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Source Apportionment for the Zinc-Containing Component of Air Particulate Matter using Automated Electron Probe Micro Analysis of Individual Particles

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Dedicated to Professor W. Haerdi on the occasion of his 60th birthday

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A methodology is described for the apportionment of zinc-containing particulate matter sampled in the vicinity of a zinc smelter to their corresponding sources in the factory. Bulk samples of particulate matter from six potential emission sources were analysed by automated electron probe microanalysis (EPMA) in order to characterize the individual particles. Based on a data set of relative peak intensities and with the aid of a binary clustering method, the most important particle classes were identified. They were used as a basis for the development of a set of disjunct identification rules (decision rules), which were able to describe the classes in a unique manner. Applying these rules upon ambient particulate data enabled the estimation of relative contributions of different types of zinc-containing particles. Evidence was found that a large number of particles was modified by a soil component or by gas phase reactions.

KEY WORDS: Source apportionment, aerosol, zinc smelter, individual particle analysis, EPMA, zinc pollution.

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INTRODUCTION

The problems associated with the apportionment of pollutants to their sources have been studied intensively during the past decade and several methods have been developed to estimate the contribution of several sources within an area of interest.¹ Most of these receptor models rely upon data obtained from bulk analysis as obtained by X-ray fluorescence (XRF), instrumental neutron activation analysis (INAA), atomic absorption spectrometry (AAS) or particle induced X-ray spectroscopy (PIXE).

Around 1980 the first studies were published on aerosol characterization on a particle-by-particle basis using an electron microscope, equipped with energy- or wavelength dispersive X-ray detectors and automated image analysis systems. The analysis of particle collections up to a 1000 could be performed within a few hours and hence, valid statistical deductions could be made.

Several particle based source apportionment studies can be found in the literature. One of the advantages is that particle sources that cause multicollinearity problems can be resolved when one takes into account particle size distribution, individual particle composition and even particle morphology for each particle class or particle source. This feature is particularly valuable when one deals with industrial processes, where there exist a large number of sources emitting particles that are chemically very alike.

The method has been used to assess the different source contributions in an urban aerosol,^{2,3} to estimate industrial source contributions to TSP^{4,5} and to identify the sources of Pb in automobile emissions.⁶ In this study, we report an alternative particle based source apportionment method using automated electron probe micro analysis data (EPMA) in combination with a supervised rule-based approach. The methodology was tested on air particulate matter sampled in the vicinity of a zinc smelter where a substantial contamination by zinc and cadmium was established.^{7,8} We focused attention on the zinc-containing particles only, in order to trace these particles back to their specific sources of emission within the plant. This limitation reduces the complexity of the aerosol data, making it possible to obtain a limited list of characteristic features for each type of zinc-containing particle and to estimate the relative contribution of each particle class.

DESCRIPTION OF THE SMELTER

The zinc smelter is situated in the North of Belgium at about 40 km to the East of Antwerp and was founded in 1889 although the present production process started in 1969. It has an annual capacity of 190,000 tons of electrolytic zinc and 700 tons of electrolytic cadmium. Figure 1 shows the flow of material in the process and numbers the possible sources of zinc-containing particles.

