E18-2008-4

E. Steinnes*, M. V. Frontasyeva, S. F. Gundorina, Yu. S. Pankratova

IDENTIFICATION OF METAL EMISSIONS FROM ADJACENT POINT SOURCES IN NORTHERN NORWAY USING MOSS BIOMONITORING AND FACTOR ANALYSIS

Submitted to «Journal of Environmental Monitoring»

^{*}Department of Chemistry, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway

E18-2008-4

Стейннес Э. и др. Идентификация источников выбросов металлов от близко расположенных заводов сталелитейного комплекса в северной Норвегии с использованием мхов-биомониторов и факторного анализа

Методом нейтронно-активационного анализа природного мха изучены атмосферные выпадения 34 следовых элементов в районе сталелитейного комплекса в одном из городов северной Норвегии в 2000 и 2005 г. Специфический вклад двух заводов, расположенных близко друг от друга, но отличных по видам выпускаемой продукции, а также изменения в характере их производства за исследуемый период были оценены с помощью факторного анализа. В 2000 г. выбросы от сталелитейного комплекса (завод I) вызвали существенные выпадения Сг и Fe, а также Al, V, Co, Ni, As, Mo, и W. Соседнее предприятие (завод II) по переплавке металлолома вызвало существенное выпадение Mn и Zn и явилось источником выбросов Sb и W. Вследствие перехода от феррохромного к ферромарганцевому производству завод I в 2005 г. показал существенное выпадение Mn. Он также явился источником выбросов Cr, Co, Ni, As, и Mo. Завод II, ответственный за существенный выброс Zn, показал возросшие выбросы Sb и W. На большую часть городской территории вклад завода I был преобладающим. Исключением являются два участка в северо-восточном направлении от предприятия, где эмиссии от завода II преобладали как в 2000, так и в 2005 г.

Работа выполнена в Лаборатории нейтронной физики им. И. М. Франка ОИЯИ. Препринт Объединенного института ядерных исследований. Дубна, 2008

Steinnes E. et al.

E18-2008-4

Identification of Metal Emissions from Adjacent Point Sources in Northern Norway Using Moss Biomonitoring and Factor Analysis

Atmospheric deposition of 34 trace metals around an iron-smelter complex in a town in Northern Norway was studied in 2000 and 2005 using neutron activation analysis of naturally growing moss. Specific contributions from two adjacent but distinct smelters and changes in operation that had occurred between the two sampling years were identified by factor analysis, and relative contributions from the two sources at different sampling sites were demonstrated by means of the factor scores. In 2000, emission from a ferroalloy smelter (Smelter I) caused substantial deposition of Cr and Fe, and this smelter was also the main source of Al, V, Co, Ni, As, Mo, and W. Another nearby plant (Smelter II) recovering metals from used materials caused considerable deposition of Mn and Zn and was also the main source of Sb and W deposition. Following a transition from ferrochrome to ferromanganese production, Smelter I in 2005 showed substantial deposition of Mn. This smelter was also still the main source of Cr, Co, Ni, As, and Mo. Smelter II maintained a considerable Zn deposition and showed increased emissions of Sb and W. In most of the urban area the contribution from Smelter I was dominant. An exception was two sites in the north-east direction from the industries, where emissions from Smelter II dominated in 2000 as well as in 2005.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

Preprint of the Joint Institute for Nuclear Research. Dubna, 2008

INTRODUCTION

Deposition of metal-containing dust from smelters may significantly affect human and environmental health in their surrounding areas. The classical approach to study the extent of such a pollution is measuring air concentrations based on aerosol collection on filters. This requires a certain technical set-up and is normally limited to one or a few sites in the areas influenced by the emissions. The information obtained, therefore, is limited with respect to the relative influence of the metal pollution in different parts of the area in question and the contribution from different sources. Moreover, air concentration measurements cannot be used to determine the atmospheric deposition of the pollutants. For that purpose bulk deposition sampling may be employed, but this approach is also limited in terms of sampling sites. The use of biomonitoring techniques has therefore proven to be a useful alternative to the conventional techniques to record detailed atmospheric deposition patterns around point sources of air pollution. Since naturally growing mosses or lichens may be frequently exterminated at conditions of high air pollution, the approach most frequently used is deployment of «moss bags» for a given period of time [7–8].

