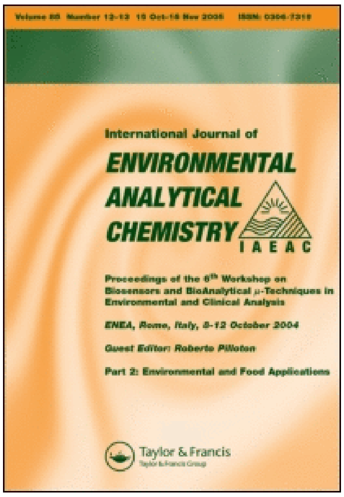

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Trace Analysis of Heavy Metals in Aerosols Over the Atlantic Ocean from Antarctica to Europe

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TRACE ANALYSIS OF HEAVY METALS IN AEROSOLS OVER THE ATLANTIC OCEAN FROM ANTARCTICA TO EUROPE

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The particulate heavy metal concentrations of Tl, Cu, Cd, Pb, Zn, Ni, Cr, and Fe were determined in the atmosphere over the Atlantic Ocean from 77°S (Antarctica) to 54°N (Europe) using the analytical method of isotope dilution mass spectrometry. The samples were collected on board of the German polar research vessel "Polarstern" during four different expedition legs from September 1987 to March 1990. Analyses of the crustal reference element Fe resulted in the calculation of enrichment factors EF(Fe), which were used for interpretation of crustal influences on heavy metal contents as well as for contamination control. The variations in concentration of the dominant crust element Fe run up to five orders of magnitude (0.22–36200 ng m^{-3}). The region between the equator and 20°N was strongly influenced by crustal material transported by the north-eastern trades out of the Sahara. EF(Fe) values around unity and the highest measured concentrations of the dominant crustal elements Fe (36200 ng m^{-3}), Cr (50.6 ng m^{-3}), and Ni (33.7 ng m^{-3}) were found in this area. The mainly anthropogenic elements Cd, Pb, and Zn reached their maximum concentration approaching the European Continent in the English Channel: Cd (1.3 ng m^{-3}), Pb (61.6 ng m^{-3}), Zn (115.9 ng m^{-3}). Elements like Tl and Cu had their highest concentration in the area influenced by Saharan mineral dust (Tl = 96.6 pg m^{-3}, Cu = 9.9 ng m^{-3}) as well as near the highly industrialized European Continent (Tl = 212 pg m^{-3}; Cu = 11.1 ng m^{-3}). A difference in contents between the South Atlantic and the North Atlantic was registered as roughly one order of magnitude for Tl, Cd and Pb. Data from former expeditions were in good agreement with respect to the corresponding meteorological and local conditions. The absolutely lowest concentrations of <0.2–4 pg m^{-3} were measured for Tl in the remote Antarctic region. The contents of the other trace elements in Antarctica were determined to be: Cu = <0.03–0.3 ng m^{-3}, Cd = 0.005–0.5 ng m^{-3}, Pb = 0.07–0.9 ng m^{-3}, Zn = <1–21 ng m^{-3}, Ni = <0.03–0.06 ng m^{-3}, Cr = <0.04–0.1 ng m^{-3}, and Fe = 0.2–9 ng m^{-3}. The high EF(Fe) values of Zn = 240–16000, of Pb = 230–1800 and especially of Cd = 800–90000 suggest that other sources than crustal material are responsible for the measured contents in this area, e.g. biogenic emissions.

KEY WORDS: Heavy metals, aerosol concentrations, Atlantic Ocean, Antarctica, isotope dilution mass spectrometry.

INTRODUCTION

A large number of publications concerning aerosols and their elemental contents appeared in the last years because of their environmental importance. Beyond the effects on climatic parameters caused by reflecting cosmic radiation,[1] the concentration of toxic heavy metals like Tl, Cd, and Pb are of great interest. It is known that the elements Tl, Cd, Pb, and Zn are mainly of anthropogenic origin, for example

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high temperature processes or the use of antiknock agents in gasoline, but there are also natural origins like volcanism and biomass burning.[2–5] On the other hand, the elements Cr, Ni, Cu and especially Fe come from mainly natural sources in the lower marine atmosphere. For example, they originate from eroded crustal material or from sea-spray.

The already existing data are derived mostly from single locations widely spread over the Atlantic and Pacific Ocean or from polar regions and often cover only a limited number of elements.[6–19] On the contrary, this work presents data of eight heavy metals, which were obtained by sampling from 77°S (Filchner Ice Shelf in Antarctica) to 54°N (Bremerhaven in Germany). Comparing these results with those from previous expeditions,[20–22] we are now able to present a more detailed picture on the global north-south pattern of heavy metals over the Atlantic Ocean.

Of additional interest is the influence of anthropogenic sources in remote areas like Antarctica or the different contributions of sources in the marine atmosphere over the Atlantic Ocean. For this purpose the determination of enrichment factors in relation to the average element content of the Earth's crust is of great importance. The element Fe is used in this work as a suitable reference element for crustal material. The derived data may serve well as an important basis for the global monitoring and modelling of element fluxes. Therefore, the results should exhibit a high standard of accuracy, which is guaranteed by the use of isotope dilution mass spectrometry (IDMS)[23,24] and strict contamination control.

EXPERIMENTAL

Sampling areas

Sampling proceeded during four expedition legs of the research vessel "Polarstern":

1) ANT VI/1 from Bremerhaven to Santander (north coast of the Spanish Peninsula) at the end of September, 1987.

2) ANT VI/5 from Cape Town to Bremerhaven during March and April, 1988.

3) ANT VII/5 from Cape Town to Bremerhaven during March and April, 1989, on a slightly different course than during ANT VI/5 (see Figure 1).

