Identification of Individual Aerosol Particles Containing Cr, Pb, and Zn above the North Sea

HANS VAN MALDEREN,
STEFAAN HOORNAERT, AND
RENÉ VAN GRIEKEN*

*Department of Chemistry, University of Antwerp (UIA),
Universiteitsplein 1, B-2610 Antwerp, Belgium*

Aerosol samples have been collected over the southern bight of the North Sea from an aircraft. In this way, 96 samples were taken for single-particle analysis during 16 flights. Almost 45 000 individual particles were analyzed with electron probe X-ray microanalysis. More than 5000 of these were found to contain significant concentrations of one or more of the heavy metals Cr, Pb, and Zn. With the help of hierarchical, nonhierarchical, and fuzzy clustering techniques, various heavy metal-containing particle types could be identified. Significant differences in abundances were detected in the North Sea heavy metal aerosol, depending on the origin of the air masses. In samples with continental influence 50 times more Zn- and Pb-containing particles were found than in samples with a marine history. For Cr, on the other hand, we found abundances in the marine sector that were one-third of the values for continental sectors. This might point to a rather undefined marine source, which could be the recycling of previously deposited material by reinjection into the atmosphere by sea spray. The highest values for Cr-, Pb-, and Zn-containing particles were always detected under southeastern wind directions.

Introduction

During the past few decades, the input of heavy metals to the North Sea has increased significantly due to the growing industrial activity and car traffic in European countries. Despite the first positive signals of improvement, e.g., the reduction of atmospheric Pb levels as a result of the use of unleaded gasoline (*1−3*), the annual total toxicity of all heavy metals mobilized was reported to exceed the combined toxicity of all of the radioactive and organic wastes generated each year (*4*). The ever increasing dispersion of heavy metals through the atmosphere, water, and soil is a major concern due to their hazardous effect on human health, the possible changes they initiate in natural biochemical processes in all ecosystems, and their inevitable accumulation in the food chain.

* Corresponding author fax: +32-3-820-23-76; e-mail address: vgrieken@uia.ua.ac.be.

It has often been demonstrated that wet and dry deposition of pollutants from the atmosphere to the North Sea is a dominant transport system for a number of elements. For several years now, efforts have been made to assess heavy metal concentrations and size distributions over the North Sea and to quantify the deposition fluxes of these elements by using a wide variety of analytical bulk techniques (*5*). Microanalysis techniques, however, have not been widely used, despite their enormous potential to characterize the morphology and composition of micrometer-sized individual aerosol particles. Observation of particular elements allows the identification of specific particle types, characterization of their source, and investigation of their abundance as a function of physical parameters. Moreover, shorter sampling times (minutes rather than hours for bulk analysis) are needed for microanalysis, which allows one to study short time variations in atmospheric composition as a result of wind direction changes and to overcome some of the problems of airborne sampling from airplanes, where shorter sampling times evidently are needed than for ship-based measurements.

The present study is part of a large investigation regarding heavy metal deposition into the North Sea. Several articles have already been published in the framework of this study on the single-particle analysis of particulate atmospheric matter using electron probe X-ray microanalysis (EPXMA) (*6*), especially for giant aerosol particles (*7*), and using laser microprobe mass analysis (*8*). Besides single-particle analysis, bulk analysis by energy-dispersive X-ray spectrometry and proton-induced X-ray emission (*9*) and by differential pulse anodic stripping voltammetry (*10*) was performed in order to obtain atmospheric concentrations of different elements. With these data, several deposition models were tested (*11, 12*), which in the end provided us with estimates for wet and dry deposition fluxes of heavy metals into the North Sea (*2*). The aim of the present article is the detailed identification and characterization of exactly the specific particle types that are responsible for the input of heavy metals Cr, Zn, and Pb.

Experimental Section

The samples were collected during several flights with a twin-engine aircraft, a Piper Chieftain PA 31-350 owned by Geosens B.V. (Rotterdam, The Netherlands), over a period of 13 months. All flights were performed under relatively cloudless and dry conditions. Wind speeds over the sampling campaign were between 2 and 13 m s^{-1}. After takeoff from Rotterdam airport, a spiral flight was initiated at the Goeree platform (51°55′30″ N, 3°40′ E) in order to localize the inversion layer. Once this was done, the aircraft flew tracks of ca. 110 km at six different heights more or less evenly spaced between sea level and the inversion layer. The lowest track, only 10−30 m above sea level, was intended to assess particle resuspension by sea spray. During these tracks, airborne particulate matter was collected on 0.4-μm-pore-size Nuclepore membrane filters using an isokinetic inlet (*13*). The flow rate was approximately 1 m^3 h^{-1}. All tracks were flown parallel with the wind direction to allow later calculation of backward trajectories. These 36-h isobaric back trajectories were provided by the Royal Dutch Meteorological Institute

(KNMI) and are shown in Figure 1. More detailed information about the sampling campaign can be found elsewhere (*14*).

In this way, 96 samples were collected during 16 flights. The analysis of almost 48 000 individual particles (500 in each sample) was done by EPXMA on a JXA-733 Superprobe of JEOL (Tokyo, Japan). For the analysis, an accelerating voltage of 20 kV and a beam current of 1 nA were used. The minimal detection limit for elemental concentration is around 1000 ppm, whereas the minimum detectable particle size is 0.2 μm. EPXMA permits one to obtain morphological parameters such as the diameter and shape factor of a particle, while the chemical composition is derived from an energy-dispersive (ED) X-ray spectrum. More detailed information on this method can be found elsewhere (*6*). The resulting data set contained both morphological and chemical information for almost 48 000 particles.

It is not difficult to imagine that, when working with such large data sets, some method of data reduction is needed. We chose a combined approach of several multivariate cluster techniques. A home-written Windows-based program, called IDAS, was used. More information about the program can be found elsewhere (*15*). Cluster analysis is a well-developed multivariate method, which has been used regularly in connection with single-particle analysis (*16*–*19*). Most of these publications dealt with hierarchical clustering methods. In our case, we applied a combination of hierarchical, nonhierarchical, and fuzzy clustering to our data set.

The clustering was performed on the X-ray elemental intensities emitted by each aerosol particle, and no normalization was done prior to the statistical treatment. Hierarchical cluster analysis (HCA) is the most simple of the three and therefore most frequently used. It has also the advantage of easy visual interpretation with the help of so-called dendrograms. Its main disadvantage lies in the fact that some hierarchical structure is presumed, and this is not always the case when working with atmospheric data sets. This might lead to the misclassification of some particles. Nonhierarchical clustering methods (NHCA) do not have these problems; however, they require prior knowledge about the data structure. This is solved by using the results of the hierarchical clustering as centroids for the nonhierarchical clustering. Both HCA and NHCA are so-called hard clustering methods: this means that one particle belongs to only one cluster after the clustering. In some cases, when dealing with overlapping clusters, this can lead to mistakes in the clustering. This problem is overcome by fuzzy clustering analysis (FCA). The main idea is to replace the procedure of splitting the multivariate data into a certain number of clusters by a procedure of determining the probability of belonging for each object to each cluster. Hard clustering therefore can be considered as a special case of fuzzy clustering, namely, when all membership coefficients but one are equal to 0. More detailed information can be found in a publication by Treiger et al. (*20*). The results of all three types of clustering very much depend on the correct choice of the number of clusters. Previously, this was done on the basis of the personal experience of the analyst rather than on the basis of statistical criteria. This problem was overcome by implementing Akaike's information criterion (AIC), which is based on the relation between entropy and ordering in an isolated system: if there is full ordering in the system,

the entropy is minimal. Further information and examples of AIC are found elsewhere (*21*).

