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

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Atmospheric deposition of 34 trace elements 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 also still was 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.

Badano zawartość 34 pierwiastków śladowych w opadzie atmosferycznym wokół kompleksu hutniczego w mieście w północnej Norwegii. Badania przeprowadzono w latach 2000 i 2005 za pomocą neutronowej analizy aktywacyjnej próbek mchu rosnącego w naturalnych warunkach. Za pomocą analizy czynnikowej zidentyfikowano wkład do tego opadu z dwóch sąsiednich ale różnych pieców hutniczych oraz zmiany w procesie produkcyjnym jakie zaszły w okresie pomiędzy dwoma czasami pobierania próbek. Względny wkład z obu źródeł w różnych miejscach pobierania próbek przedstawiono za pomocą funkcji oceniających. W roku 2000 emisja z pieca do wyrobu żelazostopów (Piec I) spowodowała istotny opad Cr i Fe a także była głównym źródłem Al, V, Co, Ni, As, Mo i W. Położony w pobliżu

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** Dedicated to Professor Rajmund Dybczynski on the occasion of his 75th birthday.
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 pollution is measuring air concentrations based on aerosol collection on filters. This requires a certain technical setup 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 [1, 2].

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 [3] and Cu–Ni smelters [4]. In Norway this technique has been used regularly since 1977 for metal deposition monitoring on a national scale [5–7]. Although the main problem of atmospheric metal deposition in Norway is associated with long-range transport from other European countries [8, 9], there are also a few industries that are sources of significant metal pollution on a 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 [10].

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.
Identification of metal emissions from adjacent point sources

EXPERIMENTAL

Materials and methods

The town of Mo i Rana is situated at 66° 20’ N, 14° 10’ E in the inner end of the eastbound Rana fjord, at about 60 km distance from the Norwegian Sea, and has around 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 Figure 1.

Figure 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 – Ferroalloy smelter (Smelter I); S – Iron smelter (Smelter II)

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 Figure 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 [5].

The moss samples were analysed 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, Sh, I, Cs, Ba, La, Sm, Tb, Yb, Hf, Ta, W, Au, Th, U) using epithermal neutron activation analysis (ENAA). ENAA was carried out at the IBR-2 pulsed fast reactor in Dubna, Russia, according to procedures described elsewhere [11–12].

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 [13]. The analyses were performed separately for the two data sets from 2000 and 2005 using principal component extraction, 1 as the eigenvalue factor selection criterion, and VARIMAX rotation of the extracted factors. Variables with factor loadings higher than 0.6 (cfr. Tab. 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 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.

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 are shown in Figures 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.

![Figure 2. Factor scores for different sampling sites in 2000](image-url)
Table 1. Factor analysis for 2000 samples

(a)

<table>
<thead>
<tr>
<th></th>
<th>Factor 1</th>
<th>Factor 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.89</td>
<td>0.25</td>
</tr>
<tr>
<td>V</td>
<td>0.97</td>
<td>0.23</td>
</tr>
<tr>
<td>Cr</td>
<td>0.92</td>
<td>-0.05</td>
</tr>
<tr>
<td>Mn</td>
<td>0.47</td>
<td>0.79</td>
</tr>
<tr>
<td>Fe</td>
<td>0.86</td>
<td>0.41</td>
</tr>
<tr>
<td>Co</td>
<td>0.97</td>
<td>0.01</td>
</tr>
<tr>
<td>Ni</td>
<td>0.98</td>
<td>0.04</td>
</tr>
<tr>
<td>Zn</td>
<td>0.47</td>
<td>0.85</td>
</tr>
<tr>
<td>As</td>
<td>0.99</td>
<td>0.11</td>
</tr>
<tr>
<td>Mo</td>
<td>0.79</td>
<td>0.57</td>
</tr>
<tr>
<td>Sb</td>
<td>-0.06</td>
<td>0.89</td>
</tr>
<tr>
<td>La</td>
<td>0.88</td>
<td>0.23</td>
</tr>
<tr>
<td>W</td>
<td>-0.08</td>
<td>0.96</td>
</tr>
<tr>
<td>Expl. Var</td>
<td>8.04</td>
<td>3.75</td>
</tr>
<tr>
<td>Prp. Totl</td>
<td>0.62</td>
<td>0.29</td>
</tr>
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</table>

Factor analysis for 2005 samples

(b)

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<th>Factor 2</th>
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</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.81</td>
<td>0.52</td>
</tr>
<tr>
<td>V</td>
<td>0.73</td>
<td>0.62</td>
</tr>
<tr>
<td>Cr</td>
<td>0.85</td>
<td>0.43</td>
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Table 1. (Continuation)

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<th>Factor 2</th>
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</thead>
<tbody>
<tr>
<td>Mn</td>
<td>0.94</td>
<td>0.20</td>
</tr>
<tr>
<td>Fe</td>
<td>0.54</td>
<td>0.73</td>
</tr>
<tr>
<td>Co</td>
<td>0.93</td>
<td>0.28</td>
</tr>
<tr>
<td>Ni</td>
<td>0.84</td>
<td>0.51</td>
</tr>
<tr>
<td>Zn</td>
<td>0.20</td>
<td>0.96</td>
</tr>
<tr>
<td>As</td>
<td>0.89</td>
<td>0.45</td>
</tr>
<tr>
<td>Mo</td>
<td>0.81</td>
<td>0.58</td>
</tr>
<tr>
<td>Sb</td>
<td>0.56</td>
<td>0.81</td>
</tr>
<tr>
<td>La</td>
<td>0.72</td>
<td>0.60</td>
</tr>
<tr>
<td>W</td>
<td>0.37</td>
<td>0.92</td>
</tr>
<tr>
<td>Expl. Var</td>
<td>7.13</td>
<td>5.08</td>
</tr>
<tr>
<td>Prp. Totl</td>
<td>0.55</td>
<td>0.39</td>
</tr>
</tbody>
</table>