4) ANT VIII/5: expedition through the Antarctic regions from Ushuaia (Argentina) via the German Antarctic station "Georg von Neumayer" and the German summer camp at the Filchner Ice Shelf to Cape Town during December 1989 until March 1990.

For more detailed information the different cruises are shown in Figure 1. The exact sampling data are given in Table 1. The first part of the sample number means the date at the beginning of sampling and the second part indicates the consecutive number together with the group of elements (A or B) analysed. The first geographic position in the second column indicates the beginning, the second position the end of each sampling.

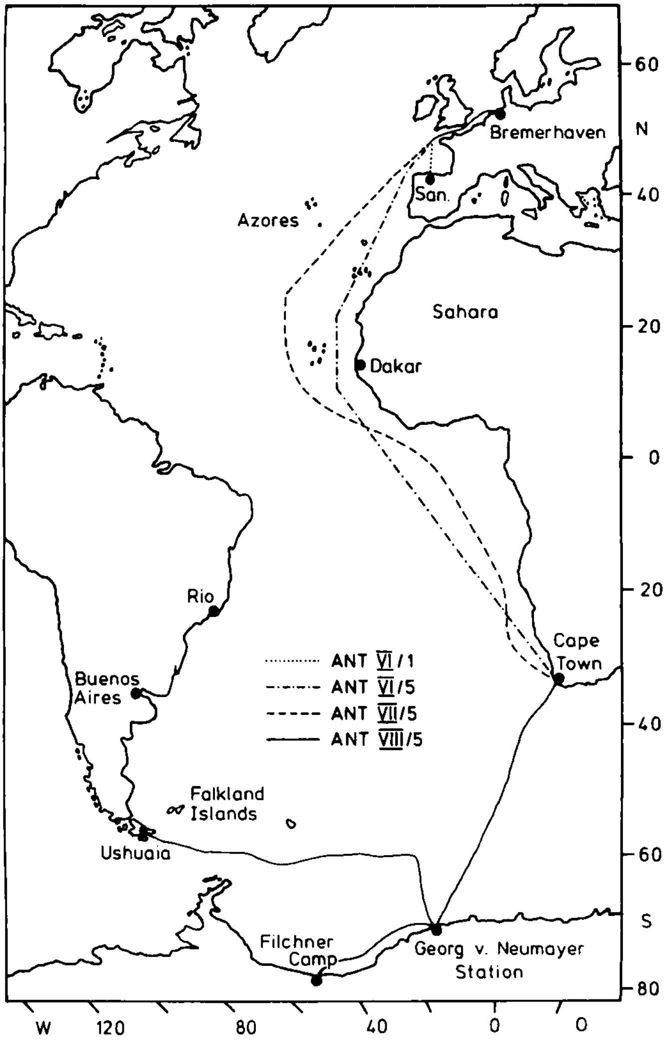

Figure 1 Cruise track of the research vessel "Polarstern" during the expedition legs ANT VI/1, ANT VI/5, ANT VII/5, and ANT VIII/5.

Sampling procedure

Sampling was carried out on board the ship approximately 20 m above sea level. The filter was mounted on top of a plastic covered high-grade steel pole 1.5 m in front of the foredeck. This sampling procedure corresponds to those of previous expeditions[20–22] in order to get comparable results. Previous samplings have shown that this procedure also guarantees the lowest risk for a contamination by the ship. During ANT VII/5 and ANT VIII/5 an automatic wind controller was used, which immediately switched off the sampling unit if the wind came from the back at an

Table 1 Sampling data for the collected aerosols over the Atlantic Ocean

Sample No.	*Geographical position* *From*	*To*	*Air volume (m^3)*
ANT VI/1:			
Element group A:			
250987 A1	53°41'N 05°33'E	52°40'N 03°35'E	16.11
250987 A2	52°40'N 03°34'E	51°22'N 01°56'E	12.00
250987 A3	51°20'N 01°54'E	50°16'N 01°28'W	13.03
260987 A4	50°15'N 01°28'W	49°32'N 03°50'W	16.29
260987 A5	49°32'N 03°50'W	48°27'N 05°32'W	37.96
260987 A6	48°25'N 05°31'W	46°56'N 04°57'W	43.06
270987 A7	46°54'N 04°57'W	45°45'N 04°32'W	35.33
ANT VI/5:			
Element group A:			
180388 A1	32°49'S 17°23'E	31°39'S 16°17'E	25.74
190388 A2	29°46'S 14°44'E	27°51'S 13°02'E	44.14
200388 A3	25°41'S 11°11'E	23°49'S 09°33'E	44.14
210388 A4	21°41'S 07°45'E	19°45'S 06°08'E	46.22
220388 A5	17°40'S 04°26'E	17°06'S 04°02'E	44.38
230388 A6	15°10'S 02°23'E	13°51'S 01°24'E	44.98
240388 A7	11°34'S 00°28'W	09°36'S 01°59'W	46.18
250388 A8	07°28'S 03°41'W	05°33'S 05°10'W	46.39
260388 A9	03°38'S 06°39'W	01°48'S 08°05'W	44.90
270388 A10	00°30'N 09°53'W	02°24'N 11°19'W	37.51
280388 A11	04°38'N 13°04'W	06°40'N 14°39'W	38.21
290388 A12	08°52'N 16°23'W	10°38'N 17°47'W	37.28
300388 A13	13°08'N 18°51'W	15°33'N 18°50'W	38.22
310388 A14	18°23'N 18°50'W	20°43'N 18°50'W	37.47
010488 A15	23°34'N 17°58'W	25°48'N 17°12'W	33.33
020488 A16	28°18'N 16°18'W	29°17'N 15°41'W	28.46
030488 A17	30°39'N 15°10'W	32°08'N 14°36'W	38.96
040488 A18	33°36'N 14°00'W	35°18'N 13°17'W	37.12
050488 A19	37°18'N 12°30'W	39°29'N 11°36'W	36.38
060488 A20	42°02'N 10°26'W	44°18'N 09°13'W	37.58
070488 A21	46°45'N 07°33'W	48°30'N 06°21'W	36.04
080488 A22	49°28'N 04°15'W	50°05'N 01°22'W	35.71
090488 A23	51°45'N 02°36'E	53°25'N 04°49'E	35.77
Element group B:			
180388 B1	31°39'S 16°17'E	29°46'S 14°44'E	41.74
190388 B2	27°51'S 13°02'E	25°48'S 11°15'E	47.03
200388 B3	23°49'S 09°33'E	21°41'S 07°45'E	50.79
210388 B4	19°45'S 06°08'E	17°40'S 04°26'E	55.19
220388 B5	17°06'S 04°02'E	15°13'S 02°26'E	47.60
230388 B6	13°51'S 01°24'E	11°34'S 00°28'W	55.95
240388 B7	09°36'S 01°59'W	07°28'S 03°40'W	51.38
250388 B8	05°33'S 05°10'W	03°38'S 06°39'W	47.99
260388 B9	01°48'S 08°05'W	00°26'N 09°50'W	53.22
270388 B10	02°24'N 11°19'W	04°38'N 13°04'W	46.26
280388 B11	06°40'N 14°39'W	08°52'N 16°23'W	43.62
290388 B12	10°38'N 17°47'W	13°08'N 18°51'W	44.29
300388 B13	15°33'N 18°50'W	18°23'N 18°50'W	44.66
010488 B15	25°48'N 17°12'W	28°18'N 16°18'W	42.95
020488 B16	29°17'N 15°41'W	30°39'N 15°10'W	37.37
030488 B17	32°08'N 14°36'W	33°36'N 14°00'W	37.79
040488 B18	35°18'N 13°17'W	37°18'N 12°30'W	34.99