Results and Discussion

To investigate the aerosol composition dependence on wind direction, we divided the 16 flights into five sectors according to the air mass history obtained from 36-h backward trajectories. Chester and Bradshaw (*22*) stressed the immense importance of the air mass origin for the aerosol composition compared to the position of the sampling location. Therefore, much care was given to the division of the samples over the five sectors, which are shown in Figure 1. Only particles containing Cr, Zn, or Pb were selected. In this way we obtained all Cr-, Zn-, or Pb-containing particles divided per sector. The distribution of the flights over the different sectors and the number of particles containing one or more of these metals in each flight are shown in Table 1. Figures 2–4 show the percentage of metal-containing particles per sector.

From these figures, it is clear that the lowest occurrences of Cr-, Pb-, and Zn-rich particles were always found in sector 1. This sector is characterized by unpolluted air masses of pure marine origin and can be considered an indicator of North Sea background values. Main sources of pollution in this sector should be ships as well as gas and oil drilling platforms, which are positioned over the central area of the North Sea, but their influence seems to be rather small. Only the percentage of Cr-containing particles is significant compared with values from sectors with continental influence (ca. one-third of pure continental values), which might support the assumption of a marine source of Cr-containing particles. The reinjection by sea spray of previously deposited particles has been proposed (*23*) as a possible source for marine-derived trace metal-containing particles, but the reality and quantification of this possible recycled marine component are still controversial (*24*). Pb and Zn values are more than 50 times lower than continental values. Sector 2 has intermediate values for Cr (1.4%) and Pb (3.0%), but the amount of Zn-rich particles is rather high (7.8%). This sector accounts for emissions from the Netherlands, the northern part of Germany, eastern Europe, and all Scandinavian countries. The highest number of heavy metal-containing particles was always encountered in sector 3. This sector is identified by air masses with pure continental history, which carry emissions from Belgium, central and southern Germany, and the eastern part of France. These high numbers are not totally unexpected, since industrial sources of heavy metals alone are thought to be 10 times higher on a global scale than all natural sources combined (*25*). Sector 4 is affected by air masses from the northwestern part of France (including the industrial centers of Dunkerque, Cherbourg, and Lille) and by emissions from the United Kingdom, but also has some influence from air masses coming from the Atlantic ocean and the English Channel. Percentages in this sector are approximately half of those in sector 3. Only Cr (2.2%) abundances are on the same level as that for sector 3 (2.1%). Samples collected on flights 4, 9, and 14 were taken under low wind speeds and variable wind conditions. Therefore, they are grouped in sector 5, called "local". The values found in this sector are also quite high.

To investigate the true chemical composition of the particles containing Cr, Zn, or Pb, we needed to identify the different particle groups and determine their abundance variations over the five sectors. This was done only for
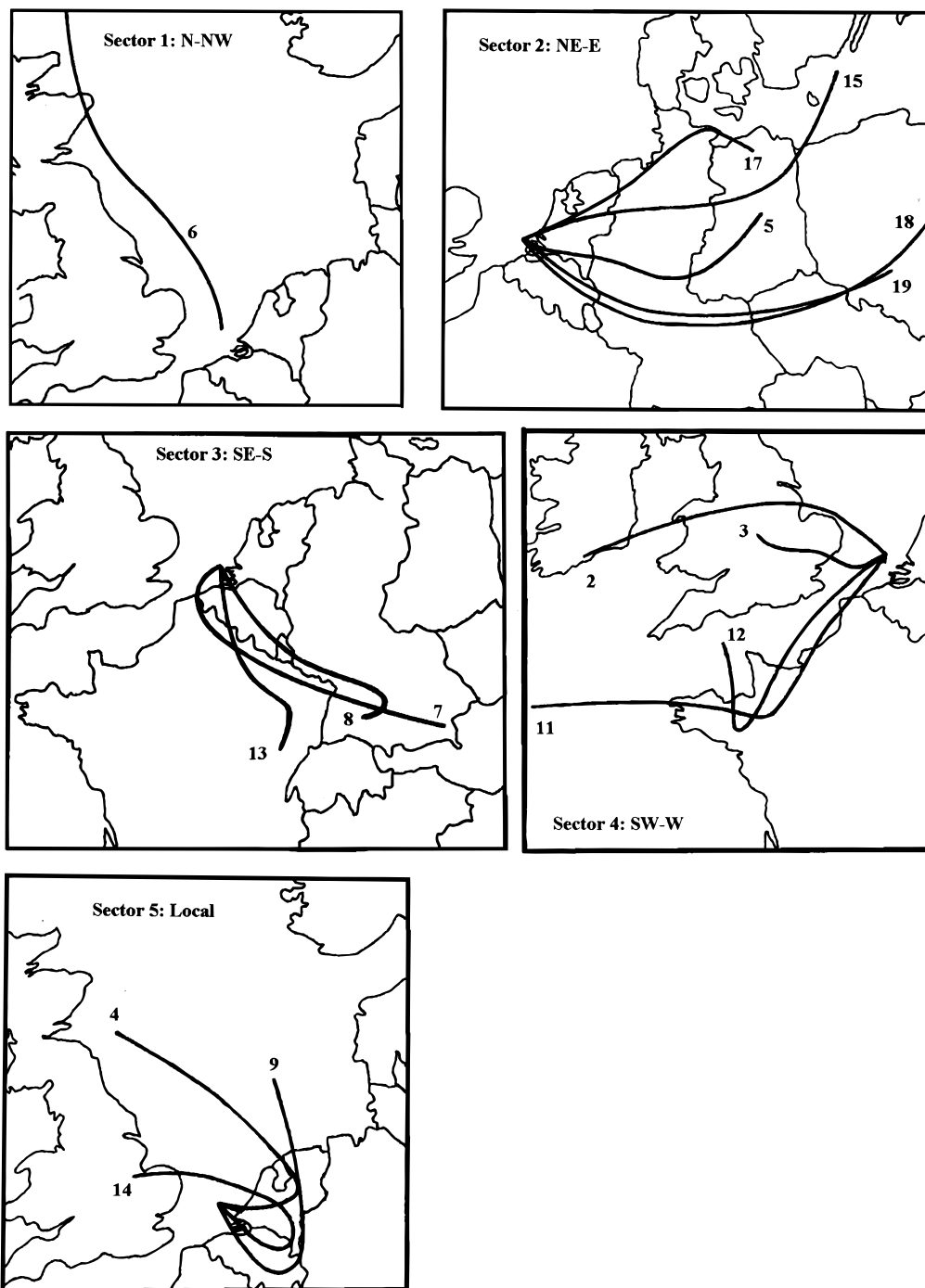
FIGURE 1. 1000-hp, 36-h air mass back trajectories at our sampling site for the five different sectors. The numbers indicate flight numbers.

