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Emission and long-range transport of trace elements in Europe

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ABSTRACT

Anthropogenic emissions of several trace elements have been estimated for European countries, using appropriate emission factors and available statistical information on industrial production and energy consumption. The emission estimates are compared with measured daily air concentrations at Birkenes in Southern Norway, using a simple trajectory model for selected days, and a statistical trajectory sector analysis for the whole period August 1978–June 1979. The results show good agreement between measured and calculated concentrations for V, Mn, Cr, Cd and Pb, while air concentrations of As, Sb and Se are not fully accounted for by the emission estimates.

1. Introduction

Many trace elements are emitted to the atmosphere because of their volatility in high-temperature combustion and metal extraction processes, or because of their industrial or technological application. The presence of these elements in aerosol and precipitation samples is well documented (e.g. Peirson et al., 1973; Rahn, 1976), and the use of these elements as tracers of long range transport of air pollutants has been demonstrated (Rahn and McCaffrey, 1980; Lannefors et al. 1980). However, no systematic comparison of emissions, with measured air concentrations or depositions has been carried out so far. The reason for this has mainly been lack of relevant emission data, with appropriate spatial resolutions for calculation of ambient concentrations. In an attempt to provide this data base, Pacyna (1983), has used emission factors for thermal electric power plants and other sources of trace elements together with statistical information on industrial production and fuel consumption to provide a spatially resolved emission survey for trace elements in Europe. The purpose of this paper is to compare these emission data with measured air concentrations, with the help of trajectory model calculations (Eliassen, 1978) and trajectory sector statistics.

2. Anthropogenic emission of trace elements in Europe

14 trace elements: As, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, V and Zn are considered in this work. Selection was based on their enrichment in ambient aerosols relative to the earth's crust and biological impacts on the environment. Fuel combustion, non-ferrous metal manufacturing, ferrometallurgical processes, waste incineration and cement and fertilizer production are involved, as the major European sources of trace element emission. Based on: (1) trace element emission factors estimated separately for all the sources considered, and (2) statistical information on the consumption of ores, rocks and fuel, and the production of various types of industrial goods, the emission of trace elements in Europe was calculated (Pacyna, 1984). The results are presented in Table 1. Information on types of fuel, ores and rock and differences in manufacturing techniques used in the European countries have been considered. Different types of dust removal installations and their

Table 1. *Emission of trace elements in 1979 ($t \cdot year^{-1}$)*

Europe	As	Be	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Sb	Se*	V	Zn
coal combustion	460	50	146	851	2,390	1,870	2,030	595	2,970	1,670	276	208	1,500	2,350
oil combustion	218		110	1,150	384	1,550	363	250	9,080	1,120		165	32,900	790
wood combustion	40		25			1,500			375	562				4,590
gasoline combustion			31				92		1,330	74,300				
mining			1			192	275		1,640	1,090		0.2		460
primary non-ferrous metal production														
copper-nickel smelters	4,490		595			7,850				9,250				2,500
zinc-cadmium smelters	910		1,550			440	13			7,880		13		48,800
lead smelters	300		8			120	3		140	10,450				180
secondary non-ferrous metal production														
copper			2			61				55	1			660
zinc														2,630
lead			1							387				150
iron, steel and ferro-alloy manufacturing			58		15,400	1,710	14,770		340	14,660				10,250
refuse incinerators	11		84	4	53	260	114		10	804	100	32	19	5,880
phosphate fertilizers			27			77			77	6		v.s.		230
cement production			15		663					746				
industrial applications	136													
TOTAL	6,500	50	2,700	2,000	18,900	15,500	17,600	850	16,000	123,000	380	420	34,500	80,000

* The Se emission with particles. An additional amount of 560 t $year^{-1}$ of selenium emitted in the vapor phase should also be considered when calculating the long-range transport of this element.

v.s. = very small.

effectiveness have been taken into account, as well as import-export relations of fuels and ores between particular countries. The details about a methodology of calculation and statistical data used were published elsewhere (Pacyna, 1984). The % contribution of particular sources in the total anthropogenic emission of trace elements in Europe is presented in Table 2.

As can be seen from Tables 1 and 2, beryllium, cobalt, molybdenum, antimony and selenium are emitted chiefly from combustion of coal, while nickel and vanadium are released mainly from oil combustion. Smelters and secondary non-ferrous metal plants release the largest amounts of arsenic, cadmium, copper and zinc. Chromium and manganese are emitted mainly from factories producing iron, steel and ferro-alloys. Finally, lead enters the environment primarily as a result of gasoline combustion. Interesting results were obtained when calculating the trace element emissions in particular countries in Europe (Pacyna, 1984). The results are presented in Table 3.

It must be admitted that for some sources as well as for certain countries the information necessary for calculations was difficult to obtain or simply lacking. The uncertainties included data on: (1) trace element concentrations in fuels and other materials, (2) industrial technologies, and (3) the efficiences of control devices. Assumptions made in this work simplify the emission calculations. However, we believe that the additional emissions of trace elements not considered in this paper are low and can be neglected when considering the estimation of total emission in Europe.

3. Natural sources of trace elements

Our knowledge about emission of several elements from natural sources is limited, because there have been very few direct measurements of emission rates or mobilization rates from these processes. Wind erosion, volcanoes, forest wildfires, vegetation and seasalt sprays release trace elements to the atmosphere. The world-wide emission of trace elements from the above-mentioned sources is compared to the anthropogenic emission of these pollutants in Europe and is presented in Table 4 (Nriagu, 1979; Walsh et al., 1979; Pacyna, 1982).