Table 1 (*continued*)

Sample No.	*Geographical position*		*Air volume (m^3)*
	From	*To*	
050488 B19	39°29'N 11°36'W	42°02'N 10°26'W	40.22
060488 B20	44°18'N 09°13'W	46°45'N 07°33'W	41.30
070488 B21	48°30'N 06°21'W	49°28'N 04°15'W	40.59
080488 B22	50°05'N 01°22'W	51°45'N 02°36'E	42.27
090488 B23	53°25'N 04°49'E	53°39'N 08°24'E	38.56
ANT VII/5:			
Element group A:			
130389 A1	31°23'S 13°04'E	30°04'S 10°04'E	37.63
140389 A2	27°58'S 09°12'E	22°51'S 09°10'E	31.76
160389 A3	19°05'S 08°23'E	16°12'S 06°12'E	44.90
170389 A4	14°01'S 04°33'E	11°56'S 02°55'E	33.71
180389 A5	10°59'S 02°12'E	08°27'S 00°19'W	36.04
190389 A6	06°02'S 01°31'W	03°52'S 03°05'W	34.37
200389 A7	01°34'S 04°51'W	00°21'N 06°25'W	38.60
210389 A8	00°48'N 07°18'W	02°13'N 09°52'W	39.58
220389 A9	03°32'N 12°15'W	04°42'N 14°29'W	35.08
230389 A10	05°43'N 16°20'W	06°40'N 18°07'W	43.34
240389 A11	08°00'N 20°32'W	09°25'N 23°09'W	37.20
250389 A12	10°40'N 25°32'W	12°09'N 28°01'W	38.06
270389 A13	16°04'N 28°05'W	18°31'N 29°18'W	34.02
280389 A14	20°44'N 28°54'W	23°28'N 28°26'W	36.78
290389 A15	25°20'N 28°04'W	25°58'N 27°40'W	39.32
300389 A16	28°01'N 25°51'W	30°15'N 23°56'W	38.15
310389 A17	32°11'N 22°06'W	34°30'N 19°57'W	37.40
010489 A18	36°32'N 18°00'W	38°13'N 16°21'W	37.90
020489 A19	39°52'N 14°40'W	41°44'N 12°49'W	34.81
030489 A20	43°29'N 10°57'W	45°43'N 08°34'W	38.84
Element group B:			
130389 B1	30°04'S 10°04'E	28°23'S 09°12'E	28.60
160389 B2	22°51'S 09°10'E	19°29'S 08°35'E	41.03
170389 B3	16°12'S 06°12'E	14°09'S 04°35'E	29.94
180389 B4	11°56'S 02°55'E	11°19'S 02°27'E	26.88
190389 B5	08°27'S 00°19'W	06°13'S 01°24'W	29.44
100389 B6	03°05'S 03°05'W	01°44'S 04°46'W	33.76
210389 B7	00°21'S 06°25'W	00°48'N 07°18'W	29.59
220389 B8	02°13'N 09°52'W	03°26'N 12°06'W	32.77
230389 B9	04°42'N 14°29'W	05°43'N 16°20'W	32.27
240389 B10	06°40'N 18°07'W	08°00'N 20°32'W	33.87
250389 B11	09°25'N 23°09'W	10°40'N 25°32'W	31.46
260389 B12	12°09'N 28°01'W	16°04'N 28°05'W	49.50
270389 B13	18°31'N 29°18'W	20°44'N 28°54'W	27.77
280389 B14	23°28'N 28°26'W	25°20'N 28°04'W	33.47
290389 B15	25°58'N 27°40'W	28°01'N 25°51'W	33.38
300389 B16	30°15'N 23°56'W	32°11'N 22°06'W	31.77
310389 B17	34°30'N 19°57'W	36°32'N 18°00'W	36.35
010489 B18	38°13'N 16°21'W	39°52'N 14°40'W	40.86
020489 B19	41°44'N 12°49'W	43°29'N 10°57'W	36.59
030489 B20	45°43'N 08°34'W	47°06'N 06°44'W	36.27
ANT VIII/5:			
Element group A and B			
201289 AB1	61°06'S 42°04'W	60°03'S 30°05'W	269.17