particles containing one or more of the elements Cr, Zn, and Pb. Other heavy elements such as Ni, V, Sn, Cd, and Cu were not investigated, because the number of particles containing one or more of these elements was too small to obtain statistically significant information. For each of the three elements we performed hierarchical, nonhierarchical, and fuzzy clustering for each of the five sectors. The results of the hierarchical clustering were used as centroids for the nonhierarchical and fuzzy clustering. The number of groups was chosen after careful evaluation of Akaike's criterion. The fuzzy clustering was employed for studying the internal overlap between the different groups. The final interpretation was carried out on the basis of the combination of the information obtained for the three clustering techniques. The results for Cr-, Zn-, and Pb-containing

particles for each of the five sectors are given in Tables 2–4.

Chromium-Containing Particles. In total, 750 particles were found containing Cr, which is 1.7% of the entire number of particles analyzed. After the clustering, several different Cr-containing particle types were detected, embodying a variety of compositions, but some frequently occurring types could be identified. The results of the clustering for the five sectors are shown in Table 2. All sectors are dominated by the appearance of Fe−Cr particles, sometimes in combination with other elements. Pure Cr particles (these are most likely Cr oxides, but since only elements with Z above 11 are detected with energy-dispersive EPXMA, O is not measured) were only encountered in sectors 2 and 4. In most sectors Cr was also detected

TABLE 1

Number of Particles Containing Cr, Pb, and Zn as a Function of the Total Number of Particles Analyzed per Flight and per Sector

flight no.	particles analyzed per flight	Cr-containing particles	Pb-containing particles	Zn-containing particles
		Sector 1: North/Northwest		
6	2922	21	4	0
total (sector 1)	2922	21 (0.7%)	4 (0.1%)	0 (0.0%)
		Sector 2: Northeast/East		
5	3401	36	88	305
15	2851	52	25	141
17	3000	39	106	234
18	1980	31	119	260
19	3000	40	87	163
total (sector 2)	14232	198 (1.4%)	425 (3.0%)	1103 (7.8%)
		Sector 3: Southeast/South		
7	3000	50	244	414
8	3000	52	176	243
13	3000	83	130	216
total (sector 3)	9000	185 (2.1%)	550 (6.1%)	873 (9.7%)
		Sector 4: Southwest/West		
2	1573	28	101	69
3	2844	41	135	164
11	2655	25	13	35
12	2880	127	38	104
total (sector 4)	9952	221 (2.2%)	287 (2.9%)	372 (3.7%)
		Sector 5: Local		
4	1764	28	156	100
9	2455	74	68	264
14	3000	50	80	103
total (sector 5)	7219	152 (2.1%)	304 (4.2%)	467 (6.5%)
total (all sectors)	43325	750 (1.7%)	1570 (3.6%)	2815 (6.5%)

FIGURE 2. Percentage of Cr-containing particles per sector. The encircled numbers indicate the sector number.
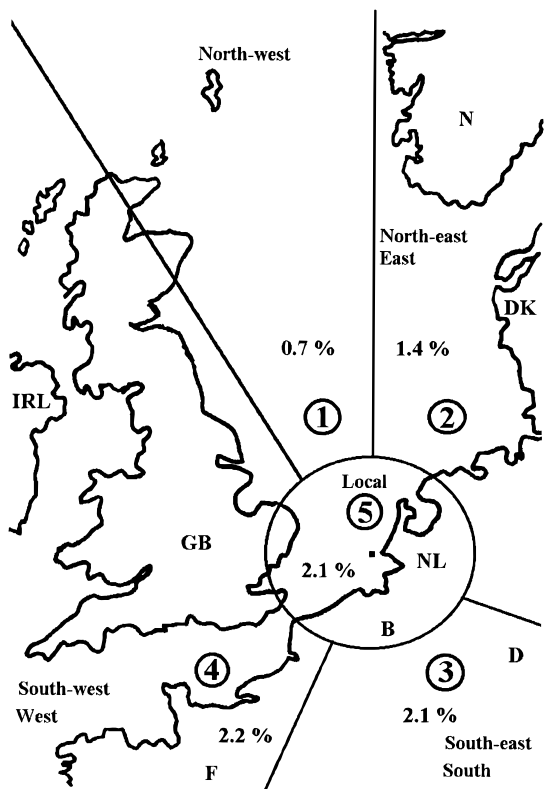

FIGURE 3. Percentage of Pb-containing particles per sector. The encircled numbers indicate the sector number.

in combination with the elements S, Ca, Cl, and K. In Table 2 they are indicated as Cr/medium-Z. In some sectors Cr was associated with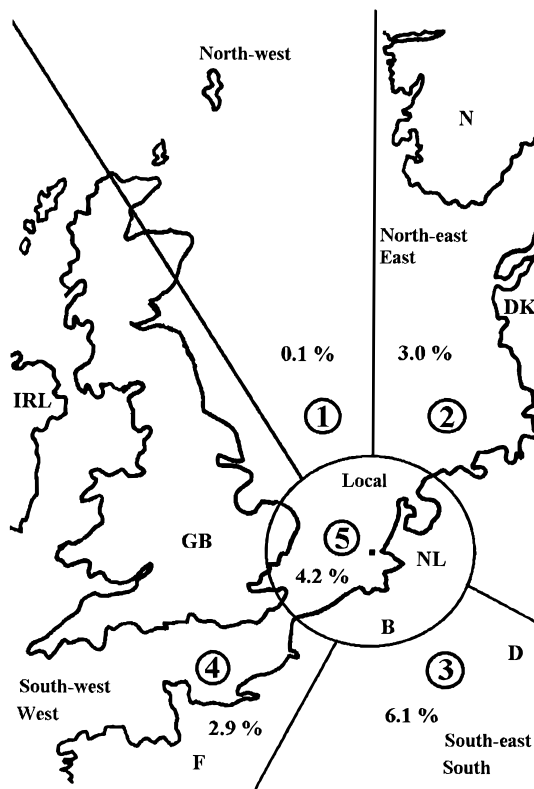 high-Z elements such as Ni, Zn, Cu, and Pb. Another frequently occurring particle type is Cr associated with Si. In Table 2 these particles are noted as Si/Cr. The size of the different particle types varies between
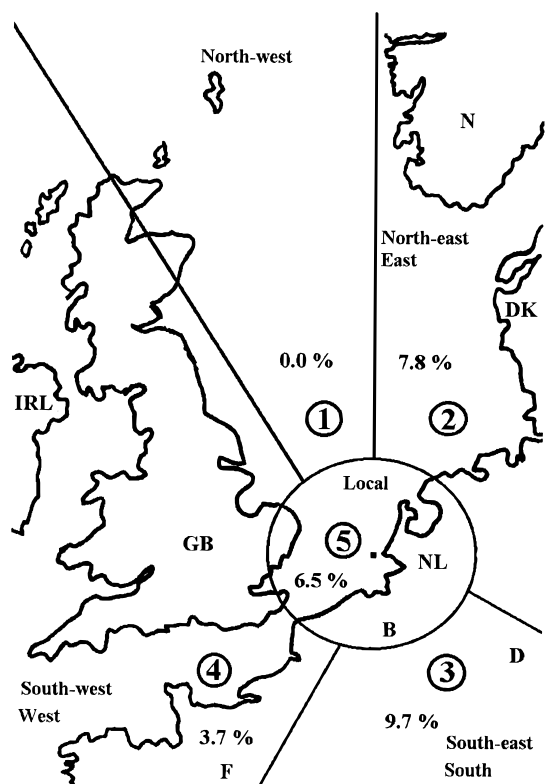
FIGURE 4. Percentage of Zn-containing particles per sector. The encircled numbers indicate the sector number.