The most important natural source of trace elements is windblown dust. This process occurs mainly in desert areas and these are far from the study region. Thus, the world-wide manganese emission from windblown dust exceeding by more than 24 times the anthropogenic emission of manganese in Europe, is still to be

Table 2. *Main anthropogenic emission sources of trace elements in Europe in 1979*

Metal	Main sources (% contribution to the total emission)
As	copper-nickel smelters (68), zinc-cadmium smelters (14), combustion of fuels (10)
Be	coal combustion (almost 100)
Cd	zinc-cadmium smelters (60), copper-nickel smelters (23), combustion of fuels (10), refuse incinerators (3)
Co	combustion of fuels (almost 100)
Cr	iron, steel and ferro-alloy making (80), combustion of fuels (15)
Cu	copper-nickel smelters (50), combustion of fuels (22), iron, steel and ferro-alloy making (11), wood combustion (11)
Mn	iron, steel and ferro-alloy making (84), coal combustion (11)
Mo	combustion of fuels (almost 100)
Ni	oil combustion (60), coal combustion (17), mining and refining (10)
Pb	gasoline combustion (60), non-ferrous metal production (22), iron, steel and ferro-alloy making (12)
Sb	coal combustion (74), refuse incinerators (25)
Se*	combustion of fuels (almost 100)
V	oil combustion (almost 100)
Zn	zinc-cadmium smelters (60), iron, steel and alloy manufacturing (13), refuse incinerators (17), wood combustion (6)

* Released with particles.

Table 3. *Emissions of trace elements for all sources in Europe in 1979 ($t \cdot year^{-1}$)*

Country	Element ... As	Be	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Sb	Se	V	Zn
Albania	31	0.1	1	3	5	71	1	1	92	134	0.4	0.5	43	72
Austria	103	0.2	137	22	200	134	182	6	184	1,933	1.1	4.5	552	4,370
Belgium	360	0.5	171	55	642	613	613	25	381	3,986	10.9	11.4	908	4,736
Bulgaria	152	1.4	67	47	181	208	218	22	291	2,234	7.5	9.7	701	1,722
Czechoslovakia	86	3.1	23	86	791	323	712	44	472	1,726	16.8	18.0	943	635
Denmark	7	0.1	9	23	50	38	37	6	185	753	12.2	3.8	596	706
Finland	127	0.2	84	23	115	246	109	7	237	1,621	1.2	4.1	565	2,460
France	228	1.4	170	103	1,095	450	1,192	34	903	10,545	30.3	18.0	2,338	6,127
German Dem. Rep.	133	4.7	37	108	528	376	432	61	549	2,084	25.1	24.1	965	746
German Fed. Rep.	782	3.9	328	136	2,153	1,552	2,054	60	1,013	9,308	49.5	46.6	2,222	11,689
Greece	10	0.2	4	17	77	55	45	6	273	1,303	1.6	3.1	372	121
Hungary	34	0.6	8	24	198	509	160	10	162	888	3.4	4.6	389	280
Iceland*	73	—	81	378	336	514	—	84	4,130	36,300	—	53	10,900	264
Ireland	2	0.1	1	8	11	13	8	2	65	456	0.4	1	199	33
Italy	93	0.8	124	150	1,055	385	925	38	1,300	9,365	16	24	3,952	4,420
Netherlands	58	0.3	88	38	255	105	253	10	321	2,427	9.3	7.9	979	3,067
Norway	36	v.s.	39	6	40	56	45	2	66	803	0.2	1.2	160	1,188
Poland	656	8.2	207	151	1,161	1,313	1,009	97	653	4,568	43.0	37.0	672	4,725
Portugal	7	v.s.	3	10	27	29	20	2	97	525	0.1	1.4	268	39
Romania	35	2.4	13	61	619	228	554	33	338	1,827	12.7	13.1	660	614
Spain	302	0.9	126	61	571	565	427	20	510	5,534	4.8	10.9	1,373	3,255
Sweden	147	0.1	16	36	195	237	172	9	323	2,270	0.4	5.4	1,003	346
Switzerland	1	v.s.	1	5	40	18	25	1	51	1,083	0.03	0.6	130	50
Turkey	62	1.1	17	30	147	427	126	15	277	1,180	6.0	5.1	419	994
USSR	2,812	15.0	816	631	7,147	6,535	6,874	257	6,014	43,842	80.0	120.0	11,262	21,281
United Kingdom	164	4	99	130	1,134	580	1,032	60	899	10,098	40.0	36.0	2,074	3,488
Yugoslavia	134	0.8	65	40	205	287	177	16	284	2,423	5.3	7.6	718	2,013
Luxemburg	0.4	v.s.	1.1	1.3	196	24	192	0.4	15	301	0.6	0.2	30	158
Total	6,500	50	2,700	2,000	18,900	15,500	17,700	850	16,000	123,000	380	420	34,500	80,000

* kg year $^{-1}$

v.s. = very small.

Table 4. *World-wide emission trace elements to the atmosphere from natural sources and the European emission from anthropogenic sources in 1979 (in 10^3 t · year^{-1})*

	World-wide emission from natural sources					
Element	Windblown dust	Volcanoes	Forest wildfires	Vegetation	Seasalt sprays	Anthropogenic emission in Europe
As	0.2	7.0	0.2	0.3	0.1	6.5
Cd	0.1	0.5	n.d.	0.2	n.d.	2.7
Co	4.0	1.4	n.d.	n.d.	n.d.	2.0
Cu	12.0	3.6	0.3	2.5	0.1	15.5
Cr	50.0	3.9	n.d.	n.d.	n.d.	18.9
Mn	425.0	82.5	n.d.	n.d.	n.d.	17.6
Ni	20.0	3.8	0.6	1.6	0.1	16.0
Pb	16.0	6.4	0.5	1.6	n.d.	123.0
Se	0.3	0.1	n.d.	n.d.	n.d.	0.4
V	50.0	6.9	n.d.	n.d.	n.d.	34.5
Zn	25.0	7.0	2.1	9.4	n.d.	80.0

n.d. = no data available.

neglected when considering the total emission of the metal in Europe.

Volcanoes seem to be the major natural source of cadmium and arsenic in the atmosphere. In Europe, there has been a few investigations on trace element emission from Mount Etna in Sicily. Buat-Mènard and Arnold (1978) estimated that about 10 t yr^{-1} cadmium was discharged into the atmosphere from this volcano as particulate matter.