In northern Europe however sampling of naturally growing terrestrial moss may sometimes be feasible also on the local scale, as shown, e.g., in studies related to thermal power plants [4] and Cu–Ni smelters [1]. In Norway this technique has been used regularly since 1977 for metal deposition monitoring on the national scale [2, 10, 11]. Although the main problem of atmospheric metal deposition in Norway is associated with long-range transport from other European countries [3, 12], there are also a few industries that are sources of significant metal pollution on the local scale. One of those is the iron industry at Mo i Rana, Nordland county (Fig. 1), established in 1946 and operated for four decades as a regular iron smelter. Financial and other considerations led to the decision to close this smelter in 1989 and use the available facilities for some alternative industries, including a ferrochrome smelter. This considerably affected the air pollution situation at Mo during the 1990s [13].

In 2000, the Norwegian State Pollution Control Authority required a deposition survey of selected metals to be carried out around 15 industries in Norway employing naturally growing moss, and the survey was repeated in 2005 at some of the sites. In the present work, moss samples collected in 2000 and 2005 around the metal industries at Mo were investigated for the contents of 34 elements by instrumental neutron activation analysis.

MATERIALS AND METHODS

The town of Mo i Rana is situated at $66^{\circ} 20'$ N, $14^{\circ} 10'$ E in the inner end of the eastbound Rana fjord, at about 60 km distance from the Norwegian Sea, and has about 20 000 inhabitants. The Rana fjord and the Rana valley stretching eastwards from Mo are shielded to the north and south by high mountains (700–1400 m altitude). Correspondingly, the prevailing local wind directions are either westerly or easterly. The location of the metal industries, which are situated within the town area, is indicated in Fig. 1.

Samples of the feather moss *Hylocomium splendens* were collected in 2000 and 2005, respectively, at the same 10 sites, all located at distances of about 0.5–4 km from the factory site within the area considerably affected by industrial emissions as evident from earlier studies. The locations of these sites are shown in the map in Fig. 1. In addition, three sampling sites representing the regional background values for the studied elements in moss were included. The moss samples were collected and further prepared for analysis according to a standard procedure described elsewhere [11].

The moss samples were analyzed for their concentrations of 34 elements (Na, Mg, Al, Cl, K, Ca, Sc, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Br, Rb, Sr, Mo, Sb, I, Cs, Ba, La, Sm, Tb, Yb, Hf, Ta, W, Au, Th, U) using epithermal neutron activation analysis (ENAA). The ENAA was carried out at the IBR-2 pulsed fast reactor in Dubna, Russia, according to procedures described elsewhere [5–6]. The accuracy of the analyses was checked by means of international standard reference materials run together with the moss samples.

The underlying relations between the chemical parameters for the moss samples were investigated using factor analysis [9]. The analyses were performed separately for the two data sets from 2000 and 2005 using principal component extraction, as the eigenvalue factor selection criterion, and VARIMAX rotation of the extracted factors. Variables with factor loadings higher than 0.6 (cfr. Table 1) were assumed to contribute significantly to a given factor. Since the number of elements considerably exceeded the number of samples collected each year, the data were first subjected to correlation analysis (results are not shown). From the observed correlations and previous knowledge about emissions from this kind of industry, thirteen elements (Al, V, Cr, Mn, Fe, Co, Ni, Zn, As, Mo, Sb, La, W) were selected for the treatment by factor analysis, and the following discussion of sources is based on these elements.