0.3 and 2.5 μm. This variation is larger than that for Pb- and Zn-rich materials. This might point to a natural source of Cr, which is not present for Zn and Pb.

More than 10 million tons of chromite (FeOCr$_2$O$_3$), the only economically important Cr mineral, is used globally each year, divided over three main industries: 76% for metallurgical, 13% for refractory, and 11% for chemical applications (26). The different industrial applications call for different forms of Cr, such as chromite, ferrochromium, Cr metal, and several other Cr compounds. Each of these industries emits Cr in one form or another. The closest Cr-emitting industries are probably the steel factories in Boulogne, Dunkerque, Lille, and Roubaix, approximately 300 km distant from the sampling location. The industrial center of the Ruhr area, with many steel factories, lies ca. 500 km east. The source identification of all of these particles types is quite complex, considering the relatively small differences between some of the particle groups. Moreover, due to the high boiling point, Cr vapors from chromium steel production and coal combustion rapidly condense as oxides on the surface of different sorts of airborne particles (27). During the combustion of fuels, the volatile species in coal evaporate in the furnace and subsequently condense as submicrometer-sized particles or on ash particles. Cr was found to be significantly concentrated on the surface of combustion particles (28). These processes give rise to a wide variety of Cr-containing particles and complicate source identification. Several particle groups with low Cr content are probably created in this way. The influence of particle size on the occurrence of this particle type is rather unclear: sizes vary between 0.5 and 1.5 μm.

The differences in abundances between the various particle groups shown in Table 2 are not to be interpreted as final, since classification of some of the clusters was difficult and subject to personal interpretation. They do,

however, give a good indication of the occurrence of the various groups.

Fe−Cr clusters are the most abundant in all of the sectors. The values vary between 39% (sector 3) and 57% (sector 1). Several publications (4, 27, 29) suggest metallurgical industries, which are the main consumers of chromite for the production of iron, steel, and stainless steel (Cr improves corrosion resistance), as the primary source of Fe−Cr-rich particles. Pacyna (30) also pinpoints the steel industry as the major emitter of Cr in Europe (15 000 tons year^{-1}). The mineralogical composition of dusts released in the different phases of iron and steel production has been identified as consisting of a significant part of Fe minerals as hematite (Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$), which sometimes contain very high concentrations (on the order of 100−1000 ppm) of heavy metals including Cr (31).

Cr-rich groups, which are correlated with Si and sometimes Al, were found in all sectors as well. They could be natural windblown soil dust particles. Some Saharan dusts are known to contain high levels of Cr, up to 3000 ppm. Long-range transport of such soils was expected to contribute to Cr release, even in Europe (32). On the other hand, they might also be the result of Cr condensation on airborne soil dust. Evidently, this Cr-containing particle type is rather large in size, often larger than 1.0 μm. This might point to a natural origin for this group. Another, and probably important, possibility is quartz (SiO$_2$) particles released in the steel production process, which may contain high Cr concentrations (31).

The main medium-Z elements that are found in combination with Cr are Ca, S, Cl, and K. Here again the emission from the metallurgical industry is probably the main contributor to this type of particles. Significant quantities of Ca minerals such as calcite (CaCO$_3$), dolomite (CaMg(CO$_3$)$_2$), and gypsum (CaSO$_4$·2H$_2$O) enriched with Cr are released during the production process. Calcite is known to react with SO$_2$ and results in gypsum. The cement industry is another potential source of atmospheric Cr. Manufacture of cement is a high-temperature process using more than 30 raw materials, with limestone, which contains Cr concentrations in the ppm range, as a major ingredient (32).

Pure Cr particles were only found in the northeastern and southwestern wind directions, and not in the southeastern direction. It is possible that this is partly an artifact of the clustering, which incorporated pure Cr particles into groups with high Cr content. Metallic Cr is used primarily in nonferrous alloys, where the use of less expensive ferrochromium alloys can introduce undesirable amounts of Fe (26). Cr particles associated with heavy metals are also likely to originate from this source. Presumably this is also the reason why they are found in higher quantities in sectors 2 and 4. The closest important nonferrous industry in the southeastern direction is much more distant than in the other directions. The occurrence of Cl in some groups is most likely explained by the coagulation of anthropogenic Cr particles and sea salt. The size of these particles is very small (around 0.4 μm).

Lead-Containing Particles. Over the five sectors together, 1570 particles were found containing Pb. This is 3.6% of the total number of particles analyzed. Again, we tried to discover the various particle types by means of a combined clustering approach. This resulted in the identification of five major Pb-containing particle types, shown in Table 3. Approximately 50% of the particles were

TABLE 2

Abundances, Diameters, and Composition of Cr-Containing Particle Groups According to Their Different Source Sectors as Found by Statistical Clustering