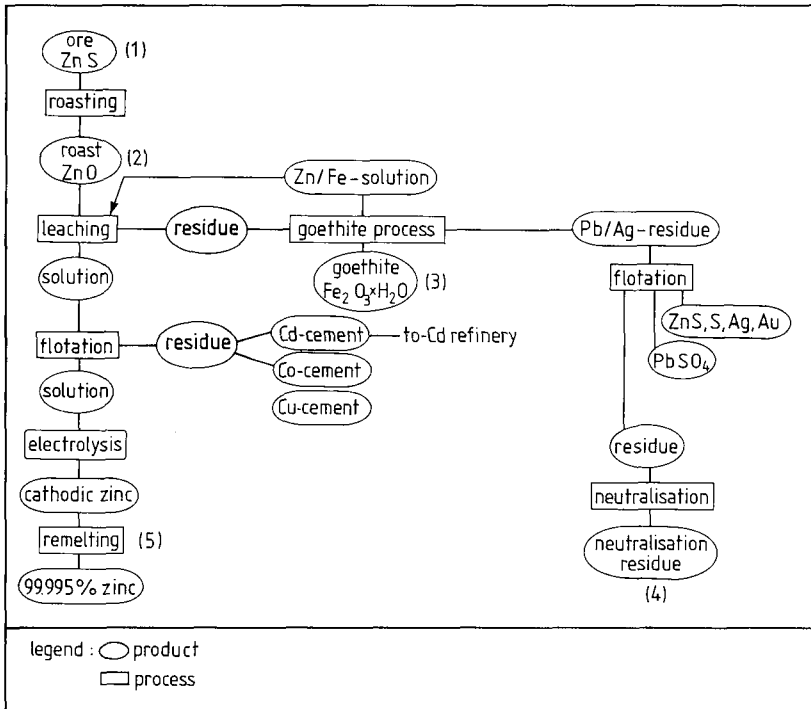


Figure 1 Description of the zinc smelter production process. The numbers between brackets refer to Table 1.

Zinc sulfide concentrates are the principal raw materials. They are stored in the zinc ore storage yard. The ore is transported by a

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shielded transport band to the fluidized bed ovens where it is oxidized to zinc oxide, the roasted ore. The evolved gas, containing SO_2 , passes to a contact process sulfuric acid plant. The roasted ore is transported to the leaching plant, where it is leached in sulfuric acid. The residues are worked up in a process, known as goethite process because it produces goethite as a residue, to recover some metals as Zn, Ag, Au and Pb. The residues are dumped locally. The zinc solution is purified in the flotation process by adding metallic zinc and antimony to the solution and Cd, Co and Cu are recovered. The acidic residues are now neutralized by CaO and O_2 and also dumped within the premises. The purified zinc solution is electrolysed to obtain a cathodic zinc that is remelted in the remelting ovens to 99.995% pure zinc. Within the plant a 40m high terril is present containing slag, a residue from a former production process.

SAMPLING

Source samples

Grab samples of the six potential dust sources were obtained in the plant (Table 1). They consisted of 250 g of bulk material and were considered to be representative for the production process. Small portions were suspended in *n*-hexane, ultrasonically treated during 5 minutes and filtered over a $0.4\ \mu\text{m}$ pore size Nuclepore polycarbonate filter. They were mounted on plexiglass stubs and carbon coated before analysis.

Table 1 Name and origin of the source samples

<i>Name</i>	<i>Origin</i>
1. Concentrated Zn-ore	Storage yard for the concentrated ore
2. Roasted Zn-ore	Roast ovens
3. Goethite residue	Storage yard for the goethite residue
4. Neutralization residue	Storage yard for the neutr. residue
5. Ashes	Filter bags of the remelting ovens
6. Slag	Slag pile

Receptor samples

Samples of ambient particulate matter were sampled in two different ways and at two different periods of the year.

By the end of January 1985, when a snow layer covered the area for at least two weeks, samples of snow were taken at 18 different locations within an area of 5×3.5 km around the zinc smelter. After lyophilization the particles were suspended in *n*-hexane, ultrasonically treated during 5 minutes, filtered over a $0.4 \mu\text{m}$ pore size Nuclepore filter and processed in the way as mentioned above. These samples are referred to as S-series (from snow).

Meteorological data showed temperature extremes between -13.1°C and -1.4°C indicating little melt off of the snow cover. The wind speed varied between 2 and 6 m/s and came from the North and the Southwest in the first half of this sampling period and from the East in the second half of the campaign.

