Mixed metal pollution from smelter industries studied by moss biomonitoring, INAA and ICPMS: Mo i Rana (Norway) case study

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Mosses :

- have a high capacity to bind metals
- have no root system (unlike higher plants)
- are easy to sample
- are widely distributed
- concentrate metals 100-1000 times their levels in bulk deposition

Therefore they are useful biomonitors of atmospheric metal deposition

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Moss biomonitor

Hylocomium splendens



Moss annual segments

Metal deposition surveys in Norway:

Ca. 500 sites

Hylocomium splendens

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



Temporal trends 1977-2010



As in moss in Norway (µg g⁻¹):

Temporal trends 1977-2010



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

Temporal trends 1977-2010



Objectives of the Norwegian national moss survey:

A. Mapping geographical patterns in atmospheric deposition of trace elements (1977 - present)

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

C. Testing the feasibility of moss samples for monitoring levels of selected groups of persistent organic contaminants (2010) 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 populated areas, and comparing results with data from previous surveys

Extent:

Sixteen industries distributed among 13 towns

Sampling:

5-10 sites around each enterprise

Elements:

59 elements determined by ICP-MS (2010)

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

- A. Ferroalloy smelter (since 2005 ferromanganese)
- 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



Iron in moss - Mo i Rana 2000 (left) and 2005 (right)



Chromium in moss - Mo i Rana 2000 (left) and 2005 (right)



Manganese in moss - Mo i Rana 2000 left) and 2005 (right)



Tungsten in moss - Mo i Rana 2000 (left) and 2005 (right)



General conclusions - Mo i Rana smelters:

- A great number of elements (including Be, V, Cr, Mn, Fe, Co, Ni, Zn, Mo, Cd, W, Hg, Pb, Bi) are deposited in the vicinity of these smelters.
- In 2000 large amounts of <u>chromium</u> were released from the ferrochrome smelter. After transition to ferromanganese production the chromium deposition was reduced but replaced with a similar release of <u>manganese</u>.
- Emissions of zirconium, niobium, molybdenum, tellurium, and tungsten increased significantly between 2000 and 2010. For other elements the difference was less appreciable.

Investigation of air pollution in Mo i Rana:

Collaboration JINR - NTNU

A. Comparison of data from previous surveys 1989 and 1993:

E. Steinnes, M.V. Frontasyeva, T.E. Sjøbakk and P. Varskog: "Metal pollution around an iron smelter complex in northern Norway at different modes of operation". Russ. J. Environ. Chem., St. Petersburg <u>13</u> (2), 100-111 (2004) (In Russian).

B. Statistical analysis of data from 2000 and 2005:

E. Steinnes, M.V. Frontasyeva, S.F. Gundorina and Yu.S. Pankratova: "Identification of metal emissions from adjacent point sources in Northern Norway using moss biomonitoring and factor analysis". Chem. Anal. (Warsaw) <u>53</u>, 877-886 (2008).

C. Statistical analysis of data from 2010:

Present work - based on data from INAA (JINR) and ICPMS (Norway)

















Results from factor analysis:

	Zr	0,256	0,456	0,795
Factor 1:	Nb	0,081	0,926	0,364
	Мо	0,835	0,384	0,388
	Ag	0,583	0,508	0,605
AI, Mn, Cu, Zn,	Cd	0,786	0,509	0,324
As, Cd, Sb, Ba	Sb	0,798	0,531	0,259
	Ba	0,964	0,145	0,194
	W	0,316	0,870	0,368
Factor 2:	Pb	0,656	0,642	0,347
	Bi	0,815	0,478	0,276
.,	Th	0,658	0,257	0,616
V, Nb, W	AI	0,922	0,271	0,265
	V	0,491	0,762	0,403
	Cr	0,285	0,151	0,897
	Mn	0,862	0,056	0,499
Factor 3:	Fe	0,431	0,418	-0,095
	Cu	0,868	0,380	0,302
	Zn	0,783	0,562	0,225
Cr, Zr, Hg	As	0,833	0,080	0,535
	Hg	0,261	0,377	0,870
	Explained			
	variance(%)	45.8	24.6	23.4