particle type	total abun	abundance (%)	diameter (μm)	relative concentration (weight %) of main elements detected by EPXMA
Sector 1: North/Northwest				
Fe/Cr	57.0	57.0	0.8	**Cr**(20), Fe(73), Ni (7)
Cr/high-Z	28.6	28.6	1.2	S(10), Cl(26), Ca(18), **Cr**(15), Cu(23)
Si/Cr	14.3	14.3	2.5	Si(16), **Cr**(84)
Sector 2: Northeast/East				
Fe/Cr	45.6	14.6	0.5	**Cr**(17), Fe(80)
		14.0	0.6	Si(6), **Cr**(18), Mn (6), Fe(62)
		12.3	1.4	Si(21), S(6), Cl(6), **Cr**(14), Fe(43)
		4.7	0.4	Si(11), **Cr**(48), Fe(29)
pure Cr	31.0	31.0	0.4	**Cr**(100)
Cr/high-Z	11.1	6.4	0.5	S(12), Cl(10), **Cr** (10), Fe(57), Zn (7)
		4.7	0.6	S(24), K(7), Ca(11), **Cr**(20), Fe(17), Zn (10)
Cr/medium-Z	9.3	5.8	0.3	S(14), **Cr**(81)
		3.5	0.3	S(26), Ca(53), **Cr**(7)
Si/Cr	2.9	2.9	0.4	Mg(7), Al(6), Si(58), S(9), **Cr**(12)
Sector 3: Southeast/South				
Fe/Cr	40.0	23.8	0.6	**Cr**(25), Fe(65)
		10.3	0.9	**Cr**(11), Fe(85)
		5.9	0.7	Si(7), S(6), **Cr**(11), Mn(32), Fe(34), Zn(7)
Cr/high-Z	30.2	15.1	0.4	Si(5), **Cr**(39), Fe(34), Ni(4), Zn(12)
		15.1	0.7	Si(4), **Cr**(11), Fe(60), Zn(12)
Si/Cr	16.2	9.2	0.9	Si(7), **Cr**(81), Fe(6)
		7.0	0.6	Si(47), S(6), **Cr**(25), Fe(14)
Cr/medium-Z	13.5	9.2	1.7	Al(6), Si(10), S(12), Cl(16), K(5), Ca(6), Ti(6), **Cr**(17), Fe(21)
		4.3	0.9	S(48), Ca(37), **Cr**(10)
Sector 4: Southwest/West				
Fe/Cr	39.0	18.1	1.5	**Cr**(18), Fe(73), Ni (4)
		10.9	0.5	**Cr**(46), Fe(40)
		10.0	0.9	Si(14), **Cr**(14), Fe(51), S(5), Cl(3)
pure Cr	24.0	24.0	0.4	**Cr**(100)
Cr/medium-Z	23.9	14.9	1.4	Cl(64), **Cr**(28)
		9.0	0.4	Ca(9), **Cr**(64), Fe(8)
Cr/high-Z	7.7	5.0	0.9	S(20), Cl(7), Ca(19), Ti(7), V(7), **Cr**(15), Fe(9), Cu(14)
		2.7	0.4	S(52), **Cr**(43), Cu(5)
Si/Cr	5.4	5.4	1.0	Si(83), **Cr**(6)
Sector 5: Local				
Fe/Cr	53.3	23.0	0.9	**Cr**(25), Fe(68), Ni(6)
		12.5	0.6	**Cr**(49), Fe(42)
		9.2	0.6	**Cr**(13), Fe(84)
		8.6	0.7	Cl(9), S(7), Si(5), Fe(52), **Cr**(17)
Si/Cr	20.7	11.8	1.0	Si(11), **Cr**(85)
		7.9	1.1	Si(87), **Cr**(13)
Cr/medium-Z	17.8	12.5	0.7	S(42), Ca(45), **Cr**(12)
		5.3	0.5	S(50), K(11), **Cr**(25)
Cr/high-Z	9.2	5.9	1.0	Si(7), Cl(15), **Cr**(20), Pb(4)
		3.3	1.4	Cl(4), **Cr**(17), Cu(76)

found to be "pure" Pb particles, most likely metallic Pb and Pb oxides. Other groups with high abundances were Pb chlorides, Pb associated with medium-Z elements such as P, Ca, and K, and Pb-containing particles with high-Z elements (mostly Zn, sometimes Cu and Sn). Pb correlated with Si, identified as Si/Pb in Table 3, accounted for only a few percent in most sectors.

Pb is an element that is used very extensively in a wide variety of applications. The average emission for all sources was estimated to be around 123 000 tons year^{-1} in Europe (30). The total deposition flux of Pb in the southern bight of the North Sea was estimated to be 13.8 kg km^{-2} year^{-1}, which is 2200 tons year^{-1} (2). Gasoline combustion accounts for more than 50% of the Pb emission, but the introduction of unleaded gasoline should have reduced this number dramatically. Other major emitters are coal combustion, Pb production, Cu−Ni production, Zn−Cd production, the steel industry, and cement factories (4). The size of Pb-containing particles varies between 0.3 and 0.8 μm and seems to be generally smaller than for Cr-containing particles.

Table 3 shows the high abundance of "pure" Pb particles (45% in sector 5, up to 54% in sector 2). The results for sector 1 are only based on four particles, so no statistical conclusions can be made. According to Fergusson (33), metallic Pb, $PbCO_3$, or Pb oxides (all of which could be the so-called "pure" Pb, because only elements with $Z > 11$ are detected in ED EPXMA) are created in various processes: emissions of coal-fired power stations, cement and fertilizer production, base metal smelting, and even automotive exhaust can eventually result in such species. The main components in aged vehicle aerosols are oxylead species: $PbCO_3$, $(PbO)_2 \cdot PbCO_3$, $PbSO_4$, and PbO (34). Therefore, it is rather complicated to assign these "pure" Pb particles to one particular source. The size of these particles is rather small (0.4 μm).

TABLE 3

Abundances, Diameters, and Composition of Pb-Containing Particle Groups According to Their Different Source Sectors as Found by Statistical Clustering

particle type	total abun	abundance (%)	diameter (μm)	relative concentration (weight %) of main elements detected by EPXMA
			Sector 1: North/Northwest	
pure Pb	75	75	0.4	**Pb**(100)
Al/Pb	25	25	0.6	Al(60), **Pb**(40)
			Sector 2: Northeast/East	
pure Pb	53.6	53.6	0.4	**Pb**(100)
Pb/high-Z	24.1	8.7	0.5	K(4), Zn(64), **Pb**(27)
		5.6	0.5	Zn(46), **Pb**(52)
		4.7	0.7	Fe(56), Zn(19), **Pb**(12)
		3.5	0.5	Cu(54), Zn(5), **Pb**(38)
		1.6	0.8	Si(5), Cl(3), Sn(66), **Pb**(23)
Pb chlorides	12.3	9.9	0.7	Cl(58), **Pb**(39)
		2.4	0.6	Cl(40), K(11), Zn(22), **Pb**(27)
Pb/medium-Z	6.6	3.8	0.6	P(4), Ca(47), **Pb**(34)
		2.8	0.4	K(63), Zn(4), **Pb**(33)
Si/Pb	3.3	3.3	0.5	Al(5), Si(56), Fe(6), Zn(4), **Pb**(22)
			Sector 3: Southeast/South	
pure Pb	48.4	48.4	0.4	**Pb**(100)
Pb chlorides	32.7	9.6	0.4	Cl(73), **Pb**(27)
		9.5	0.7	Cl(60), **Pb**(40)
		6.5	0.8	Cl(49), **Pb**(51)
		4.2	0.6	Cl(54), **Pb**(23)
		2.9	0.7	Cl(40), **Pb**(18), P(4), Ca(5), Fe(10), Zn(25)
Pb/medium-Z	10.9	3.8	0.3	P(40), Cl(5), **Pb**(53)
		3.3	0.8	Ca(55), Zn(8), **Pb**(35)
		2.0	0.5	Al(27), P(13), Ti(4), Cr(8), Sn(3), **Pb**(40)
		1.8	0.4	Cl(15), K(40), Ca(6), **Pb**(38)
Pb/high-Z	6.9	4.2	0.7	Fe(56), Zn(13), **Pb**(19)
		2.7	0.4	Zn(55), **Pb**(43)
Si/Pb	1.1	1.1	1.0	Al(6), Si(47), K(4), Fe(7), Zn(14), **Pb**(20)
			Sector 4: Southwest/West	
pure Pb	49.8	49.8	0.5	**Pb**(100)
Pb chlorides	23.3	23.3	0.7	Cl(52), Zn(3), Br(4), **Pb**(38)
Pb/high-Z	18.1	10.5	0.5	Fe(3), Zn(46), **Pb**(48)
		6.6	0.5	P(13), Ca(11), Cu(16), **Pb**(47)
		1.0	0.7	Ca(11), Sn(59), **Pb**(31)
Si/Pb	6.3	6.3	0.6	Si(38), Ca(3), Fe(29), Zn(8), **Pb**(20)
Pb/medium-Z	2.4	2.4	0.7	Cl(4), K(62), **Pb**(35)
			Sector 5: Local	
pure Pb	44.7	44.7	0.4	**Pb**(100)
Pb chlorides	34.9	21.1	0.6	Cl(68), **Pb**(28)
		13.8	0.7	Cl(48), Zn(3), Br(3), **Pb**(38)
Si/Pb	11.2	11.2	0.5	Al(1), Si(8), P(5), Mn(2), Fe(13), Zn(24), **Pb**(36)
Pb/medium-Z	6.2	3.9	0.3	P(6), Ca(50), **Pb**(38)
		2.3	0.3	K(60), Zn(2), **Pb**(37)
Pb/high-Z	3.0	3.0	0.4	Cl(6), Cu(54), **Pb**(38)