During June and July 1985, three sampling campaigns provided the necessary material for ambient particulate measurements. Samples were taken on adhesive tape, mounted on 3 cm diameter polyvinylchloride rods and shielded against rainfall by a PVC-disk on top of it. Sampling took place by inertial impaction onto these tapes from ambient air. The first sampling campaign lasted from 4 to 7 June 1985 in 5 places near the major storage yards in the plant. The second and third campaign took place from 4 to 20 June 1985 and from 20 June till 3 July in 8 different locations in the vicinity of the plant, the nearest sampling point about 100 m, the furthest about 5 km away from the plant. Two sections were cut out of the tapes after removing them from the rods, one out of the side that was oriented towards the plant, the other from the opposite side. They were mounted on plexi stubs, carbon coated and analysed by the described method. The samples obtained in these campaigns are referred to as the A, B, B*, C and C*-series, where the asterisk refers to the sections oriented towards the plant. Wind direction varied between the South and Northwest.

METHODOLOGY

The outline of the methodology is summarized in Figure 2. The procedure involves 3 main steps: particle analysis, particle class

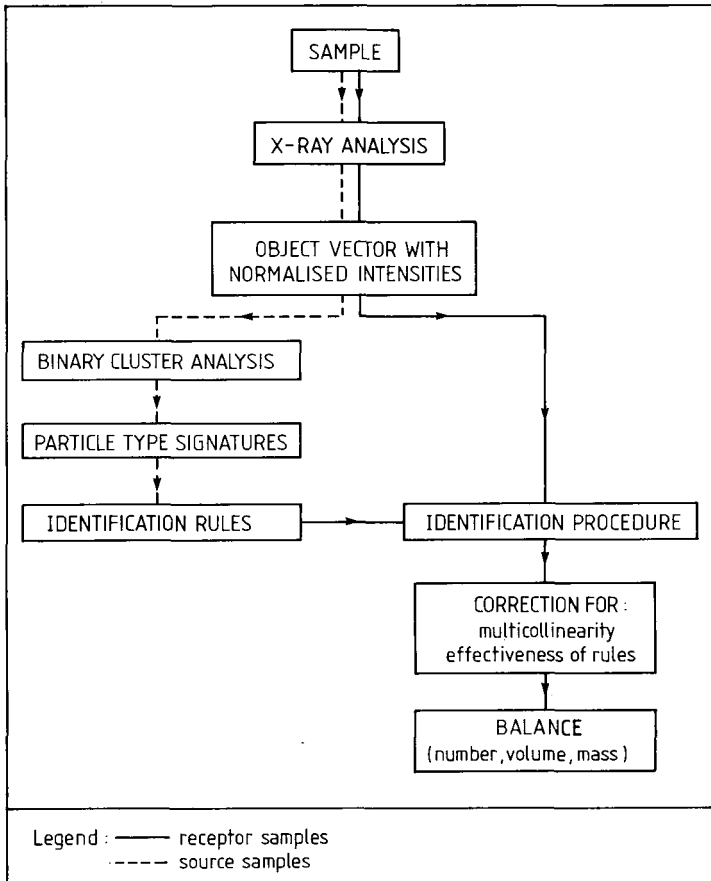


Figure 2 Outline of methodology.

definition and particle classification, including the calculation of the relative contribution of each particle class to the total particle content of the sample.

Particle analysis

All analyses were performed by electron probe microanalysis (EPMA) using a JEOL JXCA-733 Superprobe (Jeol Ltd, Tokyo,

Japan), equipped with an energy dispersive X-ray detector and a Tracor Northern TN 2000 automation system, running on a LSI 11/23 minicomputer. Analysis, beam- and stage control are performed by particle analysis software, developed at the author's laboratory, and is fully automated. A detailed description is given by Raeymaekers.⁹ Data manipulation was performed by Fortran implemented software on a Dec VAX 11/780 computer.

Particle class definition

The most common approach for the definition of particle classes is the particle class balance (PCB) method where one predefines individual particle classes on the basis of particle composition and morphology and then uses these classes to calculate their respective mass fractions within a particular sample.² These classes can be developed over time from experience obtained while examining many particles from a variety of locations and industrial activities. However, as due to the specific nature of the problem no prior knowledge about occurring particle types was available, in this study it was necessary to develop a specific set of particle classes.