(*continued*)

Table 1 (*continued*)

Sample No.	*Geographical position*		*Air volume (m^3)*
	From	*To*	
231289 AB2	60°00'S 15°20'W	63°37'S 08°45'W	231.19
301289 AB3	72°46'S 20°06'W	73°33'S 25°39'W	187.38
010190 AB4	73°58'S 27°22'W	75°47'S 33°51'W	190.39
030190 AB5	76°09'S 38°17'W	76°59'S 49°25'W	184.23
190290 AB6	75°29'S 34°59'W	73°45'S 25°40'W	178.06
200290 AB7	73°45'S 25°32'W	73°16'S 20°25'W	147.78
220290 AB8	72°37'S 19°40'W	70°48'S 15°33'W	190.02
230290 AB9	70°47'S 15°31'W	71°03'S 14°04'W	199.73
240290 AB10	71°02'S 14°00'W	70°25'S 08°44'W	213.58
010390 AB11	70°32'S 07°43'W	64°36'S 03°13'W	297.71
040390 AB12	58°35'S 00°16'W	51°20'S 05°07'E	272.92

angle of more than 112° relative to the ship's direction of movement. During ANT VI/1 and ANT VI/5 sampling was switched off manually or possible contaminations were checked by the analysis of the Ni concentration.

For sampling during ANT VI and ANT VII approximately 40 m^3 were sucked through cellulose nitrate filters with a pore size of 8 μm and a diameter of 5 cm (Sartorius, type SM 11301) during a 12-hour collection period. In the remote Antarctic area during ANT VIII about 200 m^3 were sucked through the filters with a pore size of 0.8 μm and a diameter of 10 cm (Sartorius, type SM 11304) during a 72-hour collection period. The temperature of the air stream passing the gasmeter was measured and the air volume was corrected for a temperature of 25°C assuming ideal gas conditions (values in the last column of Table 1). For the sampling of air particles we used celluose nitrate filters with pore sizes of 8 μm to obtain comparable results to investigations carried out during previous expeditions.[20–22] It is already known that the collection efficiency even of 0.01–0.1 μm particles at 8 μm pore size filters is about 95–98% due to impaction and due to electrostatic interactions between the small particles and the filter material.[25] We confirmed the evidence of this assumption in a previous paper[21] and we also confirmed this by a new series of aerosol samplings in Regensburg for the heavy metals Tl, Cu, Pb, Zn, Ni, Cr, and Fe. For these elements we found concentration differences between 0.8 μm and 8 μm filter samplings which were within the normal variations of parallel collections. Only in the case of Cd three different series of parallel collections did show significant differences (0.8 μm filters: 15.0 ng m^{-3}, 41.3 ng m^{-3}, 25.9 ng m^{-3}; 8 μm filters: 9.9 ng m^{-3}, 2.6 ng m^{-3}, 5.1 ng m^{-3}). Independent investigations of aerosols with a six-stage impactor system at different locations resulted in a preferable association of Cd with the smallest aerosol particles.[26] Because these small particles are especially subjected to long range transport mechanisms, we used 0.8 μm filters in the remote area of Antarctica.

Sample treatment

Reagents Bidistilled water was used throughout this work. Subboiled HNO_3 was produced from conc. HNO_3 of analytical grade. NaOH (30%) and NH_3 (25%) were of suprapure grade, H_2O_2 (30%) of analytical grade.

Isotope dilution technique Isotope dilution mass spectrometry (IDMS), which is known as a method with a high probability for accurate results if contamination is under control, was applied. A detailed description of this method is given elsewhere.[27–29] For the mass spectrometric measurements by positive thermal ionization two different versions of the silica gel technique are recommended.[30,31] Therefore, the elements Tl, Cu, Cd, Pb, and Zn were combined to one group measured by the silica gel technique with the addition of phosphoric acid (group A), whereas the elements Ni, Cr, and Fe were combined to another group measured by the silica gel technique with the addition of boric acid (group B). Both techniques use single-filaments, which consist of Re and were loaded with the elements of one of the mentioned groups. The determination of the isotope ratios $^{203}Tl/^{205}Tl$, $^{63}Cu/^{65}Cu$, $^{114}Cd/^{116}Cd$, $^{206}Pb/^{208}Pb$, and $^{66}Zn/^{68}Zn$ as well as of $^{60}Ni/^{62}Ni$, $^{52}Cr/^{53}Cr$, and $^{56}Fe/^{57}Fe$ were performed with a thermal ionization mass spectrometer (Finnigan MAT, type MAT 261) by a stepwise increase of the filament temperature.[21,32]

Filter treatment Due to the mass spectrometric measurement of two element groups the digestion procedure of the loaded filters (and of the unloaded ones for blank determinations) was also handled in two different ways (group A: NaOH dissolution followed by acidification with HNO_3; group B: treatment with HNO_3). The procedure is described in detail elsewhere[21] and was applied to all samples of ANT VI/1, ANT VI/5, and ANT VII/5. The sample preparation for the group A elements was already done in a clean bench on board the ship, whereas the samples designed for the analysis of group B elements were preserved in polyethylene foil until their treatment in our home laboratory in Regensburg.