No measurements have been made to assess the quantity of cadmium in the gaseous state. However, Hutton (1982) suggests after Buat-Mènard that the annual cadmium emission from Mount Etna is within the range of 10–40 t. These values are rather low even compared to the annual cadmium emission of 124 t from anthropogenic sources in Italy, calculated in this work. No published information exists on trace element emission from other volcanoes in Europe. Hutton (1982) indicates that these volcanoes are far less important than Mount Etna due to the quantity of particulate matter released.

Taking into account both the absence of desert areas in Europe and low emission of trace elements from European volcanoes, it was found in this work that emission of trace elements from natural sources in Europe is insignificant compared to that from anthropogenic sources.

4. Spatial distribution of trace element emissions in Europe

Application of trace elements as indicators of origin for aerosols in remote areas requires not only knowledge of the amounts of trace elements emitted from particular European countries but the spatial distribution of these emissions as well. In this work, the spatial distributions of the trace elements were based on location and capacities of power plants, smelters, mines, incinerators, steel and iron factories, and other industrial plants. The EMEP grid system was used (Dovland and Saltbones, 1979). The grid length was 150 km. Further details on the EMEP grid system are available from previous reports (Amble, 1981; Semb and Amble, 1981).

2 examples of the trace element emission distribution in Europe are given in Figs. 1 and 2, for vanadium and beryllium, respectively. Vanadium released mostly from oil combustion is emitted mainly in Western Europe and in the European part of the USSR. The largest amounts of beryllium are released in eastern Europe and in the European part of the USSR. Places dashed in Figs. 1 and 2 show areas with higher emission than the average emissions of vanadium and beryllium in Europe. The spatial distributions of all elements considered in this work are available in other report (Pacyna, 1983).

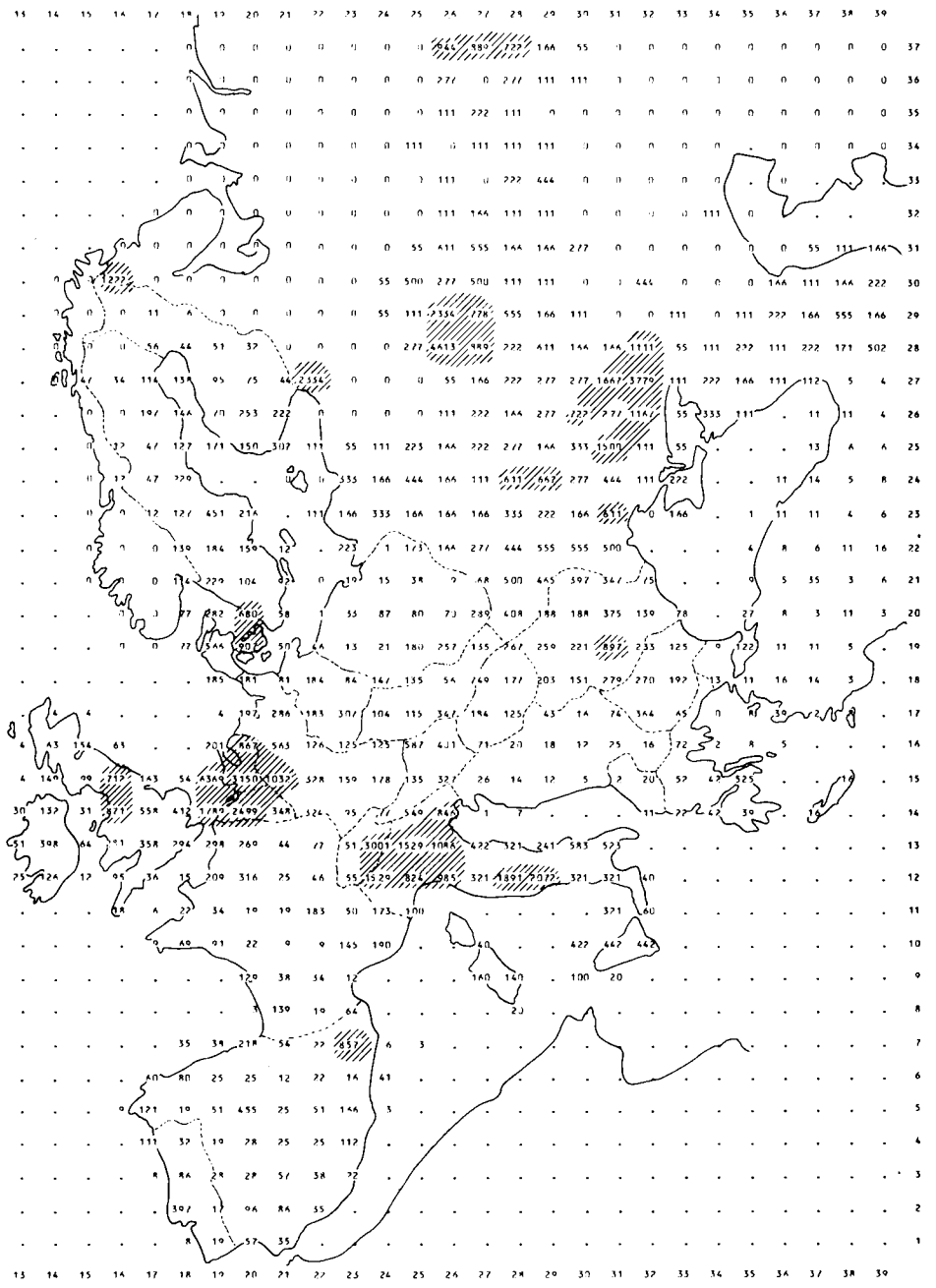

Fig. 1. Spatial distribution of vanadium emission in Europe in 1979 in 10^2 kg year^{-1}. The shaded areas represent locations with emissions higher than the average for the grid area.