The second most abundant particle type was Pb chlorides. These particles originate from car exhaust emissions and have been studied extensively (*35, 36*). The primary material from the exhaust of cars is PbClBr. However, PbO, Pb(OH)Cl, Pb(OH)Br, and sometimes $PbSO_4$ and Pb may occur. PbClBr reacts in the atmosphere with many products, all resulting in the loss of halides and finally producing Pb sulfates, nitrates, and oxides (*33*). The detected percentages of traffic-related particles in the different sectors correlate quite well with the amount of car traffic in these sectors: sector 5 (35%) and sector 3 (33%) had air masses passing over densely populated areas in Belgium, The Netherlands, and Germany. Sector 4 (23%) also has a lot of traffic, but it is much more distant from the sampling area. Therefore, the particles had much more time to react with atmospheric compounds. No Pb halides were found in sector 1 (marine sector).

Another detected particle type was Pb associated with P, Ca, or K. Particles containing P and/or Ca are probably linked to emissions by cement manufacturing or fertilizer production. Zn and Cl were sometimes found in association with Pb particles holding K. They might be connected to emissions from refuse incineration, which is known to be a major source of airborne heavy metals (*37*). Pb was found together with Zn in a lot of particles classified as Pb/high-Z, but also with other heavy metals such as Sn and Cu. Ferroalloy production is probably the main emitter of these types of particles. Their abundances varied between 3.0% in sector 5 and 24% in sector 2. Pb particles in correlation with Si can be associated with soil. This might be partly true since windblown soil dust is known to bring 20 000 tons of Pb into the atmosphere globally every year (*30*), but they could also be fly ash particles, containing high amounts of heavy metals (*38*). These particles sometimes constitute up to 50% of the particle abundance in the North Sea atmosphere (*6*). Other possibilities for Pb silicates are base metal smelting and refining (*33*).

TABLE 4

Abundances, Diameters, and Composition of Zn-Containing Particle Groups According to Their Different Source Sectors as Found by Statistical Clustering

particle type	total abun	abundance (%)	diameter (μm)	relative concentration (weight %) of main elements detected by EPXMA
Sector 1: North/Northwest				
no Zn-containing particles encountered				
Sector 2: Northeast/East				
Fe/Zn	48.5	30.9	0.5	Fe(72), **Zn**(18)
		17.6	0.5	S(19), Fe(41), **Zn**(27)
Zn sulfides	25.8	13.5	0.4	S(38), **Zn**(58)
		12.3	0.5	S(60), **Zn**(26)
pure Zn	8.7	8.7	0.4	**Zn**(100)
Si/Zn	7.8	7.8	0.8	Al(6), Si(23), S(12), K(10), **Zn**(90), Sn(4)
Zn/high-*Z*	5.7	5.7	0.5	Cl(4), **Zn**(51), Pb(38)
Zn/medium-*Z*	3.4	3.4	0.5	Cl(12), Ca(59), **Zn**(11)
Sector 3: Southeast/South				
Fe/Zn	59.6	59.6	0.5	S(4), Fe(65), **Zn**(20)
Zn chlorides	16.0	16.0	0.6	Cl(28), **Zn**(48), Pb(9)
Zn sulfides	15.6	15.6	0.5	S(48), Cl(5), Fe(7), **Zn**(26)
Si/Zn	8.8	8.8	0.5	Si(42), Mn(6), Fe(17), **Zn**(18)
Sector 4: Southwest/West				
Fe/Zn	45.5	29.6	0.6	Fe(73), **Zn**(14)
		15.9	0.6	Si(6), S(10), Fe(45), **Zn**(22)
Zn sulfides	18.8	11.0	0.5	S(59), Ca(6), **Zn**(20)
		7.8	0.4	S(40), **Zn**(57)
Zn/high-*Z*	15.1	6.2	0.7	P(8), Cu(5), **Zn**(58), Sn(9), Pb(10)
		6.2	0.5	**Zn**(38), Pb(59)
		2.7	0.4	Cr(58), Fe(28), **Zn**(8)
Si/Zn	10.5	10.5	0.9	Al(13), Si(50), S(7), Fe(8), **Zn**(11)
Zn chlorides	10.2	10.2	0.7	Si(7), S(12), Cl(49), **Zn**(20), Pb(5)
Sector 5: Local				
Fe/Zn	39.8	16.7	0.5	Fe(63), **Zn**(28)
		15.8	0.6	Fe(83), **Zn**(10)
		7.3	0.6	Si(2), S(9), Ca(3), Mn(26), Fe(40), **Zn**(18)
Zn sulfides	32.1	11.1	0.5	S(34), Cl(30), **Zn**(32)
		9.2	0.4	S(65), **Zn**(28), As(4)
		6.0	0.4	S(44), **Zn**(51)
		5.8	0.6	S(29), Fe(37), **Zn**(26)
Si/Zn	8.1	4.9	0.7	Al(16), Si(19), S(9), Fe(25), **Zn**(13)
		3.2	0.7	Al(8), Si(54), S(6), Fe(6), **Zn**(16)
pure Zn	7.3	7.3	0.3	**Zn**(100)
Zn chlorides	6.9	6.9	0.7	Cl(53), **Zn**(30), Pb(7)
Zn/high-*Z*	3.6	3.6	0.4	P(7), K(7), **Zn**(44), Pb(34)
Zn/medium-*Z*	2.1	2.1	0.9	P(12), S(13), Ca(55), **Zn**(16)