The enrichment factors for the group A elements with regard to the iron concentration (EF(Fe) values, see equation (1)) were calculated by the results of two successive samplings (A and B). This was acceptable for sampling periods up to 12 h. However, in the remote area of Antarctica the sampling period was increased to 3 days because of the very low concentration levels (ANT VIII/5). This was the reason why a new procedure for the filter treatment was developed, which enables the analysis of all eight heavy metals from the same filter.

Figure 2 represents the new procedure for the sample treatment. About 0.8–1 ml spike solution containing the enriched isotopes of group A elements (concentration Tl, Cd $\sim 0.5\,\mu g\,ml^{-1}$; Cu, Pb, Zn $\sim 5\,\mu g\,ml^{-1}$) and the same quantity of spike solution containing the enriched isotopes of group B elements (concentration Cr $\sim 5\,\mu g\,ml^{-1}$; Ni, Fe $\sim 10\,\mu g\,ml^{-1}$) were added to the filter stored in a 50 ml polyethylene flask. Afterwards, a mixture of 1 ml NaOH (30%) and 9 ml bidistilled water was added. The filter material was digested at a temperature of 70°C over

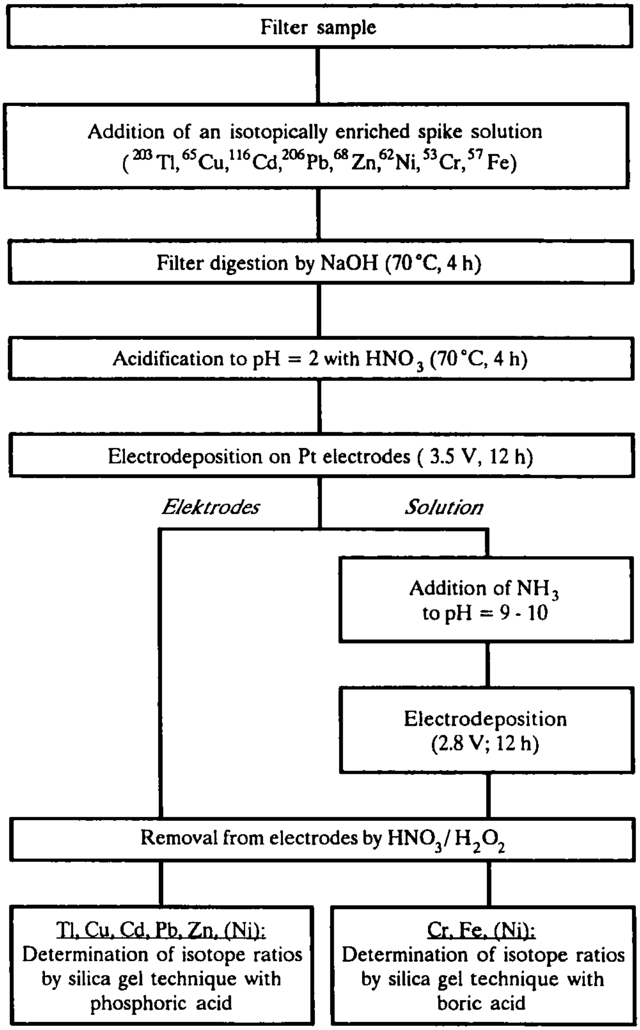

Figure 2 Schematic diagram of the sample treatment for the determination of Tl, Cu, Cd, Pb, Zn, Ni, Cr, and Fe in filter samples with IDMS.

4 h by occasional shaking until the filter was dissolved. The digestion of aerosol particles was continued by acidification with conc. HNO_3 to pH = 2 and further stirring at 70°C over a period of 4 h. Afterwards, the solution was transferred to a 25 ml polyethylene flask, where the first electrodeposition at a potential of 3.5 V for 12 h took place. The deposits were removed from both electrodes using 20 μl of a 4:1 mixture of conc. HNO_3/H_2O_2 (30%). This solution was transferred to a 1.5 ml Eppendorf cup and evaporated to dryness. The residue was used for the isotopic measurement of Tl, Cu, Cd, Pb, Zn and also of Ni in some cases. The remaining solution of the first electrodeposition step was adjusted to a pH of 9–10 by NH_3

(25%). A second electrodeposition was carried out at 2.8 V for 12 h. The electrodes were treated in the same way as already mentioned and the remaining residue was used for the isotopic measurement of Cr, Fe, and possibly Ni. In most cases Ni was measured from the first electrodeposition. In cases where the Ni amount of the first electrodeposition was too small for reproducible mass spectrometric measurements, Ni was determined together with Cr and Fe. This digestion method was carried out in our home laboratory in Regensburg in a clean bench.

Using the NaOH digestion method, a total dissolution of the filter material was obtained. In the case of the HNO_3 digestion method the filter material was not dissolved, so that the dissolution of the collected aerosol particles could not visibly be followed. In the case of silicate particles there is a risk that part of the heavy metals will not be dissolved,[33–35] although our previous investigations using alternative NaOH and HNO_3 digestions did not show any significant differences in the results by applying IDMS.[21] However, we did not use a digestion with hydrofluoric acid to limit all additional chemical steps, which could contribute to the blank. Moreover, the determination of EF(Fe) enrichment factors around unity in aerosols, influenced mainly by Saharan sand (Figures 3 and 4) evidently shows the relevance of the analytical method used.

Blank control

In general, several precautions were taken for contamination control. Every receptacle for filter materials or for solutions were treated twice with diluted HNO_3 and rinsed with bidistilled water. The filterholder was cleaned with diluted HNO_3 prior to its first use and washed with bidistilled water between each sampling. After the cleaning procedure the whole sampling equipment was preserved in polyethylene foil until its next use. In order to obtain comparable results with our previous aerosol investigations over the Atlantic Ocean,[20–22] the cellulose nitrate filters during the expeditions ANT VI and ANT VII were not precleaned by leaching them with an acid. In contrast to this procedure the larger filters of 10 cm diameter used in Antarctica (ANT VIII/5) were leached with a 2 mol l^{-1} HNO_3 solution and twice with bidistilled water prior to their application to reduce the blank contribution by the filter material. Most of the chemical steps were carried out in a clean bench.