First, individual particles from the six potentially most important pollution sources in the plant, which correspond to different steps in the production process, were analysed. For each particle an X-ray spectrum was accumulated for 20 seconds, using an electron beam intensity of 1 nA, an accelerating voltage of 25 kV and a take-off angle of 40 degrees. After on-line spectrum deconvolution, net peak intensities were calculated and stored on disk as an object vector together with the projected diameter of the particle. For each individual source about one hundred particles were analysed.

The X-ray intensities were not corrected for particle size effects, nor were the intensities converted into concentration using e.g. a ZAF correction procedure, because each spectrum was assumed to represent within a predetermined small variation a fingerprint for a particular type of particle. No conversion of the results to mass fractions was performed. In fact, it appeared that the correction of each particle or particle class with its bulk density as roughly estimated would only increase the overall uncertainty of the data.

In order to perform the classification of the analysed particles according to their similarity in elemental composition, the spectral

intensity of each detected element was normalized to the sum of the intensities of all the elements in the particular spectrum. Then, for each particular sample, a matrix was constructed, consisting of 25 relative intensities for the K lines of the elements Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Cu, Zn, Ge and Br and the L lines of the elements Ag, Cd, Sn, Sb and Hg together with the projected diameter for all particles analysed.

This matrix was then subjected to binary clustering analysis. In this method zero or one is assigned to each element based on the condition that the relative X-ray intensity is below or above a preselected threshold, which is in this case set to 10%. Particles with the same binary pattern are then classified in the same class, which is labelled after the elements it contains.

As an example, Table 2 lists the results of such a clustering for the sample taken from the source corresponding with the emissions of the zinc ore from the zinc ore storage yard. The sample contains two major classes, marked respectively Ore1 and Ore2, which together constitute up to 88% of all particles analysed. Secondary elements in the table are those with an intensity below the preselected 10% threshold; they are not systematically found in every particle analysed.

Table 2 Results of a binary clustering analysis, applied onto the data matrix of the zinc ore sample. The numbers between brackets are standard deviations

<i>Group (Ore)</i>	<i>Main elements</i>	<i>Secondary elements (infrequently detected)</i>	<i>Rel. intensities main elements (standard deviation)</i>	<i>Particles (%)</i>
1	S/Zn	Al, Si, Ca, Ti Mn, Fe, Cu, Pb	39(8)/46(7)	62
2	S/Fe/Zn	Si, Mn, Cu, Pb	40(7)/15(6)/35(10)	26
3	S/Fe/Cu	—	42(2)/20(1)/23(1)	3
4	Zn	—	100	3
5	Al/Zn	—	49/51	1
6	S/Ca/Zn	—	41/14/44	1
7	Ca	Zn	84	1
8	S	—	100	1
9	S/Fe	Zn	51/37	1
10	Al/Si/K	Fe	25/49/13	1

For each class of particles that was included into the identification procedure a characteristic fingerprint was obtained, which was expressed as a *Particle Type Signature* (PTS). These are shown in Figures 3a–l. Each PTS is built up of the five elements which are the most commonly detected in all the individual classes. Specific trace elements, characteristic for one given class were not found and hence could not be used in the classification, except for one specific case. The particles from the Ash-class, were the only ones to contain significant amounts of chlorine. Because of secondary reactions of many particles with atmospheric chlorine—presumably originating from the remelting ovens—this criterium was not unique and therefore could not be used in the identification. The dashed line in Figures 3a–l represents the 10% threshold while the shaded areas are 69% variance levels. This way of expressing results can be compared to the way source signatures in source apportionment are expressed for bulk air particulate matter samples.¹⁰