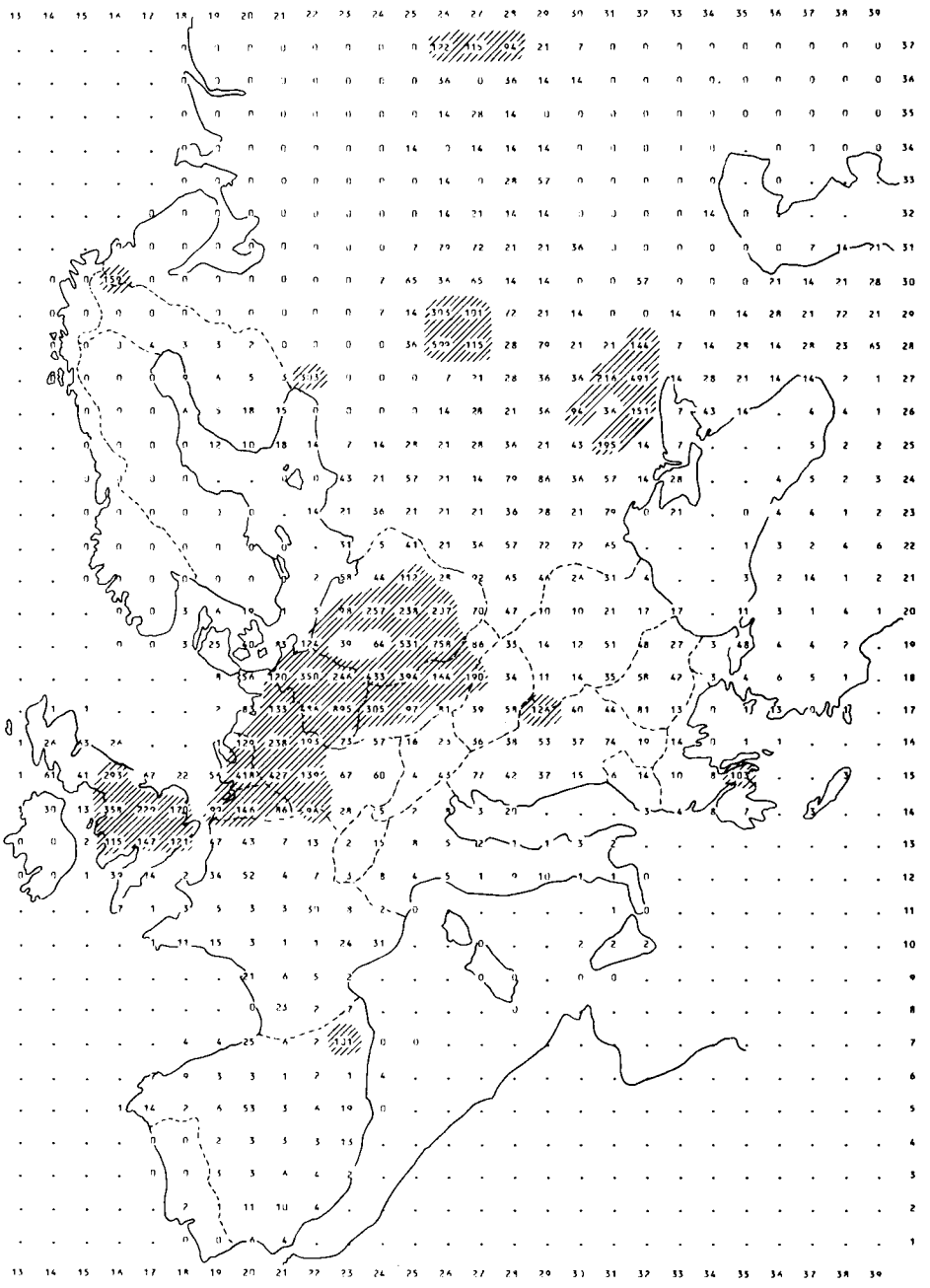

Fig. 2. Spatial distribution of beryllium emission in Europe in 1979 in kg year^{-1}. The shaded areas represent locations with emissions higher than the average for the grid area.

5. Measured concentrations of trace elements at Birkenes

Sampling of aerosols for subsequent trace element analysis was carried out in the period August 1978–June 1979 at 3 rural sites in Norway. Approximately 1900 m^3 of air were drawn through a 142 mm diameter Whatman 41 cellulose fibre filter, using a fan pump with brushless motors. The sampling period was 24 h for the results which are to be considered here. After sampling, the filter was segmented in 4 parts. Instrumental neutron activation analysis on one of the segments was used for the determination of Na, Al, Sc, ti, V, Cr, Mn, Fe, Cu, As, Se, Br, Sb, Ba, La, and W. A nitric acid extract of another segment was used for the determination of Pb, Cd and Zn by atomic absorption spectrometry, using a Massman furnace with automatic injection for the two former elements.

Weekly bulk precipitation samples were also analysed by instrumental neutron activation analysis (INNA) and atomic absorbtion spectrophotometry (AAS). A summary of the results has been presented earlier (Hanssen et al., 1980). Table 5 gives the observed monthly mean concentrations for the Birkenes site. This station has served as a monitoring station for long-range transport of air pollutants in Norway since 1972 and receives polluted air from most of the countries in Europe (OECD, 1979).

The observed concentration levels, and particularly the ratios between the individual elements, are comparable with earlier observations of trace elements in Norway (Semb, 1978), as well as with observations at Lerwick, Shetland (Peirson et al., 1973) and in Sweden. The values for zinc on the air filters from Birkenes are very high, however, and may be due to contamination by the sampling equipment. This is supported by comparison with precipitation samples. Washout factors are generally around 1 $m^3 \cdot cm^{-3}$ for most of the elements, from which it may be inferred that the "true" airborne zinc concentration is probably around 20 $ng \cdot m^{-3}$ as a yearly mean value. The results for selenium are also anomalous in that the apparent concentration of this element in the air samples is less than would be expected from the precipitation samples. It is possible that the selenium found in the precipitation is derived from volatile compounds not retained on the air filters. The detection limits of the analytical method are also given in Table 5. Daily mean concentrations at, or below, the cited detection limits occur mainly for the elements Cr and Sb, but are of little consequence for the calculated monthly, or yearly, mean concentrations.