Blank determinations were always carried out parallel to the sample analyses. In this case the filter was placed into the filterholder, which was covered by polyethylene foil mounted to the sampling unit without starting the pump. The digestion procedure was exactly the same as described for loaded filters. The results of these investigations are listed in Table 2. The detection limits listed in Table 3 were calculated by the standard deviation of the blank determinations ($2 \times s$ definition with s as the standard deviation of the blank). The Tl detection limit was always below 1 pg m^{-3}, whereas the other heavy metals—except the ubiquitous elements Fe and Zn—resulted in values in the low pg m^{-3} range. Due to the higher air volume, which was sucked through the sampling system during ANT VIII/5, for most of the heavy metals a better detection limit could be obtained in Antarctica even if larger—but precleaned—filters were used.

Table 2 Blank values in ng for used filter material and total sample treatment during different expedition legs (in parantheses: number of parallel determinations)

Element	*ANT VI/1*	*ANT VI/5*	*ANT VII/5*	*ANT VIII/5*
Tl	<0.021 (3)	<0.021 (5)	<0.048 (5)	<0.048 (6)
Cu	7.8 ± 0.9 (3)	8.6 ± 0.8 (5)	13 ± 2 (5)	20 ± 3 (6)
Cd	0.3 ± 0.5 (4)	0.1 ± 0.1 (5)	0.4 ± 0.2 (5)	0.4 ± 0.4 (6)
Pb	3.2 ± 0.6 (3)	10.7 ± 0.9 (5)	36 ± 1 (5)	6.3 ± 0.9 (6)
Zn	190 ± 50 (4)	40 ± 10 (6)	70 ± 10 (2)	230 ± 90 (6)
Ni	—	6 ± 1 (5)	9 ± 1 (5)	23 ± 4 (5)
Cr	—	9 ± 1 (5)	8.0 ± 0.7 (5)	21 ± 6 (6)
Fe	—	240 ± 20 (5)	230 ± 60 (5)	650 ± 20 (6)

Table 3 Detection limits in ng m^{-3} with regard to the mean air volumes collected during different expedition legs

Element	*ANT VI/1* *40 m^3*	*ANT VI/5* *40 m^3*	*ANT VII/5* *40 m^3*	*ANT VIII/5* *200 m^3*
Tl	<0.0005	<0.0005	<0.001	<0.0002
Cu	0.05	0.04	0.1	0.03
Cd	0.03	0.005	0.01	0.004
Pb	0.03	0.05	0.05	0.009
Zn	3	0.5	0.5	0.9
Ni	—	0.05	0.05	0.04
Cr	—	0.05	0.04	0.06
Fe	—	1	3	0.2

RESULTS AND DISCUSSION

Review of results and EF(Fe) values

The analytical results of the Atlantic longitudinal section from 33°S to 54°N are given in Table 4 arranged by their expedition legs and their consecutive numbers, which correspond with Table 1. During ANT VI/1 only the group A elements were determined. The heavy metal concentrations of the marine Antarctic surface aerosol are listed in Table 5. According to the different regions, the determined aerosol concentrations vary over the Atlantic Ocean from 33°S to 54°N up to a factor of 10^2–10^3. Fe shows the largest variation by a factor of more than 10^4. The concentrations in the marine aerosol of Antarctica are in average still a factor of $10^2 - 10^3$ lower than over the Atlantic Ocean at latitudes north of 20°S. The element concentration at different sampling sites in Antarctica normally do not differ by more than a factor of 10.

The determination of enrichment factors EF serves as an important tool for source identification. Due to its high natural abundance, Fe is one of the most commonly used reference elements for crustal material.[36–38] The EF(Fe) value for any heavy

Table 4 Heavy metal concentrations in the surface aerosol over the Atlantic Ocean (8.0 μm pore size filters)

