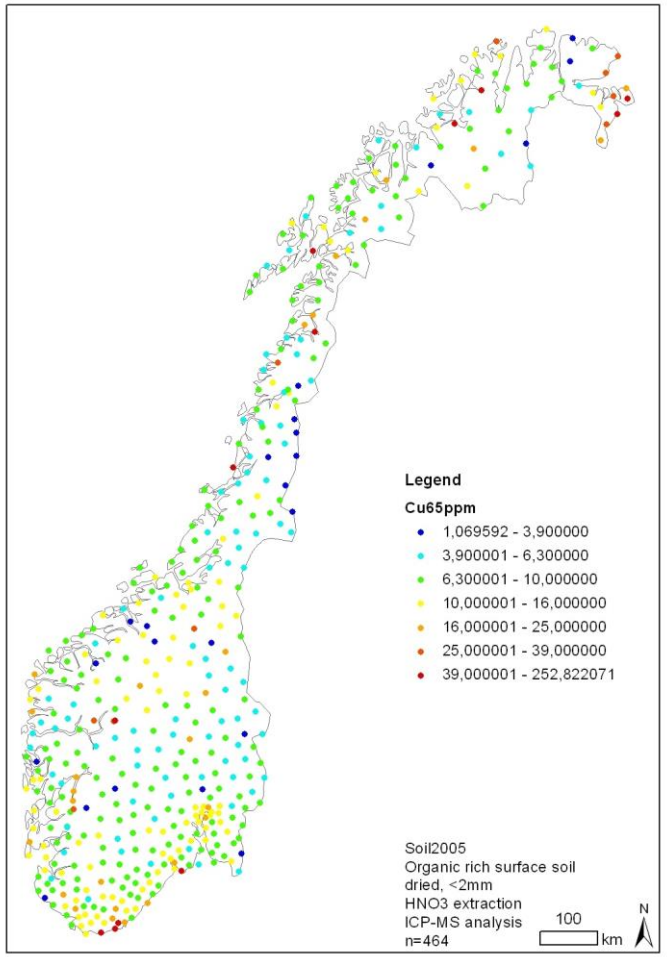


# Concentrations of metals in natural surface soils 2005

**Ni**

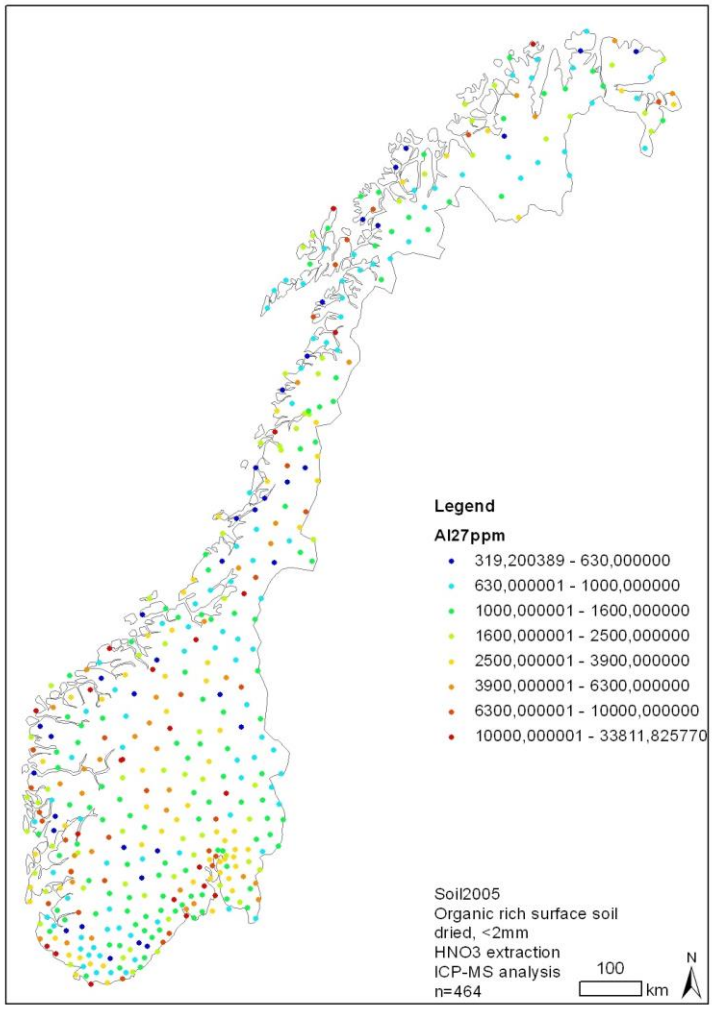



**Cu**

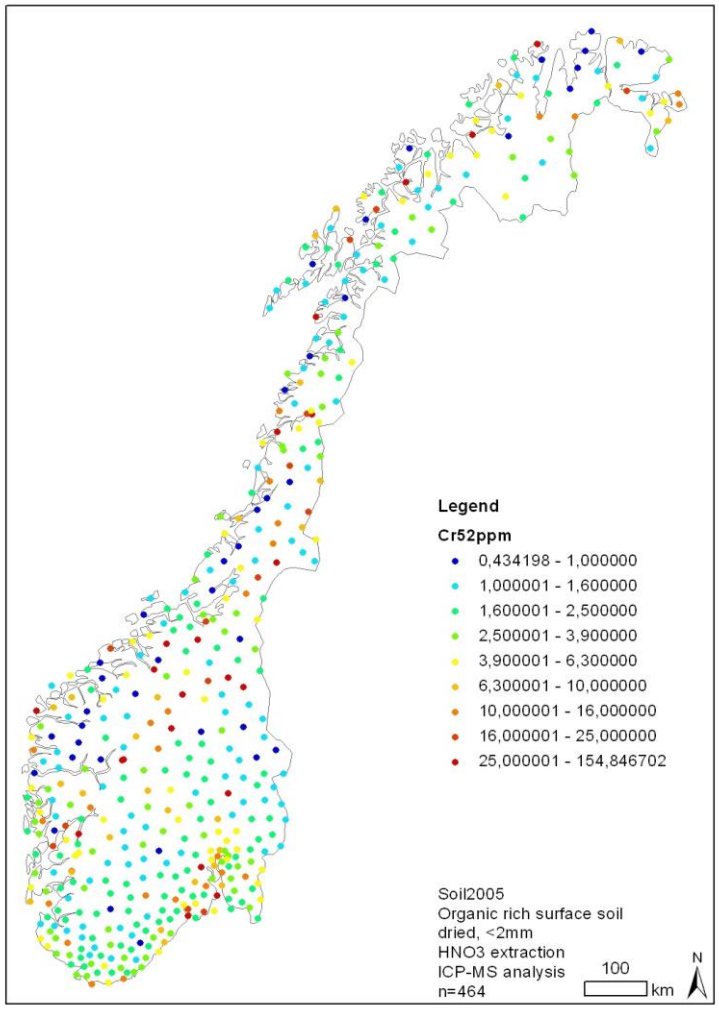


# Concentrations of metals in natural surface soils 2005

## Al

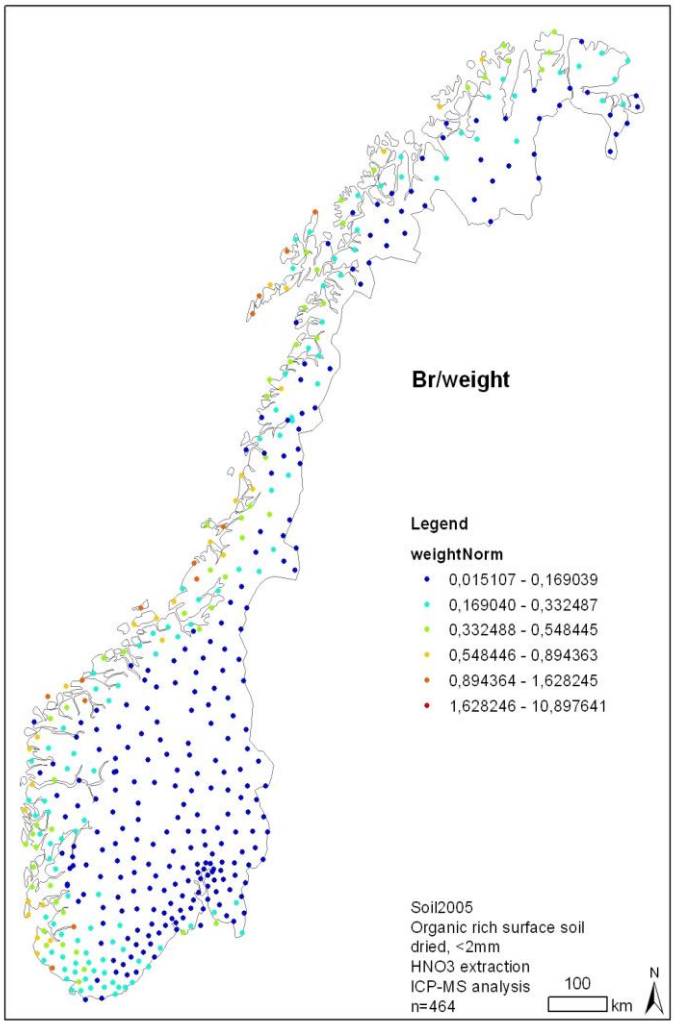



## Cr

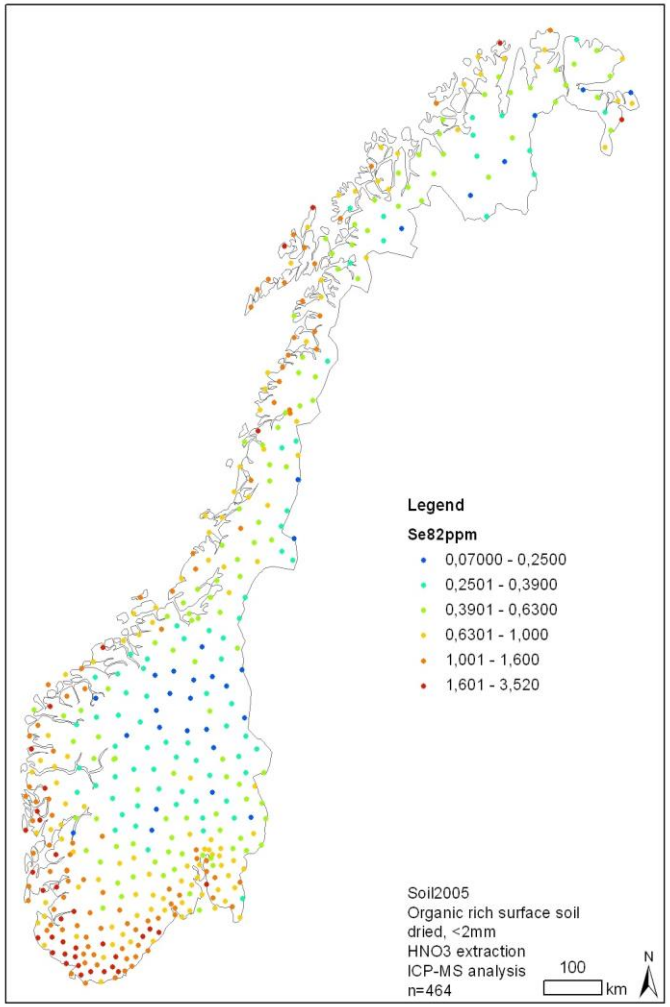