Particle classification

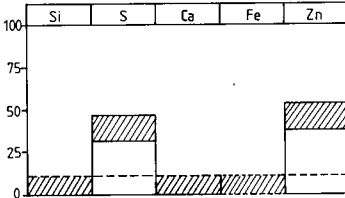
The PTS were used as a basis to develop a set of identification (or decision) rules which describe the respective particles uniquely. This approach differs from the one used by Johnson *et al.*,¹¹ in that the classification is not dependent on the order of chemistry definition files in a linear file structure. It is rather an alternative to the *a priori*

Table 3 Set of identification rules

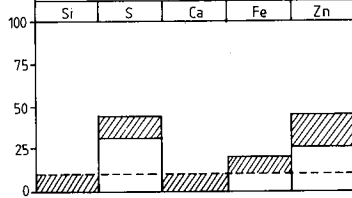
Nr. Rule	Relative X-ray intensities (%)					Relations
	Si	S	Ca	Fe	Zn	
1. Ore	<5	>10	<5	>0	>0	$0.19 < k < 2.5$
2. Roast	<5	0	0	>0	$0 < p < 71$	$40 < l < 100$
3. Neutr.	>5	>10	>5	>0	<10	$0.19 < k < 2.5$
4. Goeth.	<10	>0	<10	>0	>0	$k > 3.2$
5. Ash	0	<10	0	0	>71	
6. Slag	$17 < p < 27$	<10	>10	$27 < p < 43$	<10	
7. Ore-like	>5	>0	<5	>0	>0	$0.19 < k < 2.5$
8. Roast-like	>5	0	0	>0	$0 < p < 71$	$40 < l < 100$

$$k = (p_{Zn} + p_{Fe})/p_S, \quad l = p_{Fe} + p_{Zn}, \quad p = \text{relative intensity.}$$

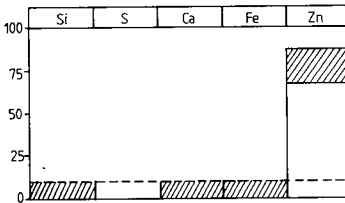
Sample : Ore
 Particle type : Ore 1 id% : 62
 Identificationrule : Ore



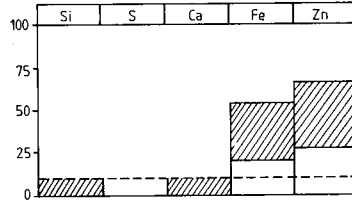
Ore
 Ore 2 id% : 26
 Ore



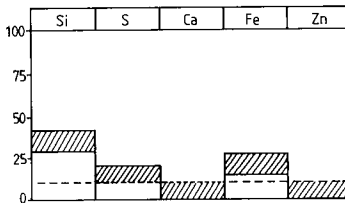
Roasted Ore
 Roasted Ore 1 id% : 46
 Roast



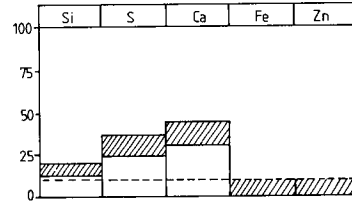
Roasted Ore
 Roasted Ore 2 id% : 37
 Roast



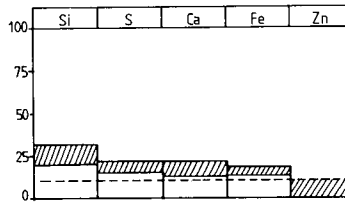
Neutralisation residue
 Neutralisation 1 id% : 8
 Neutr



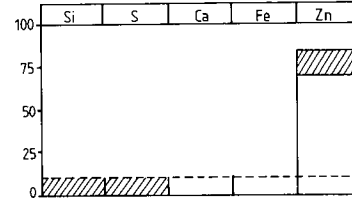
Neutralisation residue
 Neutralisation 2 id% : 8
 Neutr