6. Application of the emission data to model longe-range transport of trace elements over Europe

Emission data calculated in earlier sections have been used to estimate concentrations of trace elements. Then, the estimated concentrations were compared with measurements.

6.1 *Estimation of trace element concentrations using a simple trajectory model*

A simple trajectory model has been used to calculate the trace element concentrations in air over southern Norway. The following trace elements were considered for calculations: arsenic, cadmium, copper, chromium, manganese, lead, antimony, vanadium and zinc. These are elements for which measurement data were available. The model describes the horizontal dispersion of trace elements within an atmospheric boundary layer. Calculations are based on trajectories followed for 96 h, arriving at the centre of all emission grid elements every 6 h. The model is very similar to the model that was used in the OECD program on long-range transport of sulphur compounds (OECD, 1979; Eliassen, 1978; Eliassen and Saltbones, 1982).

The mass-balance equation is:

$$\frac{dq}{dt} = (1 - \alpha) \cdot \frac{Q}{h} - k \cdot q, \qquad (1)$$

where:

q = trace element concentrations in air (ng/m^3);
Q = trace element emissions per unit area and time ($ng \cdot m^{-2} \cdot s^{-1}$);
h = mixing layer (m);
k = decay rates for trace elements (wet and dry deposition) (s^{-1});
α = part of trace element emission deposited in the same grid element as it is emitted; this local

Table 5. *Monthly mean concentrations in air (A) (ng m^{-3}) and precipitation (P) ($\mu g l^{-1}$) at Birkenes, Norway for some elements during the period August 1978–June 1979*

Element ...	Na		Al		V		Cr		Mn	
Period	*A*	*P*	*A*	*P*	*A*	*P*	*A*	*P*	*A*	*P*
Aug. 1978	452	515	155	26	2.6	1.2	1.0	—	6.4	<5
Sept. 1978	551	675	46	19	1.8	0.7	0.6	—	4.2	<5
Oct. 1978	637	1,200	56	27	4.4	2.1	1.0	—	6.2	8
Nov. 1978	1,099	2,285	27	29	1.1	1.3	0.4	—	3.3	16
Dec. 1978	236	3,650	34	155	3.2	3.6	0.9	—	4.3	10
Jan. 1979	288	1,320	38	29	4.0	2.0	1.0	—	5.8	<5
Feb. 1979	393	1,755	62	29	3.9	4.1	1.6	—	8.0	10
Mar. 1979	1,122	1,065	80	26	4.3	1.1	1.2	—	8.3	5
Apr. 1979	286	500	96	40	3.5	1.6	1.2	—	5.2	<5
May 1979	532	400	105	81	2.9	1.1	1.1	—	3.6	8
June 1979	248	555	94	38	1.7	1.4	0.6	—	4.7	9
Aug. 1978–June 1979	523	1,270	71	53	3.1	1.8	1.0	—	5.4	7.4
detection limit	10	—	10	5	0.05	0.2	0.3	—	0.5	5

Element ...	As		Sb		Br		Cu		Pb	
	A	*P*	*A*	*P*	*A*	*P*	*A*	*P*	*A*	*P*
Aug. 1978	0.79	0.5	0.42	0.7	5.6	7.7	10	—	15	7
Sept. 1978	0.41	0.5	0.27	0.7	5.8	8.4	5	—	12	4
Oct. 1978	1.6	1.0	0.65	1.8	7.0	16.9	23	—	31	13
Nov.1978	0.39	0.9	0.23	2.3	4.1	24.8	5	—	11	7
Dec. 1978	0.94	0.5	0.19	0.4	2.3	23.4	<5	—	16	11
Jan. 1979	1.1	0.8	0.31	0.3	3.7	13.7	<5	—	18	11
Feb. 1979	1.8	0.7	0.80	0.6	5.1	20.0	6	—	27	14
Mar. 1979	1.4	0.8	0.57	0.2	7.8	9.5	5	—	27	10
Apr. 1979	1.0	0.9	0.41	0.4	2.8	7.2	<5	—	17	12
May 1979	1.4	1.1	0.54	0.3	4.1	8.7	7	—	23	14
June 1979	0.55	0.6	0.31	0.2	3.1	8.9	<5	—	13	9
Aug. 1978–June 1979	1.0	0.8	0.43	0.6	4.6	12.9	7	—	19	11
detection limit	0.1	0.1	0.1	0.1	0.5	0.1	5	—	0.2	1

Element ...	Cd		Zn			
Period	*A*	*P*	*A**	*P*	SO_2–S	SO_4–S
Aug. 1978	0.36	0.16	(210)	9	0.7	0.61
Sept. 1978	0.17	0.10	(50)	7	0.3	0.43
Oct. 1978	0.57	0.36	(276)	23	1.0	1.13
Nov. 1978	0.19	0.26	(43)	12	0.4	0.23
Dec. 1978	0.20	0.28	(46)	29	1.5	1.0
Jan. 1979	0.19	0.22	(46)	19	1.5	1.09
Feb. 1979	0.35	0.29	(97)	24	2.3	1.63
Mar. 1979	0.32	0.23	(150)	12	4.2	2.68
Apr. 1979	0.22	0.21	(85)	13	1.5	2.20
May 1979	0.32	0.46	(200)	22	1.1	1.89
June 1979	0.16	0.19	(51)	24	0.6	1.41
Aug. 1978–June 1979	0.28	0.27	(112)	15	1.6	1.43
detection limit	0.01	0.05	1	0.1	0.1	0.01

* The zinc concentrations in parenthesis are unreliable as explained in the text.

deposition supplements the deposition included in the decay rate k.