Sample	*Tl*	*Cd*	*Cu*	*Pb*	*Zn*	*Ni*	*Cr*	*Fe*
	(pg m^{-3})		*(ng m^{-3})*					
ANT VI/1								
A1	25	—	1.00	2.42	—			
A2	—	—	0.59	4.28	—			
A3	20	51.9	1.37	7.36	12.7			
A4	—	89.1	1.37	6.91	18.6			
A5	13.5	—	1.48	—	—			
A6	—	233	2.05	21.45	11.9			
A7	—	76.2	0.42	7.10	5.3			
ANT VI/5								
A/B1	<0.8	96.0	0.73	0.09	47.5	0.33	0.36	6.7
A/B2	18.1	—	—	1.62	14.6	12.23	0.09	7.0
A/B3	<0.5	57.5	0.44	0.20	4.9	4.42	0.14	7.4
A/B4	73.1	39.0	—	18.73	67.1	1.22	<0.04	1.2
A/B5	<0.5	—	0.58	0.97	—	1.36	0.07	23.7
A/B6	<0.5	—	0.12	0.67	2.5	0.99	0.07	25.9
A/B7	<0.5	—	—	0.85	—	2.61	<0.04	16.7
A/B8	<0.5	8.2	0.18	1.13	3.4	0.39	0.45	329.4
A/B9	1.0	—	—	1.90	—	0.86	1.14	753.4
A/B10	7.4	18.5	0.45	1.08	2.5	—	1.47	991.4
A/B11	5.2	<5	0.20	0.91	6.3	22.0	40.43	21900
A/B12	96.6	—	—	12.81	—	33.66	50.58	36200
A/B13	80	—	—	8.11	14.1	17.4	22.79	17300
A/B14	33.1	114.3	2.32	12.04	73.7	—	—	—
A/B15	6.7	—	—	1.94	—	0.67	0.89	644.2
A/B16	<0.7	—	0.57	—	13.3	0.30	0.37	219.9
A/B17	<0.5	<5	0.06	0.23	7.3	0.06	<0.05	12.0
A/B18	9.4	130	0.73	13.0	6.1	1.6	0.79	469.8
A/B19	16	97	2.03	1.27	6.8	2.0	0.53	140.4
A/B20	91.7	1300	2.35	33.8	40.7	2.55	0.86	216
A/B21	200.6	1220	6.21	61.64	69.7	4.33	1.52	543.3
A/B22	212	—	11.08	—	115.9	1.2	0.39	271.0
A/B23	<0.6	<6	1.09	1.38	18.1	1.6	0.43	10.4
ANT VII/5								
A/B1	<1	16.1	<0.1	0.060	<0.5	<0.07	<0.05	<4
A/B2	2.8	58.4	<0.1	<0.06	<0.6	0.19	0.62	6.6
A/B3	9.0	<9	0.49	<0.04	0.8	0.11	0.12	21.8
A/B4	1.9	13	<0.1	0.14	<0.6	0.12	<0.05	10.7
A/B5	3.8	<10	0.11	0.31	<0.6	0.21	0.07	28.5
A/B6	—	16	—	0.33	<0.6	<0.06	0.10	38.2
A/B7	<1	<10	<0.1	0.22	8.3	0.10	0.10	45.6
A/B8	<1	<10	0.30	0.17	17.7	0.22	0.18	135
A/B9	10	—	—	—	—	8.6	12.4	7830
A/B10	16	107	9.89	4.55	19	—	8.90	4450
A/B11	23	290.1	2.63	10.08	—	6.29	8.66	4950
A/B12	20	—	—	28.29	95.5	—	3.46	2500
A/B13	—	—	—	—	—	—	0.21	—
A/B14	<1	—	<0.1	—	132.4	0.07	<0.04	14.4
A/B15	2	<10	<0.1	0.30	11.6	0.07	0.30	12.6
A/B16	<1	<10	<0.1	0.14	6.6	<0.06	<0.04	5.4
A/B17	<1	<10	0.44	0.18	5.8	0.17	<0.04	11.6
A/B18	19	—	<0.1	—	—	<0.05	0.13	15.8
A/B19	6	<10	<0.1	0.07	5.0	0.06	<0.04	<3
A/B20	2	<10	<0.1	0.91	3.2	1.9	0.34	57.7

— Not determined.

Table 5 Heavy metal concentrations and EF(Fe) values of the marine Antarctic surface aerosol during ANT VIII/5 (0.8 μm pore size filters)

Sample	*Tl*	*Cu*	*Cd*	*Pb*	*Zn*	*Ni*	*Cr*	*Fe*
Concentrations (pg m^{-3})								
AB1	0.5	143	49	112	9510	39	<40	1050
AB2	4	83	46	168	8300	<30	<50	429
AB3	0.9	<30	12	71	<1000	<40	<60	221
AB4	0.5	172	500	440	16800	<40	<60	1570
AB5	<0.03	80	6	107	1510	<40	<70	2110
AB6	2	267	5	81	<1000	<40	<70	982
AB7	1	313	39	528	2670	55	<80	8780
AB8	1	199	100	379	3920	53	<60	5940
AB9	0.8	78	29	214	2200	<40	<60	1400
AB10	<0.2	233	20	595	2690	<40	104	2140
AB11	0.2	150	101	909	20500	—	96.9	4650
AB12	2	206	479	5413	21400	55	—	1520
EF(Fe) values								
AB1	62	140	13000	480	7300	28	<20	
AB2	1000	200	30000	1800	16000	<50	<70	
AB3	510	<140	15000	1400	<4000	<100	<200	
AB4	42	110	90000	1300	8600	<20	<20	
AB5	<20	39	800	230	570	<10	<20	
AB6	250	280	1500	370	<800	<30	<40	
AB7	14	37	1300	270	240	4.7	<5	
AB8	21	34	4700	290	530	6.7	<6	
AB9	72	57	5900	690	1300	<20	<20	
AB10	<10	110	2700	1300	1000	<10	27	
AB11	5.3	33	6100	880	3500	—	12	
AB12	160	140	89000	16000	11000	27	—	

— Not determined.

metal Me is given by

$$\mathrm{EF(Fe)} = \frac{(c_{\mathrm{Me}}/c_{\mathrm{Fe}})_{\mathrm{sample}}}{(c_{\mathrm{Me}}/c_{\mathrm{Fe}})_{\mathrm{crust}}} \qquad (1)$$

with $c_{\mathrm{Me,Fe}}$ as the concentration of the metal of interest and of iron, respectively.

The EF(Fe) values calculated in this work are based on the data given for the mean abundances of the elements in the Earth's crust by Taylor.[39] Due to natural variations of the Earth's crust composition the enrichment factors should significantly exceed a value of about 10 to clearly indicate the influence of another source than crustal material in the aerosol. The EF(Fe) results are listed in Table 5 and Table 6. The sign " < " indicates a calculation with the detection limit of the metal of interest and, therefore, respresents maximum values. Data with the sign " > " are calculated with the detection limit of Fe and, therefore, represent minimum values.