Neutralisation residue
 Neutralisation 3 id% : 10
 Neutr



Zinc remelting furnace ashes
 Ash id% : 90
 Ash



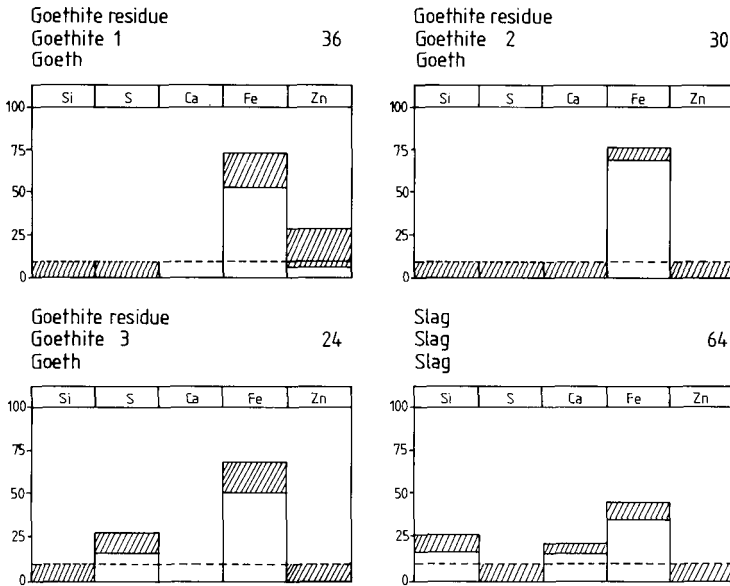


Figure 3a-1 Particle Type Signatures (PTS) for the main classes of particles found in the 6 source samples. In the upper left corner are noted the name of the source sample, the particle type (or particle class) and the identification rule. In the upper right corner is noted the percentage of particles belonging to that class.

utilization of chemical information in the definition file structure, proposed by Karcich *et al.*,¹² but easier to use with the applied data processing program structure.¹³

Table 3 gives an outline of the set of rules. Each consists of a combined condition for the relative intensities or a supplementary relationship between these intensities. It should be noticed that:

1) The names of the rules are printed in small letters; the particle classes, defined by these rules are not exactly the same as the previously defined particle classes and are therefore printed in capitals, when used throughout the text.

2) Several rules are the combined description of several classes within the same source to minimize multicollinearity among the sources.

3) The rules have a broader range of application than one standard deviation on the intensities used, would allow for. This is

because of the—statistical—need to account for a maximum number of particles, i.e. more than the ca. 69% that the Gaussian distribution would predict. Furthermore, the rules were slightly adjusted to the ambient particulate matter in the sample because it appeared that the composition of the ambient particles varied in comparison with the source derived particle composition.

4) The rules, as they are formulated, are disjunct; i.e. there is no overlap between them.

5) Additional rules were established on an empirical basis because their formulation was shown to allow for slightly more complete identification percentages than when these additional rules were omitted from the set; k and l are defined as follows:

$$k = (p_{Zn} + p_{Fe}) / (p_S)$$

$$l = p_{Zn} + p_{Fe}$$

p = relative intensity.

When the identification rules are applied to the matrices of the source data a contingency matrix can be calculated.¹⁴ This matrix is an indication of the extent to which a rule τ classifies those particles it is supposed to classify in class R and misclassifies particles similar to particles from class R but belonging to a minor class in another source. Another way to state this is that the contingency matrix is a measure of the probability that a particle e.g. a roast particle that is

Table 4 Contingency matrix for the zinc fraction of the aerosol; the figures between brackets are the elements of a diagonal matrix that corrects for the effectiveness of the identification rules

Source	Rule					
	Ore	Roast	Neutr.	Goeth.	Ash	Slag
Ore	0.93[1.03]	0	0	0.01	0	0
Roast	0	0.68[4.0]	0	0.27	0	0
Neutr.	0	0	1[1.27]	0	0	0
Goeth.	0.07	0.04	0	0.72[1.14]	0	0
Ash	0	0.28	0	0	1[1.11]	0
Slag	0	0	0	0	0	1[1.41]

classified into the ROAST class, is really a roasted ore source particle.