The trace element emissions per unit area and time were calculated using spatial distributions of trace element emissions presented in previous chapters. Eliassen and Saltbones (1982) have a scheme for estimating the variable mixing height for Europe from the information provided by radiosonde data. However, since this is a preliminary study it was decided in this work, to assume constant mixing height of 1000 m. Decay rates for trace elements have been estimated applying deposition velocities of the pollutants and a constant mixing height. Further, the effect of precipitation was not considered in this work. Our knowledge of complicated physical and chemical processes leading to wet deposition of trace elements is very incomplete. Thus, the wet deposition process has not been considered when calculating decay rates of trace elements, leading to a slight overestimation of trace element concentrations. The following dry deposition velocities for aerosols containing the respective trace elements were assumed to be representative for decay rate calculations in the study region: 0.1 cm s^{-1} for cadmium and lead; 0.2 cm s^{-1} for arsenic and antimony; 0.3 cm s^{-1} for vanadium; 0.4 cm s^{-1} for copper, chromium and zinc; and 0.5 cm s^{-1} for manganese (Welsh Office, 1975; Cawse, 1981).

A part of the trace element emission is deposited in the same grid element as it is released, being an additional local dry deposition. For the purpose of this work, a value of 0.05 for the local deposition was subjectively inferred, based on the literature (OECD, 1979). This value represents a first approximation and can be underestimated for highly industrialized areas or overestimated in areas with emissions from very tall stacks.

Two other simplifications were also made when calculating the trace element concentrations: (1) no exchange of pollution between the boundary layer and the free troposhere, and (2) uniform concentrations within the mixing layer.

The mass balance equation (1) can be integrated along the calculated trajectories. Since eq. (1) is linear in the concentration q, the contributions from the emissions at individual positions along a trajectory were considered separately, and added to give complete concentrations. For a trajectory section consisting of N positions or time-steps Δt, one obtains

$$q(N\Delta t) = q(0) \cdot e^{-k \cdot N \cdot \Delta t} + \sum_{i=0}^{N=1} (1 - \alpha) \frac{Q_i \cdot \Delta t}{h} \cdot e^{-k \cdot \Delta t}, \quad (2)$$

where:

$q(N\Delta t)$ = trace element concentrations at the end of the trajectory (ng m^{-3});
$q(0)$ = trace element concentrations at the start of the trajectory;
Q_i = trace element emission in the "i" grid, (ng m^{-2} s^{-1});
N = number of trajectory sections, being 24 in this work;
Δt = time-step of 4 hours, (s).

The 850 mb "return-flow" trajectories were calculated for the Norwegian station at Birkenes, using the algorithm given by Petterssen (Petterssen, 1956, OECD, 1979). Then, 15 two-day periods were selected as "episodes". During these periods, the high measurement concentrations were noticed and trajectories were very clearly defined with respect to their origin. 4 representative cases are shown in Fig. 3.

The concentrations of vanadium, manganese, arsenic, antimony, copper, zinc, cadmium, chromium and lead calculated during the episodes are presented in Table 6. In the same table, measurement concentrations of the above-mentioned elements are also included.

6.2 *Comparison of the trace element concentrations measured at Birkenes with the trace element concentrations calculated using a simple trajectory model*

As can be seen from Table 6, differences between calculations and measurements are rather small. To quantify these differences, the relative differences have been calculated using the equation:

$$x = \frac{C_{cal} - C_{meas}}{C_{meas}} \cdot 100\%, \quad (3)$$

where:

x = relative difference (%);
C_{cal} = calculated concentration (ng m^{-3});
C_{meas} = measured concentration (ng m^{-3}).