# Concentrations of metals in natural surface soils 2005

**Br**

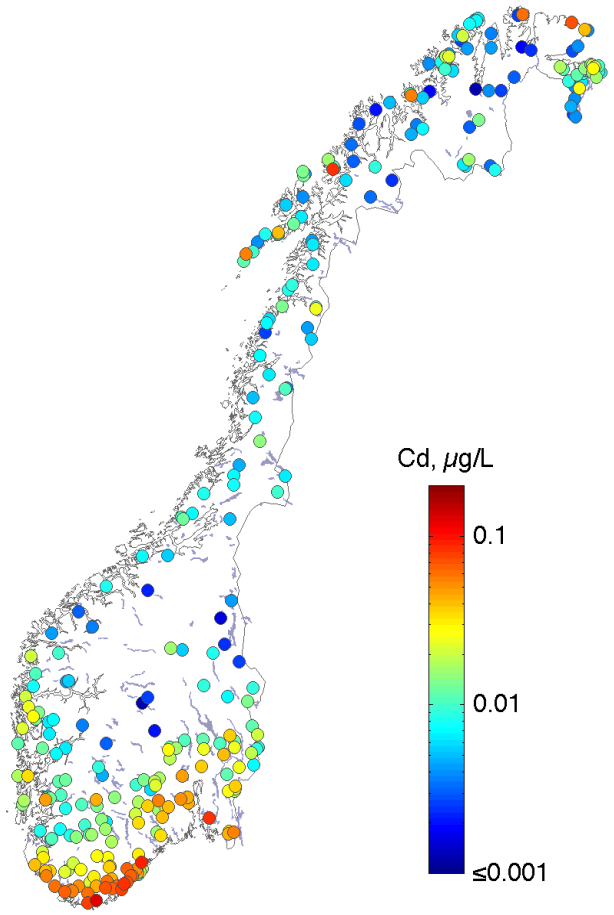



**Se**



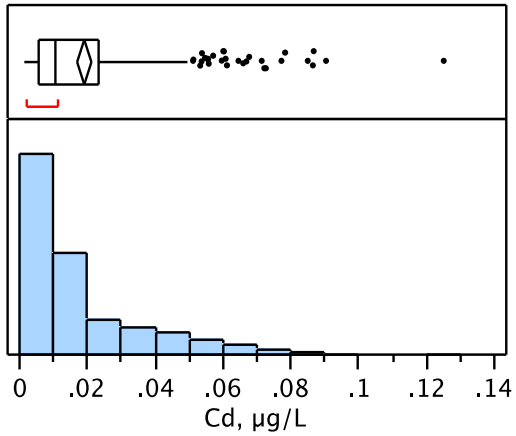
# Cadmium in Norwegian lake water (µg $L^{-1}$)

Data from Norwegian Institute for Water Research (NIVA)




Cd, overflatevann, n = 316

| Percentiles | µg/L | Moments | µg/L |
|---|---|---|---|
| 100.0% | 0.125 | Mean | 0.019 |
| 97.5% | 0.074 | Std Dev | 0.020 |
| 90.0% | 0.049 | Std Err Mean | 0.001 |
| 75.0% | 0.024 | upper 95% Mean | 0.021 |
| 50.0% | 0.011 | lower 95% Mean | 0.017 |
| 25.0% | 0.006 | | |
| 10.0% | 0.004 | | |
| 2.5% | 0.002 | | |
| 0.0% | 0.001 | | |



**Characterizing atmospheric deposition of metals around major industries in Norway (2000 - 2005 - 2010)**

Purpose:

Mapping of local deposition of metals from industries, mostly aluminium and iron alloy manufacturing plants situated within or adjacent to densely built-up areas - and comparing with data from previous surveys

Extent:

Sixteen industries distributed among 13 towns

Sampling:

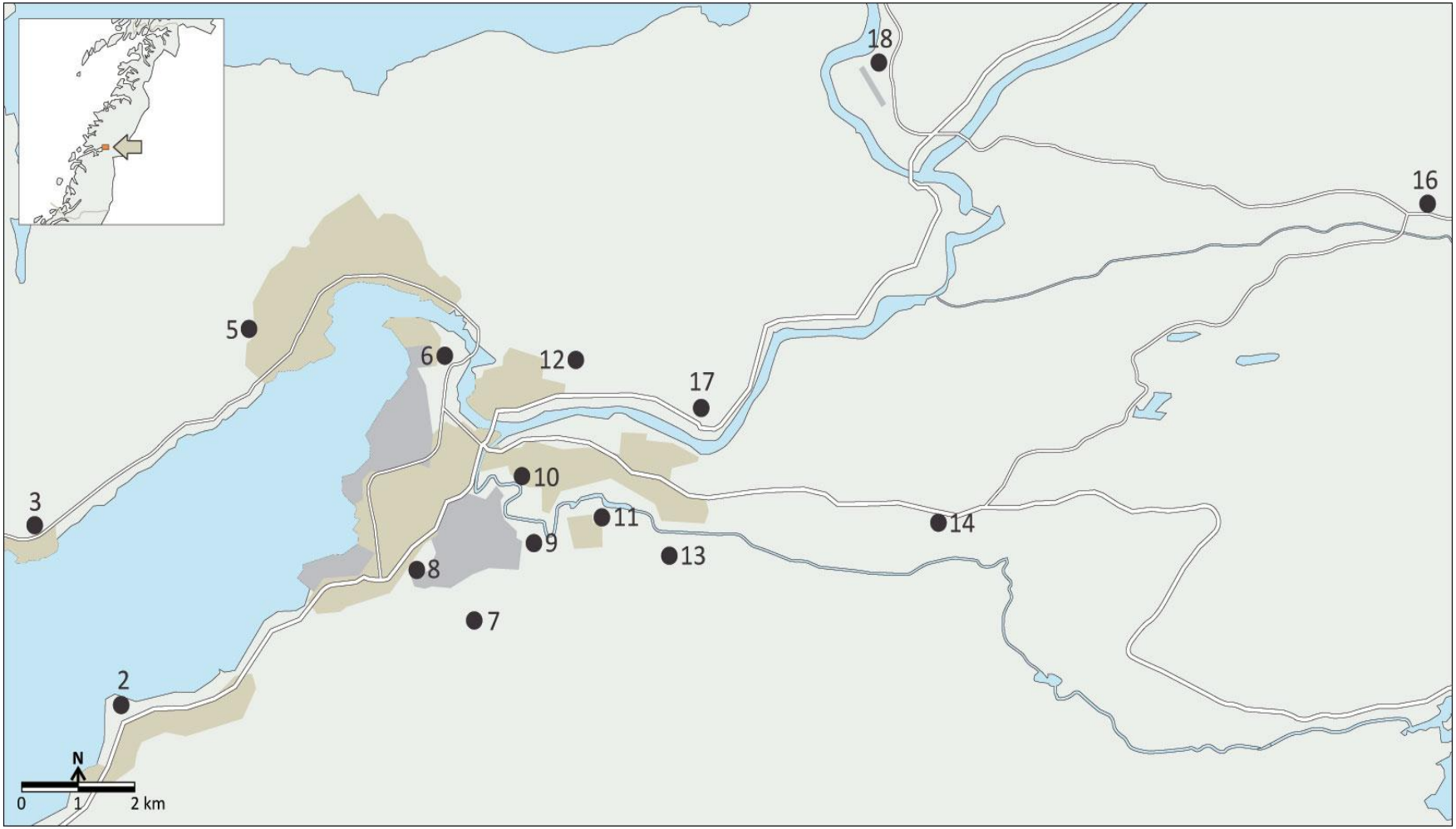
Five sites around each enterprise

Elements:

59 elements determined by ICP-MS

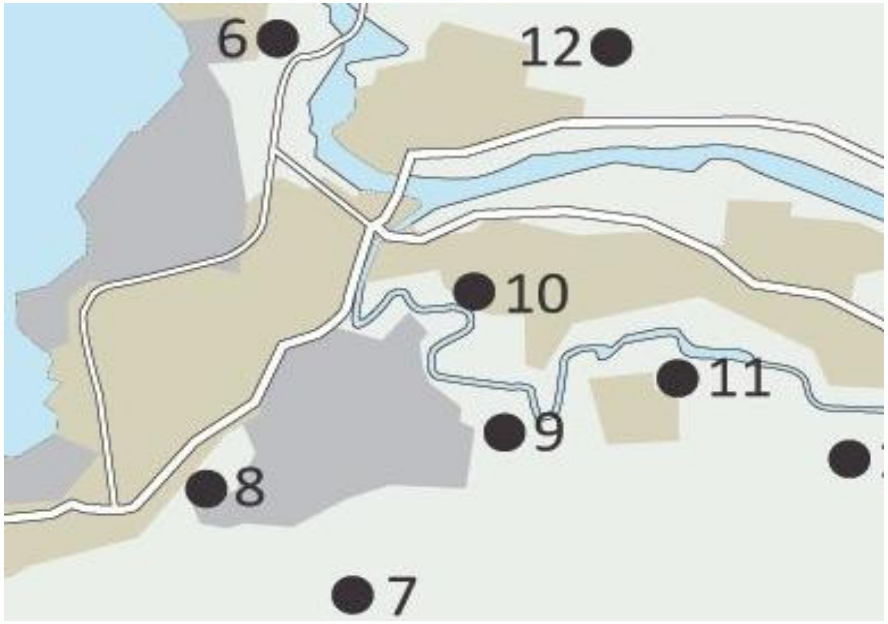
Sampling network around the mixed metal industries in Mo i Rana:

A. Ferromanganese smelter
B. Ferrosilicon factory
C. Recovery of metals from mixed scrap metal



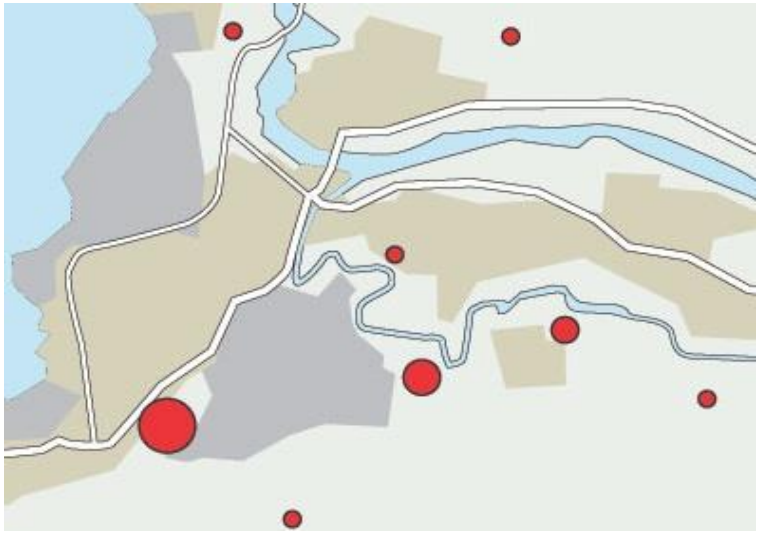
Distribution of some elements among sites close to the Mo industrial area:

A closer look

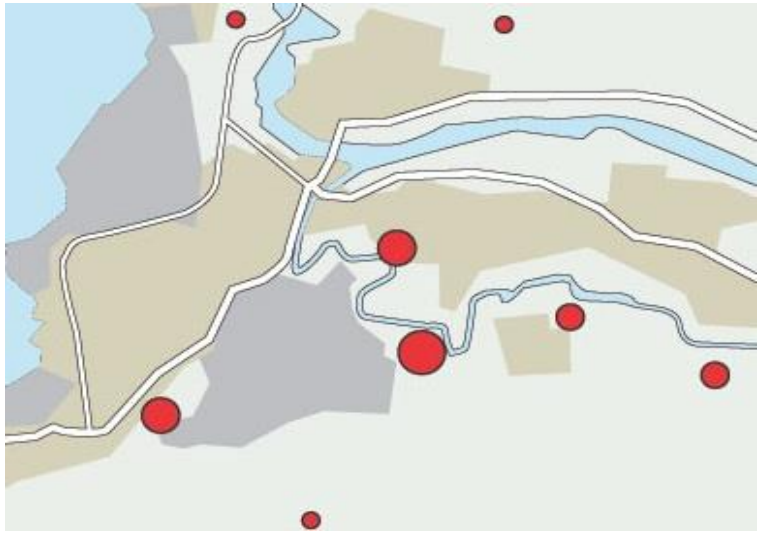


Distribution of four metals in moss at sites surrounding the Mo industries

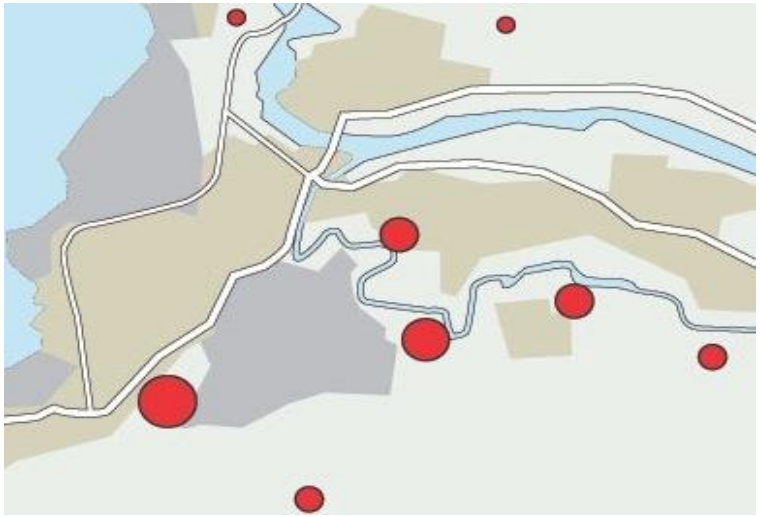
**Be**



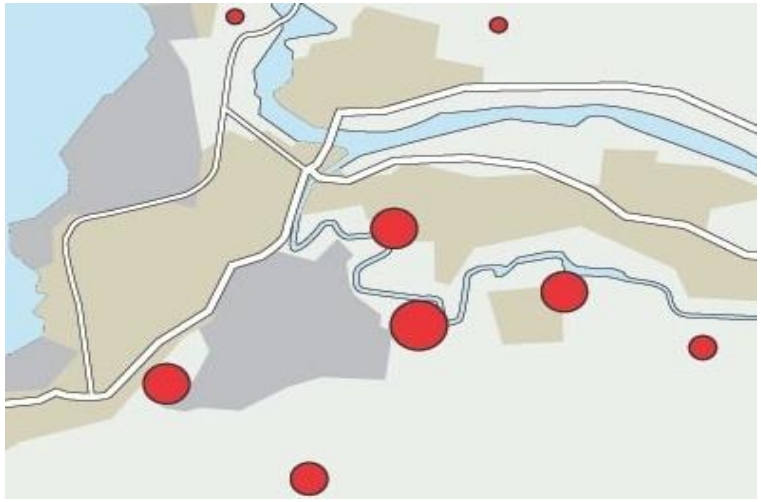
**Cr**



**Mn**



**Zr**



Some results from the study of emissions from local industries:

- Some factories have reduced their emissions substantially over the period 2000-2010.

- In other cases no appreciable improvement is noted, and still much remains to be done to achieve satisfactory levels.

- In several cases appreciable emissions of elements normally receiving little attention in industrial emissions were observed. Examples are Be, Zr, Nb, Mo, Ag, In, Te, W, Bi.

- In one particular case with three different enterprises located within the same industrial area the distributions of elements among sampling sites may help to identify the major source of each element.