The figures between brackets are the elements of the diagonal matrix that corrects for the effectiveness of the identification rules. They are defined for a class as the ratio of the number of zinc-containing particles, that are identified by the identification rule, to the number of particles, that should be identified by the identification rule if the rule had not to be adjusted to assure a set of disjunct rules. These elements are calculated as the ratio of the number of all identified particles to the number of particles the identification rule applies to (the main classes that were initially used as a basis).

The size of a class S_{class} can now be calculated as:

$$S_{\text{class}} = A \cdot B \cdot C$$

where

S = matrix of all corrected class sizes for all classes j and samples i ,

A = contingency matrix,

B = correction matrix for the effectiveness of the decision rules,

C = matrix of all class sizes for all classes j and samples i .

The class size can now be calculated as number, volume or mass fraction, according to the needs of the particular problem. However, the correction matrix B should then be calculated on the same basis unless one assumes that the total particle volume is equal to the mean particle volume times the number of particles.

RESULTS AND DISCUSSION

Particles collected in ambient samples were analysed under the same experimental conditions and for each particle an object vector was constructed, as described previously. Then the identification rules were applied onto the resulting data matrices in order to trace back the emission particles described by these rules. After identification and classification, corrections were carried out in order to estimate the relative contributions for each particle class in each ambient particulate sample by number and by volume, the latter using the projected

diameter as obtained in the electron micrographs and assuming a spherical shape.

Statistical analysis

The results of the statistical analysis are summarized in Table 5. For all samples analysed, the mean percentage of zinc-containing particles was 21% by number. Assuming that the fall-out and snow-out was not particularly enhanced for zinc-containing particles, this figure has to be regarded as high, since at residential non-contaminated locations typical values of 0.5% were observed. The percentage of zinc-containing particles was slightly higher for the S-series than for the B or C-series of measurements and was highest for the A-series, because these samples were taken in the more immediate vicinity of some of the potential sources of pollution.

The average median projected diameter for the zinc aerosol as obtained for the S-samples equals $1.8 \pm 0.7 \mu\text{m}$ and agrees fairly well with the mass median diameter of $1.5 \mu\text{m}$ obtained by Rahn *et al.*,¹⁵ in Liège, Belgium from bulk analysis of cascade impactor samples. Size distributions measured near sources are expected to have significant fractions of large particles when compared to non-source data. This is consistent with the measured median diameter obtained for the A-series, which is slightly higher than for the B- and C-series.

Table 5 Median projected diameters and zinc particle content for all samples in series S, A, B*, B, C* and C. Series marked with an asterisk contain the sample sections oriented towards the plant. The numbers between brackets are 1 standard deviation.

Series	Total aerosol (μm)	Zn-aerosol (μm)	Zn-particles (number %)
S	1.6(0.3)	1.8(0.7)	24
A	4.0(2.4)	4.7(2.6)	30
B*	3.9(4.0)	4.6(4.6)	15
B	3.4(0.9)	5.1(2.0)	19
C*	2.5(0.6)	2.8(0.7)	15
C	3.6(1.0)	2.5(1.8)	21
Mean			21

Median diameters obtained with the inertial impactor device (series A, B, and C) are significantly larger than those obtained in the S-series. This indicates that the inertial impactor device samples another fraction of the ambient particulates, with, presumably, a lesser collection of the micron size and submicron size particles.

Source apportionment

The results of the identification procedure for the particle classes are summarized in Table 6 for the zinc-containing component of the air particulate matter. Several remarks can be made:

When considering the results of rules 1 to 6 only, an overall degree of identification of 46%, which is defined for the zinc-containing particles as the volume of identified particles to the total volume of particles, could be achieved. This is rather low and points to the fact that at least one other important zinc particle component is present in the aerosol. This could well be one of the known source components which is modified by chemical atmospherical reactions or else a resuspended soil component which is present with high abundance in the top soil in the area around the plant. Therefore, after manual scanning through the data files and looking up non-identified particles, two extra identification rules were defined, obeying the same conditions as originally put forward. They differ from the ones obtained for the ore and roast PTS in that the Si-signal is much higher, pointing to contamination by crustal components. They were