Fig. 1. Maps showing the location of Mo i Rana in Norway and moss sampling sites (•) in 2000 and 2005. Dashed grey colour in the right map: main urban area. The locations of the two main industrial sources: F - f ferroalloy smelter (Smelter I); S - i iron smelter (Smelter II)

RESULTS AND DISCUSSION

Results from factor analyses of the moss data from 2000 and 2005, respectively, are shown in Tables 1a and 1b, and the distribution of the two prominent factors in each case among the sampling sites is shown in Figs. 2 and 3. The 2000 moss factor analysis shows two distinct components. Factor 1 has high loadings for Al, V, Cr, Fe, Co, Ni, As, Mo, and La, and is obviously associated with the ferrochrome production (Smelter I), and the highest factor scores are observed at sites 5 and 6 located next to the factory in the eastward direction. Factor 2 has high loadings for Mn, Zn, Mo, Sb, and W, and is apparently due to emissions from Smelter II. This factor has the highest factor score at site 7, which is the site closest to that smelter.

Element	Factor 1	Factor 2	Element	Factor 1	Factor 2
Al	0.89	0.25	Al	0.81	0.52
V	0.97	0.23	V	0.73	0.62
Cr	0.92	-0.05	Cr	0.85	0.43
Mn	0.47	0.79	Mn	0.94	0.20
Fe	0.86	0.41	Fe	0.54	0.73
Co	0.97	0.01	Co	0.93	0.28
Ni	0.98	0.04	Ni	0.84	0.51
Zn	0.47	0.85	Zn	0.20	0.96
As	0.99	0.11	As	0.89	0.45
Mo	0.79	0.57	Mo	0.81	0.58
Sb	-0.06	0.89	Sb	0.56	0.81
La	0.88	0.23	La	0.72	0.60
W	-0.08	0.96	W	0.37	0.92
Expl.Var	8.04	3.75	Expl.Var	7.13	5.08
Prp.Totl	0.62	0.29	Prp.Totl	0.55	0.39

 Table 1a. Factor analysis for 2000 samples Table 1b. Factor analysis for 2005 samples

In 2005, the analysis also shows two well-defined factors that may be ascribed to each of the smelters, but the separation of elements between the factors is not as clear as in 2000. Factor 1 still appears to be associated with Smelter I, where extremely high emissions of Cr at this time are replaced by similarly high Mn emissions. Al, Co, Ni, As, and Mo are still mainly in this factor, whereas V and La now occur in both factors at about the same level and Fe has moved to Factor 2. Zn, Sb, and W are still strongly linked to Factor 2, indicating that it is associated with the same source as in 2000, i.e., Smelter II. As in 2000, the highest scores for Factor 1 are seen at sites 5 and 6, and the highest score for Factor 2 — at site 7.

Maximum values for all 34 elements in 2000 and 2005 are shown in Table 2 in comparison with corresponding data from background sites. Most of the elements are enriched in samples collected near Mo, indicating local sources. Only Na, Cl,



Fig. 2. Factor scores for different sampling sites in 2000



Fig. 3. Factor scores for different sampling sites in 2005

K, Ca, Se, Br, Rb, I, Cs, and Au appear to be virtually independent of industrial and other activities within the urban area. The other elements not included in the factor analysis, Mg, Sc, Sr, Ba, Sm, Tb, Yb, Hf, Ta, Th, and U, are all enriched at sites strongly exposed to the industrial emissions, particularly sites 5, 6, and 8. These elements however are all geochemically classified as lithophilic, and might be associated either by handling of raw material for Smelter I or by operations in the factory area leading to excessive release of local soil dust. Mg is most strongly associated with Cr in 2000 and Mn in 2005, i.e., with the raw material for Smelter I in both cases. Inter-correlations between the other members of this group however do not point specifically to any of the smelter processes. The group Th–Sc–Hf–REE is strongly coherent in both years. On the other hand, U is strongly correlated with Fe, Hf, and Ta (but not with Cr) in 2000 and with Ni, As, Mo, Ba, and REE in 2005.