Figure 3. Factor scores for different sampling sites in 2005
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, 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–RE is strongly coherent in both years. U on the other hand is strongly correlated with Fe, Hf, and Ta (but not with Cr) in 2000 and with Ni, As, Mo, Ba, and RE in 2005.

Table 2. Maximum values observed in moss samples from Mo i Rana 2000 and 2005 compared to data from regional background sites

<table>
<thead>
<tr>
<th>Element</th>
<th>2000</th>
<th>2005</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum ppm</td>
<td>Background level ppm</td>
</tr>
<tr>
<td>Na</td>
<td>580</td>
<td>130</td>
</tr>
<tr>
<td>Mg</td>
<td>4700</td>
<td>520</td>
</tr>
<tr>
<td>Al</td>
<td>11700</td>
<td>910</td>
</tr>
<tr>
<td>Cl</td>
<td>380</td>
<td>110</td>
</tr>
<tr>
<td>K</td>
<td>5800</td>
<td>2800</td>
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Table 2. (Continuation)

<table>
<thead>
<tr>
<th>Element</th>
<th>2000</th>
<th>2005</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum. ppm</td>
<td>Background level. ppm</td>
</tr>
<tr>
<td>Ca</td>
<td>19200</td>
<td>3000</td>
</tr>
<tr>
<td>Sc</td>
<td>3.4</td>
<td>0.08</td>
</tr>
<tr>
<td>V</td>
<td>77</td>
<td>1.5</td>
</tr>
<tr>
<td>Cr</td>
<td>19000</td>
<td>9.5</td>
</tr>
<tr>
<td>Mn</td>
<td>2500</td>
<td>380</td>
</tr>
<tr>
<td>Fe</td>
<td>21100</td>
<td>690</td>
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<tr>
<td>Co</td>
<td>16.0</td>
<td>0.24</td>
</tr>
<tr>
<td>Ni</td>
<td>95</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>Zn</td>
<td>1090</td>
<td>34</td>
</tr>
<tr>
<td>As</td>
<td>4.8</td>
<td>0.11</td>
</tr>
<tr>
<td>Se</td>
<td>0.34</td>
<td>0.20</td>
</tr>
<tr>
<td>Br</td>
<td>8.7</td>
<td>4.3</td>
</tr>
<tr>
<td>Rb</td>
<td>27</td>
<td>6.6</td>
</tr>
<tr>
<td>Sr</td>
<td>63</td>
<td>9</td>
</tr>
<tr>
<td>Mo</td>
<td>2.4</td>
<td>0.20</td>
</tr>
<tr>
<td>Sb</td>
<td>0.44</td>
<td>0.04</td>
</tr>
<tr>
<td>I</td>
<td>6.2</td>
<td>2.7</td>
</tr>
<tr>
<td>Cs</td>
<td>1.0</td>
<td>0.13</td>
</tr>
<tr>
<td>Ba</td>
<td>110</td>
<td>21</td>
</tr>
<tr>
<td>La</td>
<td>6.2</td>
<td>0.39</td>
</tr>
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(Continuation on the next page)
Identification of metal emissions from adjacent point sources

Table 2. (Continuation)

<table>
<thead>
<tr>
<th>Element</th>
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<th></th>
<th>2005</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Maximum. ppm</td>
<td>Background level. ppm</td>
<td>Maximum. ppm</td>
<td>Background level. ppm</td>
</tr>
<tr>
<td>Sm</td>
<td>0.21</td>
<td>0.04</td>
<td>1.35</td>
<td>0.05</td>
</tr>
<tr>
<td>Tb</td>
<td>0.033</td>
<td>0.006</td>
<td>0.19</td>
<td>0.009</td>
</tr>
<tr>
<td>Yb</td>
<td>0.094</td>
<td>&lt; 0.02</td>
<td>0.42</td>
<td>&lt; 0.02</td>
</tr>
<tr>
<td>Hf</td>
<td>0.86</td>
<td>&lt; 0.05</td>
<td>9.8</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>Ta</td>
<td>0.05</td>
<td>0.01</td>
<td>0.26</td>
<td>0.01</td>
</tr>
<tr>
<td>W</td>
<td>6.0</td>
<td>0.13</td>
<td>13.3</td>
<td>0.42</td>
</tr>
<tr>
<td>Au</td>
<td>0.009</td>
<td>0.002</td>
<td>0.030</td>
<td>0.005</td>
</tr>
<tr>
<td>Th</td>
<td>0.37</td>
<td>0.06</td>
<td>1.9</td>
<td>0.08</td>
</tr>
<tr>
<td>U</td>
<td>0.20</td>
<td>0.03</td>
<td>1.1</td>
<td>0.06</td>
</tr>
</tbody>
</table>

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


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