The best agreement between measurements and

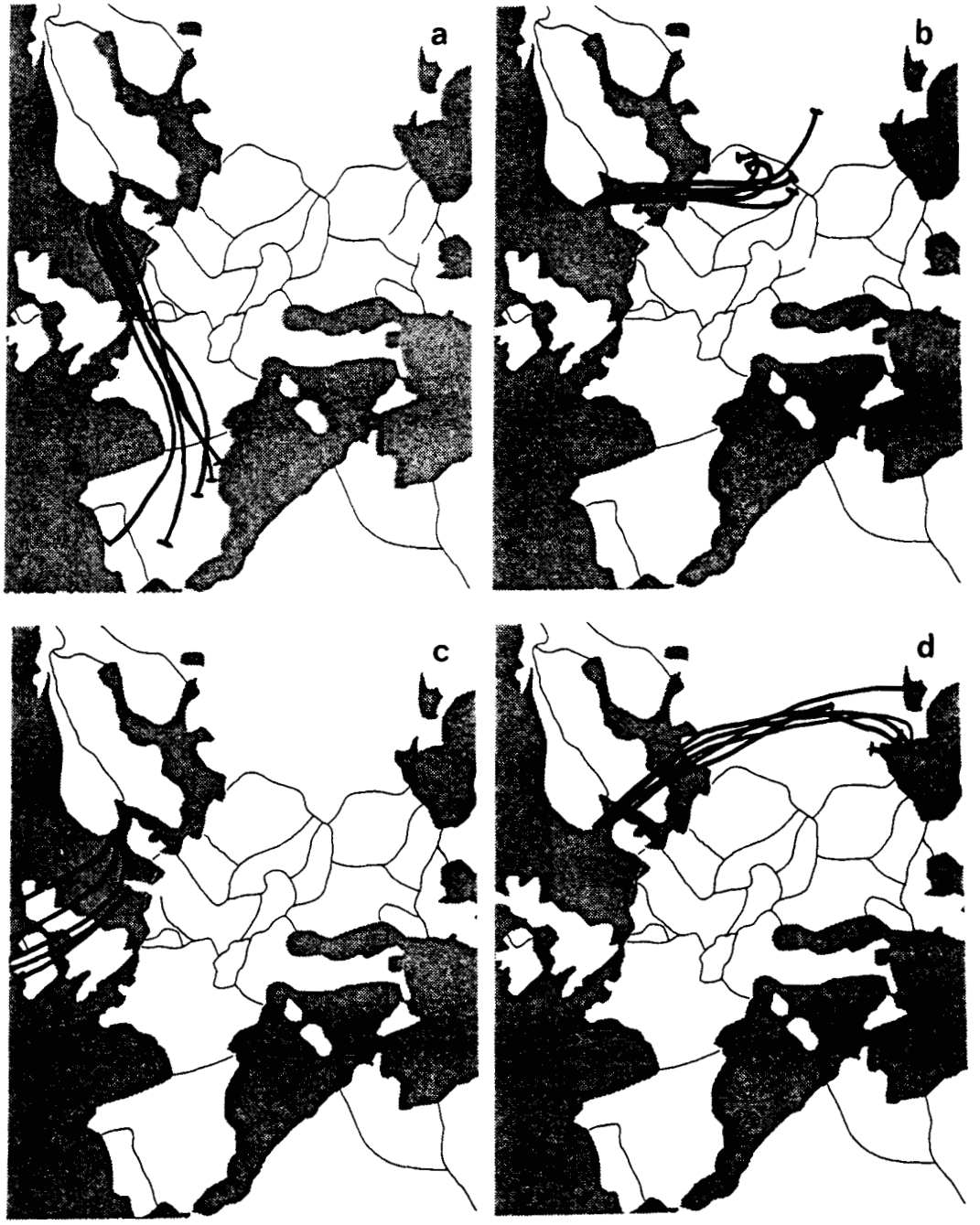

Fig. 3. 96 h, 850 mb back trajectories for events with unusually high concentrations of trace elements at Birkenes. (a) 12–13 Oct. 1978; (b) 23–24 Jan. 1979; (c) 1–2 March 1979; (d) 31 March–1 April 1979.

Table 6. *Estimated and measured concentrations of trace elements at the Birkenes station in 1978–1979 (ng/m³)*

Date	V		Mn		As		Sb		Cu		Zn		Cd		Cr		Pb	
	M	*C*	*M*	*C*	*M*	*C*	*M*	*C*	*M*	*C*	*M*	*C*	*M*	*C*	*M*	*C*	*M*	*C*
21–22 Aug. 1978	8.4	11.2	10.1	12.8	3.5	3.0	1.4	0.2	9.0	5.3	160	110	1.3	1.4	2.7	3.1	75.6	88.2
14–15 Oct. 1978	9.2	9.8	11.0	16.0	4.2	4.1	<0.02	0.2	68.0	7.0	150	146	1.8	2.5	2.0	2.9	71.0	65.2
23–24 Jan. 1979	3.9	5.0	10.0	15.6	0.7	5.3	0.2	0.3	<5.0	6.5	16	43	0.2	0.3	0.8	1.2	17.3	21.3
28–29 Jan. 1979	8.5	10.2	12.0	18.2	1.2	2.3	0.4	0.4	<5.0	6.5	51	58	0.3	0.4	0.9	1.3	16.1	23.2
21–22 Feb. 1979	9.3	8.2	15.0	14.7	2.6	3.7	1.1	0.8	11.0	11.9	152	171	0.6	1.6	3.4	3.3	44.0	38.8
22–23 Feb. 1979	10.0	9.0	14.0	16.4	3.0	3.5	1.5	0.9	6.0	5.8	140	102	0.8	1.4	6.7	7.2	45.8	59.2
01–02 Mar. 1979	19.0	29.4	34.0	51.2	12.0	11.5	2.6	1.0	12.0	21.0	131	145	1.6	2.1	6.2	9.0	22.5	26.5
06–07 Mar. 1979	17.0	16.9	34.0	31.1	5.7	7.0	2.7	0.4	15.0	11.8	545	94	1.6	2.0	4.5	4.1	23.2	19.2
20–21 Mar. 1979	11.0	12.6	6.8	9.6	2.2	2.3	0.9	0.6	5.0	4.0	139	109	0.7	1.1	2.0	3.1	51.4	69.5
29–30 Mar. 1979	4.7	4.2	10.0	8.2	1.5	1.6	0.6	0.8	5.0	3.0	27	32	0.2	0.3	1.7	1.4	24.1	40.2
31–01 Apr. 1979	7.6	7.5	18.0	15.6	2.5	5.1	0.8	0.9	<5.0	9.7	50	65	0.4	0.6	2.3	1.9	32.8	39.5
01–02 Apr. 1979	5.7	7.9	12.0	15.6	1.9	2.4	0.5	0.3	<5.0	3.4	106	88	0.3	0.4	1.5	1.8	22.0	20.6
10–11 Apr. 1979	12.0	13.9	15.0	19.7	2.7	5.3	0.2	0.9	7.0	10.0	36	61	0.6	0.7	4.7	6.5	36.6	42.1
11–12 Apr. 1979	10.0	14.5	10.0	12.3	2.5	2.4	1.0	0.9	12.0	3.4	6	30	0.5	0.64	2.4	2.8	32.0	46.5
06–07 Jun. 1979	4.2	4.8	12.0	15.6	1.3	1.9	0.8	0.7	<5.0	3.4	6	30	0.3	0.51	1.3	1.6	32.5	30.1

M = measured, *C* = calculated.

calculations has been obtained for vanadium. The relative difference of 20% has been estimated for this element. This fact can be interpreted as a confirmation of very accurate emission calculations for vanadium. Slightly higher values of relative differences have been estimated for lead, chromium, manganese and arsenic, being 24, 27, 30 and 34%, respectively. The values of 42 and 49% were calculated as the relative difference for data for copper and cadmium. The highest differences have been estimated for antimony (60%) and zinc (87%). For zinc, this may confirm the suspected contamination of the filter samples as discussed in section 5.

6.3 *Variations in trace element concentrations with direction of arriving air trajectories*

The calculated air trajectories may be used to classify the air samples with respect to emission areas. For this purpose, 8 sectors were defined as shown in Fig. 4. If more than 50% of the data points defining the trajectories during a sample period fall within one of the sectors, the sample is assigned to this sector. If not, the sample is assigned to an imaginary sector 9.

The number of samples and mean concentrations for each of the sectors are given in Table 7. This table also contains mean values of sulphur dioxide and sulphate for comparison purposes.