Table 6 Average composition (vol %) of the zinc aerosol for all series S, A, B*, B, C* and C. Samples with a zinc particle content <5% were excluded. The numbers on the top row refer to the identification rules in Table 3

<i>Series</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>	<i>8</i>	<i>Total</i>
S	10	12	15	2	1.5	2.5	29	11	83.0
A	30	2	19	7	0.2	7	18	8	91.2
B*	17	3	5	4	0.6	0.2	16	2	47.8
B	28	8	16	3	0.8	1.4	7	0.6	64.8
C*	11	6	6	12	6	0.1	17	0.4	58.5
C	16	3	11	6	1.2	0	9	14	60.2
Mean	18.7	5.7	12.0	5.7	1.7	1.9	16.0	6.0	67.7

called respectively "ore-like" and "roast-like" particles. When the identification rules for these particles were integrated in the already existing set of rules, the percentage of identification equals 67.7 volume %.

The most consistent results were obtained for the A-series, that was sampled for a short period in the immediate vicinity of the sources of ore, neutralization residue, goethite residue and slag; for the corresponding classes a high identification percentage was obtained.

A rather constant fraction of unidentified material of $42 \pm 7\%$ is obtained for all samples of series B and C, which were sampled under similar experimental and atmospheric conditions. This, together with the fact that nearly all results for a given class have the same order of magnitude, indicates towards a consistent identification procedure.

If we assume that the S-series sampled another size fraction of the particulate matter of the ambient air and if we examine this series separately, it is apparent that for the A, B and C series the main pollution source of zinc particles appears to be the ore pile, both by direct and indirect emission, the latter if we assume that the ore-like particles are resuspended and modified zinc ore particles. The second major source is the neutralization residue and the goethite residue by resuspension of these dumped materials. The emission of particles from the roast ovens is of marginal importance, a fact that can be positively correlated with the installation of a large filter unit on these ovens. Also, particles released from the remelting ovens and from the high slag terril were hardly found at all and hence, they contribute little to the overall pollution around the site.

The results of the S-series confirm these findings. However, because of the observed discrimination of small particles, higher volume fractions of small fugitive roast particles were found, indicating that these particles contribute 12% by volume to the overall zinc pollution.

Surprising is that resuspended material is more abundantly present in the S-series than in the others, despite the presence of a snow layer covering the area and effectively shielding the soil material from resuspension. This could mean that the dumping activity itself is causing this effect.

The method proposed is a straightforward, rule-based approach

using one or more main particle classes in a particle source as a tracer for the relative contribution of that source at a given receptor site. This implies the use of a non-biased or bias-adjustable sampling technique. A measure for this could be the ratio of two particle classes within a given source. If there is no bias, this ratio has to be the same for both source sampling and receptor sampling. Unfortunately, multicollinearity prohibits the verification of this statement.

CONCLUSIONS

It has been shown that it is possible to apportion the zinc fraction of the aerosol sampled in the vicinity of a zinc smelter to several emission sources on the plant, even to some previously unknown ones. However, care must be taken in the interpretation of the relative fraction of identification which vary considerably from one receptor to another, due to, on one hand statistical considerations (the number of particles must be large enough) and on the other hand to meteorological conditions.

One major drawback in the methodology as described is that the source samples were collected in a rather crude way by grab sampling of material. Improvement of this methodology should be achieved if they were taken as a resuspended fraction of the bulk material, in this way simulating the actual conditions of the emissions more closely. Indeed, fractionation could occur thus altering the particle class ratio within a given source sample. Other possible improvements reside in the use of a fast procedure to convert X-ray intensities into concentrations in order to allow the use of accurate mass fractions. This approach would allow a direct comparison of the method with the PCB approach. A procedure to do this is presently studied and the results obtained will be reported in due course.

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