		2000	2005		
Element	Maximum	Background level	Maximum	Background level	
	(ppm)	(ppm)	(ppm)	(ppm)	
Na	580	130	960	170	
Mg	4700	520	4000	610	
Al	11700	910	7800	730	
Cl	380	110	540	110	
K	5800	2800	6600	3400	
Ca	19200	3000	14400	3400	
Sc	3.4	0.08	3.4	0.11	
V	77	1.5	38	2.0	
Cr	19000	9.5	580	5.5	
Mn	2500	380	19200	390	
Fe	21100	690	20500	550	
Со	16.0	0.24	8.9	0.24	
Ni	95	< 5	205	< 5	
Zn	1090	34	1290	35	
As	4.8	0.11	4.7	0.08	
Se	0.34	0.20	0.87	0.16	
Br	8.7	4.3	11.0	4.8	
Rb	27	6.6	19	6.4	
Sr	63	9	103	16	
Mo	2.4	0.20	18.4	0.11	
Sb	0.44	0.04	3.0	0.07	
Ι	6.2	2.7	7.8	2.8	
Cs	1.0	0.13	3.8	0.19	
Ba	110	21	470	24	
La	6.2	0.39	9.2	0.42	
Sm	0.21	0.04	1.35	0.05	
Tb	0.033	0.006	0.19	0.009	
Yb	0.094	< 0.02	0.42	< 0.02	
Hf	0.86	< 0.05	9.8	< 0.05	
Та	0.05	0.01	0.26	0.01	
W	6.0	0.13	13.3	0.42	
Au	0.009	0.002	0.030	0.005	
Th	0.37	0.06	1.9	0.08	
U	0.20	0.03	1.1	0.06	

 Table 2. Maximum values observed in moss samples from Mo i Rana in 2000 and 2005

 compared to the data from regional background sites

Ē

CONCLUSIONS

In a local area affected by air pollution from more than one major source it can be very difficult to distinguish between contributions from each of these

sources, in particular if they are located close to each other and partly emit the same substances. By using several sampling points optimally located relative to the suspected sources, simultaneously recording a considerable number of relevant chemical substances, and employing factor analysis for multivariate treatment of the data, the specific contributions from each pollution source may be defined. In particular, the calculation of factor scores for each sampling site may help to solve the problem. As shown in the present paper, this approach can be particularly useful in a situation with considerable changes of operation in industrial sources affecting the air pollution situation in a local community.

REFERENCES

- 1. Äyräs M. et al. // J. Geochem. Exploration. 1997. V. 58. P. 269-281.
- 2. Berg T. et al. // Environ. Pollut. 1995. V. 88. P. 67-77.
- 3. Berg T., Røyset O., Steinnes E. // Environ. Monit. Assessm. 1994. V. 31. P. 259-273.
- 4. Folkeson L. // Ann. Bot. Fennici. 1981. V. 18. P. 245-253.
- 5. Frontasyeva M. V., Steinnes E. // The Analyst. 1995. V. 120. P. 1437-1440.
- Frontasyeva M. V., Nazarov V. M., Steinnes E. // J. Radioanal. Nucl. Chem. 1994. V. 181. P. 363–371.
- 7. Goodman G. T., Roberts T. M. // Nature. 1971. V. 231. P. 287-292.
- 8. Little P., Martin M. H. // Environ. Pollut. 1974. V. 6. P. 1-19.
- 9. Schaug J. et al. // Atmos Environ. 1990. V. 24A. P. 2625-2631.
- 10. Steinnes E. et al. // Water, Air, Soil Pollut. 1994. V. 74. P. 121-140.
- 11. Steinnes E., Rambæk J. P., Hanssen J. E. // Chemosphere. 1992. V. 35. P. 735-752.
- 12. Steinnes E. et al. // Water, Air, Soil Pollut. 1989. V.45. P. 207-218.
- 13. Steinnes E. et al. // Russ. J. Environ. Chem. St. Petersburg, 2004. V.13, No.2. P. 100–111 (in Russian).

Received on January 22, 2008.

Редактор В. В. Булатова

Подписано в печать 14.02.2008. Формат 60 × 90/16. Бумага офсетная. Печать офсетная. Усл. печ. л. 0,62. Уч.-изд. л. 0,86. Тираж 260 экз. Заказ № 56069.

Издательский отдел Объединенного института ядерных исследований 141980, г. Дубна, Московская обл., ул. Жолио-Кюри, 6. E-mail: publish@jinr.ru www.jinr.ru/publish/