Zinc-Containing Particles. Except for sector 1, particles containing Zn were found in all sectors. This clearly points to the fact that a marine source for Zn is very unlikely. In the other sectors together, 2815 Zn-rich particles were detected, what is almost twice as much as Pb-containing particles. As for Cr and Pb, we performed hierarchical, nonhierarchical, and fuzzy clustering on the combined Zn-rich particles for the five different sectors. This again resulted in the identification of seven major Zn-containing particle types (Table 4). The most important group is the Fe−Zn particles, which constitute up to 60% of the particle abundance (sector 3). Dependent on the wind direction, Zn sulfides make up between 16% and 32% of the Zn particles. Zn chlorides, often in the presence of Pb, were found to account for approximately 5−16% of the detected particles. Less abundant groups were "pure" Zn particles, Zn correlated with medium-*Z* elements such as Ca and P, high-*Z* elements such as Pb and Sn, and Zn particles with significant concentrations of Si. The particle size of Zn-containing particles seems to vary between 0.3 and 1.0 μm. These rather small variations make size-related interpretation of the data difficult.

Worldwide, most Zn production originates from ZnS minerals, which are converted into metallic Zn in a series of processes. The main use of Zn is in galvanizing iron and steel products, which are coated with a layer of Zn in order to increase the corrosion resistance. Zn is also used in numerous Zn−base alloys, which are utilized in a wide variety of applications such as Ni−Zn batteries. Other applications of Zn are in plumbing materials, as a catalyst in vulcanization processes (Zn oxides), in paints (ZnS), and in cosmetic and pharmaceutical products. Natural Zn emissions (43.5×10^6 kg year^{-1}), with windblown dust as a major contributor, are estimated to be almost 10 times lower than the combined industrial emissions (314×10^6 kg year^{-1}). Here the main sources are primary Zn production, iron and steel industries, industrial applications, coal and wood combustion, and waste incineration (*4, 39*). The yearly total deposition flux of Zn into the southern bight of the North Sea was calculated to be 28 kg km^{-2} year^{-1}, which is approximately 4432 tons per year for the total area of the southern bight (*2*).

As for Cr, the most abundant group of Zn particles is particles containing high amounts of Fe. Sometimes these

particles held small concentrations of S and Si. Rybicka (31) found significant concentrations of Zn (200–2500 ppm) in mineral dusts containing Fe (magnetite and hematite) emitted by the different stages of the metallurgical production processes by knowing that the iron and steel industries are the second most important source of atmospheric Zn (4), and considering the large amount of metallurgical complexes in a rather short distance to our sampling area (northern France, Ruhr area, Gent area, and Manchester area), this might explain the large amount of Zn-containing Fe-rich particles. Strong correlations for Fe, Zn, and Mn above the North Sea (sector 5) have been reported before by Baeyens and Dedeurwaerder (40). They recognized metallurgical emissions from Dunkerque, Gravelines, and Boulogne as point sources for these elements.

Zn sulfides are the second most abundant group in three out of four sectors. They might be partly related to windblown Zn ores, which are mostly stored uncovered and therefore easily taken up by the wind, and which easily react to yield a number of secondary minerals. These minerals, such as $ZnCO_3$, can be partly responsible for the detected "pure" Zn particles (again, low-Z elements are not detected by our method). The reaction between Zn oxides and sulfuric acid, during release in metallurgical processes, might also yield a fraction of the detected Zn–S particles.

In sectors 3–5, 7–16% of the particles were Zn chlorides. The major part is probably linked to emissions of refuse incineration. The vaporization of volatile elements, among which are heavy metals, during combustion is followed by condensation of these elements on small particles present in the exhaust. The high concentrations of Cl species in the gas stream provides an excellent opportunity to form volatile metal chlorides (37). In the coarse fraction of incinerator particles, Mamane (41) found all particles to contain at least some Zn, K, and Cl. He stated that these particles were formed through the condensation of volatile Zn, K, and Cl on existing minerals. This type of particle was the only significant heavy metal-containing giant particle type found in the North Sea aerosol (7).

In most sectors, approximately 10% of the Zn-rich particles contained a significant percentage of Si. They might be partially related to windblown soil dust, since the average Zn concentration in soil is 100 ppm, but some contain more than 1000 ppm (42). On the other hand, these Zn-rich particles are probably for a significant fraction fly ash (just as Pb/Si particles), which is known to contain important concentrations of heavy metals (38, 43). Also, the small average diameter of this group (0.5 μm) points to a significant anthropogenic fraction. Although the concentrations of heavy elements such as Cr, Pb, and Zn might not be high enough in most fly ash particles to be detected with our method, this does not mean that they do not contribute to the atmospheric input of trace metals to the North Sea.

Other less frequently occurring particle types were Zn in association with Pb, Cr, and Sn. Again, ferroalloy production is presumably the main source of these particles. Abundances were as high as 15% (sector 4). Zn associated with medium-Z elements such as Ca and P is likely derived from the manufacture of phosphate fertilizer or from cement production (30).

General Overview. The combined interpretation of the three cluster techniques produced 5–7 major particle types containing Cr, Pb, or Zn. Most of the particle types were directly or indirectly connected to emissions of the metallurgical industry, which is eminently present in the northern part of France, the German Ruhr area, and the industrial centers in the middle of the United Kingdom. A major part of Pb-rich particles was found to be associated with automotive exhaust. Less important sources were cement production and refuse incineration.

On top of this, we should not forget that concentrations lower than 1000 ppm cannot be detected with ED EPXMA. Thus, we must presume that at least a fraction of the particles containing lower concentrations of Cr, Pb, and Zn were not identified as heavy metal-containing, but indeed contribute to the atmospheric heavy metal inputs. An important example of such a particle type is fly ash, which constitutes a major part of North Sea particulate matter. Only a small fraction of these fly ash particles were found with heavy metal concentrations higher than 1000 pmm. This does not mean that they do not contribute to the heavy metal inputs, when considering the high amounts of fly ash particles in some sectors.

Our results provide ample evidence for the apparent existence of a heavy metal-containing North Sea aerosol. It was mainly overlooked in previous investigations using single-particle analysis, because these particles are "drowned" in an excess of other, more abundant, particle types such as sea salt and aluminosilicates. The enormous number of particles (48 000) obtained by our automated analysis method allows us to acquire much more statistically reliable results than by manual single-particle analysis, with which only a few hundred particles can be analyzed in a reasonable time. It is exactly this huge database that allowed us to focus on special, low-abundant particle types such as heavy metal-containing particles.

Literature Cited

(1) Katrinak, K. A.; Anderson, J. A.; Buseck, P. R. *Environ. Sci. Technol.* **1995**, *29*, 321–329.

(2) Rojas, C. M.; Injuk, J.; Van Grieken, R. E.; Laane, R. W. *Atmos. Environ.* **1993**, *27A*, 251–259.