Factor scores

		Factor	Factor	Factor
	Site no.	1	2	3
Factor 1:	2	-0,323	-0,139	-0,169
	3	-0,372	-0,308	-0,392
Al, Mn, Cu, Zn,	5	-0,211	-0,356	-0,380
As, Cd, Sb, Ba	6	0,019	0,117	-1,196
	7	-0,143	-0,191	-0,190
Factor 2:	8	3,403	0,469	-0,212
V, Nb, W	9	0,209	-1,125	2,962
	10	-0,668	3,263	0,828
	11	-0,316	-0,157	0,813
_	12	-0,260	-0,338	-0,456
Factor 3:	13	-0,404	-0,319	-0,056
Cr, Zr, Hg	14	-0,307	-0,324	-0,500
	16	-0,318	-0,462	-0,636
	17	-0,307	-0,130	-0,418

Maximum metal concentrations in moss at Mo i Rana 2000, 2005, and 2010

More than 10 times background level: Significant pollution More than 50 times background level: Serious pollution

	2000	2000	2010
Element	Maximum	Maximum	Maximum
	(ppm)	<i>(ppm)</i>	(ppm)
Mg	4700	4000	2020
Al	11700	7800	8000
K	5800	6600	5600
Ca	19200	14400	8300
V	77	38	19
Cr	19000	580	470
Mn	2500	19200	12700
Fe	21100	20500	13400
Со	16.0	8.9	6.7
Ni	95	205	29
Zn	1090	1290	780
As	4.8	4.7	2.9
Mo	2.4	18.4	2.6
Sb	0.44	3.0	0.63
Ba	110	470	580
La	6.2	9.2	9.9
W	6.0	13.3	8.9
Au	0.009	0.030	0.016
Th	0.37	1.9	2.0
U	0.20	1.1	1.2

Conclusions:

- 1. In the 2010 data most trace elements emitted by Mo i Rana industries are well separated in three factors.
- 2. Elements occurring in the same factor show similar distributions among sampling sites.
- 3. It may be assumed that these factors represent three different industrial sources.
- 4. Factor scores for the three most polluted sampling sites indicate that each of them is predominantly affected by one of those three different sources.
- 5. The high deposition levels of many metals at Mo i Rana are confirmed in the 2010 survey

2000: Use of naturally growing moss to study atmospheric deposition of metals in the vicinity of 15 industries in Norway

- Initiated by the Norwegian State Pollution Control Authority
- Financed by the industries:

5 aluminium plants
6 iron and iron alloy smelters
2 cement factories
1 zinc smelter
1 titanium factory

Ten sampling sites at each location.

Repeated at some of the sites in 2005 and most sites* in 2010

*Two additional aluminium plants participated in 2010

Deposition of some trace elements around Mo i Rana iron industries

EF: Air pollution levels at the most exposed sites relative to background

2	000		
EF		2010/2000	
Site 8	Site 10	Site 8	Site 10
65	7.7	0.85	0.86
32	40	0.42	1.49
410	520	0.02	0.39
147	28	6.7	1.13
151	122	0.73	0.93
55	11	0.75	1.17
35	9.2	0.51	1.02
14.1	6.5	1.40	0.97
46	15	1.26	0.65
18	4.9	0.56	0.78
19	27	1.9	3.4
53	160	21.5	5.4
46	22	3.8	2.7
17	15	0.74	0.95
33	20	1.71	0.81
80	95	1.26	7.2
34	5.6	8.6	1.8
75	128	31	4.3
4.0	5.7	1.9	0.60
54	46	0.90	0.59
36	21	1.8	1.6
	2 Site 8 65 32 410 147 151 55 35 14.1 46 18 19 53 46 17 33 80 34 75 4.0 54 36	2000 EF Site 8 Site 10 65 7.7 32 40 410 520 147 28 151 122 55 11 35 9.2 14.1 6.5 46 15 18 4.9 19 27 53 160 46 22 17 15 33 20 80 95 34 5.6 75 128 4.0 5.7 54 46 36 21	2000 EF 2010/ Site 8 Site 10 Site 8 65 7.7 0.85 32 40 0.42 410 520 0.02 147 28 6.7 151 122 0.73 55 11 0.75 35 9.2 0.51 14.1 6.5 1.40 46 15 1.26 18 4.9 0.56 19 27 1.9 53 160 21.5 46 22 3.8 17 15 0.74 33 20 1.71 80 95 1.26 34 5.6 8.6 75 128 31 4.0 5.7 1.9 54 46 0.90 36 21 1.8





Factor scores for 14 sampling sites

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17	-0.307	-0.130	-0.418