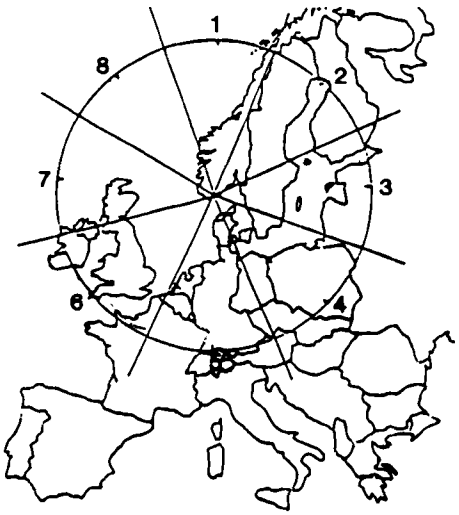

Fig. 4. Eight sectors considered in this work.

As expected, concentrations are high for sectors 4, 5 and 6. Certain elements are especially high in sector 6. This particularly applies to vanadium which is emitted mainly from power plants burning residual fuel oil, and lead, which is released from motor vehicles. The low values for lead in sector 5 may be explained by the restrictions on fuel lead in the Federal Republic of Germany (0.15 $g \cdot l^{-1}$), which is 3 times lower than the level in UK, Belgium and France (0.4 $g \cdot l^{-1}$).

The high values for zinc in sector 6 are difficult to explain. Samples contaminating zinc must have been released in connection with highly acid "white episode" aerosols (Brosset, 1976). Manganese and chromium, which are emitted mainly in connection with steel production, appear to be more equally distributed. This also applies for arsenic, while selenium and antimony are higher in sector 6.

The comparison can be carried out one step further by comparing the concentrations with estimated emissions for the respective sectors. Ideally, this would require weighting of emissions with the probability of trajectory crossings, and allowances for dry deposition and precipitation scavenging. We have chosen a simpler approach, assuming that the emissions of Poland and the USSR are representative for sector 4, and the emissions from the German Democratic Republic and the Federal Republic of Germany are representative for sector 5. For sector 6, we have considered the emissions from the United Kingdom alone, and UK with the addition of emissions from the Netherlands, Belgium, Luxemburg and Northern France. This was done as an attempt to take into account the typical wind shear between 850 mb and the surface.

The mean concentrations of each element were then divided by the total emission of that element for each sector. The ratios were divided by the concentration/emission ratio for vanadium. The results are given in Table 8.

This procedure involves the assumption that all the pollution components behave in the same way with respect to dry deposition and rain scavenging. Values less than one indicate that emissions have been overestimated relative to vanadium, higher values that emissions are underestimated.

It appears that there is reasonable agreement between measurements and estimated emissions for total sulphur, manganese, lead and cadmium. Chromium appears to have been slightly over-

Table 7. *Observed concentrations in air at Birkenes for different sectors of arriving air trajectories* ($ng \cdot m^{-3}$ *except S in* $\mu g \cdot m^{-3}$)

Sector	No. of observations	Na	Al	V	Cr	Mn	Zn	SO_2–S	SO_4–S	As	Se	Sb	Pb	Cd
1	9	295	30	0.45	0.39	3.5	11.9	0.14	0.20	1.56	0.22	0.13	3.86	0.08
2	8	136	92	1.27	0.59	5.0	51.9	1.07	0.55	5.07	0.24	0.15	9.82	0.14
3	20	156	70	4.47	1.19	7.8	30.2	2.31	2.47	8.13	0.32	0.34	13.40	0.21
4	8	164	194	4.37	1.55	7.1	31.7	2.82	2.15	11.96	0.53	0.57	24.47	0.33
5	4	206	49	3.38	0.72	3.9	126.2	1.52	2.54	6.55	0.42	0.41	18.73	0.22
6	15	829	139	7.45	1.94	8.5	530.3	2.21	2.39	7.72	1.69	1.11	48.02	0.94
7	42	818	39	1.71	0.53	3.2	105.5	0.68	0.82	3.92	0.49	0.27	13.60	0.17
8	16	391	46	0.45	0.36	4.1	27.8	0.13	0.22	1.76	0.17	0.11	3.55	0.08
9	55	508	101	4.88	1.51	7.63	92.4	2.46	1.87	1.56	0.74	0.64	27.97	0.35

estimated. A more likely explanation is that this element is emitted with relatively coarse particles with higher deposition velocity. Arsenic, antimony and selenium occur in much higher concentrations than expected for all the sectors, and the information on the emission of these 3 elements is apparently incomplete.

7. Conclusions

Preliminary calculations using a trajectory model show that measurement concentrations of trace elements from long-range transport at Birkenes in Southern Norway can be related to calculated anthropogenic emissions for a number of elements, e.g. V, Pb, Cd, Mn, Cr, for selected days with only slowly changing air trajectories. Too low values have been calculated for antimony, selenium and arsenic, indicating that information on the emission sources is incomplete for these elements. It applies specially for natural sources of selenium and additional anthropogenic sources of antimony and arsenic, such as industrial application of both elements. These sources are not included in emission calculations.

Due to internal contamination of samples, the measured Zn concentrations are believed to be much too high. Thus, it is not possible to draw conclusions for this element. However, it appears that emissions of zinc may have been underestimated.

The sector analysis confirms that element ratios may be used as indicators of origin for aerosols. Vanadium, lead and cadmium have their main emission sources in western Europe, while arsenic, beryllium and molybdenum at Birkenes originate mainly from Eastern Europe.

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Table 8. *Comparison of measured mean concentrations with expected values, using vanadium as reference elements (see text for explanation)*

	Sector 4	Sector 5	Sector 6	
Metal	Poland + USSR	Federal Republic of Germany, German Democratic Republic	UK	The Netherlands, Belgium, Luxemburg, Northern France, and UK.
V	1*	1*	1*	1*
Cr	0.5	0.25	0.5	0.5
Mn	2.4	1.5	2.3	2.2
Zn	3.3	9.6	42	25
S	1.0	1.0	0.5	0.8
As	9.3	6.8	13	8.1
Se	9.2	5.3	13	19
Sb	13	5.0	8	10
Pb	1.4	1.5	1.3	1.8
Cd	0.9	0.6	2.6	1.5

* By definition (reference element).

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