(3) Hooper, J. F.; Ross, H. B.; Sturges, W. T.; Barrie, L. A. *Tellus* **1991**, *43B*, 45–60.

(4) Nriagu, J. O.; Pacyna, J. M. *Nature* **1988**, *333*, 134–139.

(5) Ottley, C. J.; Harrison, R. M. *Sci. Total Environ.* **1991**, *100*, 301–318.

(6) Rojas, C. M.; Van Grieken, R. E. *Atmos. Environ.* **1992**, *26A*, 1231–1237.

(7) Van Malderen, H.; Rojas, C.; Van Grieken, R. *Environ. Sci. Technol.* **1992**, *26*, 750–756.

(8) Dierck, I.; Michaud, D.; Wouters, L.; Van Grieken, R. *Environ. Sci. Technol.* **1992**, *26*, 802–808.

(9) Rojas, C. M.; Van Grieken, R. E.; Maenhaut, W. *Air Soil Pollut.* **1993**, *71*, 391–404.

(10) Injuk, J.; Otten, Ph.; Laane, R.; Maenhaut, W.; Van Grieken R. *Atmos. Environ.* **1992**, *26A*, 2499–2508.

(11) Rojas, C. M.; Otten, Ph. M.; Van Grieken, R. E.; Laane, R. W. In *Air Pollution Modelling and Its Application*; van Dop, H., Steyn, D., Eds.; Plenum Press: New York, 1991.

(12) Rojas, C. M.; Van Grieken, R. E.; Laane, R. W. *Atmos. Environ.* **1993**, *27A*, 363–370.

(13) Pena, J. A.; Norman, J. M.; Thomson, D. W. *J. Air Pollut. Control Assoc.* **1977**, *27*, 337–340.

(14) Otten, Ph.; Rojas, C.; Wouters, L.; Van Grieken, R. Atmospheric Deposition of Heavy Metals (Cd, Cu, Pb and Zn) into the North

Sea. Report 2 to Rijkswaterstaat (The Hague, The Netherlands) on Project NOMIVE*2 DGW 920, University of Antwerp (UIA), Belgium.

(15) Bondarenko, I.; Treiger, B.; Van Grieken, R.; Van Espen, P. *Spectrochim. Acta Electron.*, submitted.

(16) Crutcher, H. L.; Rhodes, R. C.; Graves, M. E.; Fairbaim, B.; Nelson, A. C. *JAPCA* **1986**, *36*, 1116−1122.

(17) Saucy, D. A.; Anderson, J. R.; Buseck, P. R. *Atmos. Environ.* **1987**, *21*, 1649−1657.

(18) Shattuck, T. W.; Germani, M. S.; Buseck, P. R. *Anal. Chem.* **1991**, *63*, 2646−2656.

(19) Bernard, P. C.; Van Grieken, R. E. *Anal. Chim. Acta* **1992**, *267*, 81−93.

(20) Treiger, B.; Bondarenko, I.; Van Malderen, H.; Van Grieken, R. *Anal. Chim. Acta*, in press.

(21) Bondarenko, I.; Van Malderen, H.; Treiger, B.; Van Espen, P.; Van Grieken, R. *Chemom. Intell. Lab. Syst.* **1994**, *22*, 87−95.

(22) Chester, R.; Bradshaw, G. F. *Mar. Pollut. Bull.* **1991**, *22*, 30−36.

(23) Duce, R. A.; Liss, P. S.; Merrill, J. T.; Atlas, E. L.; Buat-Menard, P.; Hicks, B. B.; Miller, J. M.; Prospero, J. M.; Arimoto, R.; Church, T. M.; Ellis, W.; Galloway, J. N.; Hansen, L.; Jickels, T. D.; Knap, A. H.; Reinhard, K. H.; Schneider, B.; Soudine, A.; Tokas, J. J.; Tsunogai, S.; Wollast, R.; Zhou, M. *Global Biogeochem. Cycles* **1991**, *5*, 193−259.

(24) Ottley, C. J.; Harrison, R. M. *Atmos. Environ.* **1993**, *27A*, 685−695.

(25) *Toxic Metals in the Atmosphere*; Nriagu, J. O., Davidson, C. I., Eds.; Advances in Environmental Science and Technology 17; Wiley and Sons: New York, 1986.

(26) Nriagu, J. O. In *Chromium in the Natural and Human Environments*; Nriagu, J. O., Nieboer, E., Eds.; Advances in Environmental Science and Technology 20; Wiley and Sons: New York, 1988.

(27) Moore, J. W.; Ramamoorthy, S. *Heavy Metals in Natural Waters*; Springer-Verlag: New York, 1984.

(28) Natusch, D. F.; Wallace, J. R. *Science* **1974**, *86*, 695−699.

(29) Xhoffer, C.; Bernard, P.; Van Grieken, R.; Van der Auwera, L. *Environ. Sci. Technol.* **1992**, *25*, 1470−1478.

(30) Pacyna, J. M. In *Toxic Metals in the Atmosphere*; Nriagu, J. O., Davidson, C. I., Eds.; Advances in Environmental Science and Technology 17; Wiley and Sons: New York, 1986.

(31) Rybicka, E. H. *Environ. Technol. Lett.* **1989**, *10*, 921−928.

(32) Pacyna, J. M.; Nriagu, J. O. In *Chromium in the Natural and Human Environments*; Nriagu, J. O., Nieboer, E., Eds.; Advances in Environmental Science and Technology 20; Wiley and Sons: New York, 1988.

(33) Fergusson, J. E. *The Heavy Elements*; Pergamon Press: Oxford, 1990.

(34) Harrison, R. M. In *Toxic Metals in the Atmosphere*; Nriagu, J. O., Davidson, C. I., Eds.; Advances in Environmental Science and Technology 17; Wiley and Sons: New York, 1986.

(35) Harrison, R. M.; Sturges, W. T. *Atmos. Environ.* **1983**, *17*, 311−328.

(36) Hirschler, D. A.; Gilbert, L. F.; Lamb, F. W.; Niebylski, L. M. *Ind. Eng. Chem.* **1957**, *49*, 1131−1142.

(37) Greenberg, R. R.; Zoller, W. H.; Gordon, G. E. *Environ. Sci. Technol.* **1978**, *12*, 566−573.

(38) Norton, G. A.; Malaby, K. L.; Dekalb, E. L. *Environ. Sci. Technol.* **1988**, *22*, 1279−1283.

(39) Nriagu, J. O. *Nature* **1979**, *279*, 409−411.

(40) Baeyens, W.; Dedeurwaerder, H. *Atmos. Environ.* **1991**, *25A*, 1077−1092.

(41) Mamane, Y. *Atmos. Environ.* **1988**, *22*, 2411−2418.

(42) Aubert, H.; Pinta, M. *Trace Elements in Soils*; Elsevier Scientific Publishing: Amsterdam, 1977.

(43) Ondov, J. M.; Choquette, C. E.; Zoller, W. H.; Gordon, G. E.; Biermann, A. H.; Heft, R. E. *Atmos. Environ.* **1989**, *23*, 2193−2204.