It is obvious that for most of the heavy metals the marine atmosphere over the Atlantic Ocean from 33°S to 54°N can be divided into three major sections due to the EF(Fe) data: the South Atlantic, the region mainly influenced by Saharan mineral

Table 6 Enrichment factors EF(Fe) over the Atlantic Ocean

Sample	*Tl*	*Cu*	*Cd*	*Pb*	*Zn*	*Ni*	*Cr*
ANT VI/5							
A/B1	<10	110	4000	61	5700	37	30
A/B2	330	—	—	1000	1700	1300	7.1
A/B3	<8	62	2200	120	530	450	11
A/B4	7900	—	95000	73000	46000	790	<20
A/B5	<3	25	—	180	—	43	1.8
A/B6	<2	4.5	—	120	77	29	1.5
A/B7	<4	—	—	230	—	120	<1
A/B8	<0.2	0.6	7.0	15	8.4	0.9	0.8
A/B9	0.2	—	—	11	—	0.9	0.9
A/B10	0.9	0.5	5.3	4.9	2.1	—	0.8
A/B11	0.7[1]	0.2[1]	<1[1]	4.1[1]	5.1[1]	0.8	1.0
A/B12	0.3	—	—	1.6	—	0.7	0.8
A/B13	0.6	—	—	2.1	0.7	0.8	0.7
A/B14	0.2[2]	0.1[2]	1.9[2]	3.1[2]	3.4[2]	—	—
A/B15	1.3	—	—	14	—	0.8	0.8
A/B16	<0.4	2.6	—	—	49	1.0	0.9
A/B17	<5	5.3	<0.1	86	490	3.5	<2
A/B18	2.5	1.6	78	120	11	2.6	1.0
A/B19	14	15	190	41	39	11	2.1
A/B20	53	11	1700	700	150	8.9	2.3
A/B21	46	12	632	510	100	6.0	1.6
A/B22	98	42	—	—	340	3.3	0.8
A/B23	<7	110	<162	600	1400	120	23
ANT VII/5							
A/B1	—	—	>1000	>70	—	—	—
A/B2	50	<20	2500	<40	<70	22	53
A/B3	52	23	<100	<8	28	3.8	3.0
A/B4	22	<13	340	57	<50	8.4	<3
A/B5	17	4.1	100	48	<20	5.4	1.3
A/B6	—	—	120	39	<10	<1	1.4
A/B7	<3	<2	<60	22	150	1.7	1.3
A/B8	<0.9	2.2	<20	5.8	110	1.2	0.8
A/B9	0.2	—	—	—	—	0.8	0.9
A/B10	0.5	2.3	6.8	4.6	3.4	—	1.1
A/B11	0.6	0.5	16	9.2	—	1.0	1.0
A/B12	1.0	—	—	51	31	—	0.8
A/B14	<9	<7	—	—	—	3.8	<2
A/B15	20	<8	<200	110	740	4.0	13
A/B16	<20	<20	<500	110	970	<8	<4
A/B17	<10	38	<200	70	400	11	<2
A/B18	150	<6	—	—	—	<2	4.6
A/B19	>250	—	—	>100	>1000	>10	—
A/B20	4.3	<2	49	71	45	25	3.3

[1] Calculated using Fe content of sample B10.

[2] Calculated using Fe content of sample B13.

dust and the North Atlantic with the anthropogenically influenced area of Europe (Figures 3 and 4). Whereas the EF(Fe) values in aerosols over the South and North Atlantic significantly exceeds one, the region influenced by Saharan mineral dust shows the expected low values near unity or in some cases even less. This trend can

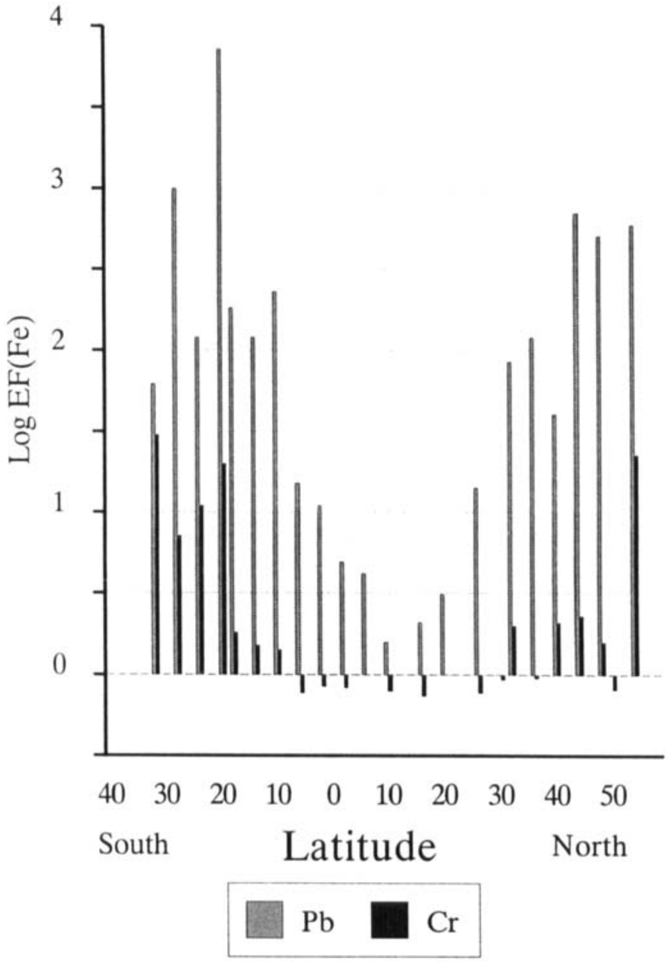

Figure 3 EF(Fe) values of Pb and Cr for the marine aerosol over the Atlantic Ocean from 33°S to 54°N determined during ANT VI/5 (March–April 1988).

clearly be seen for Pb, Cr, and Ni in Figures 3 and 4, although the magnitude of the EF(Fe) values is evidently different for various heavy metals. For example, Cr and Ni exceed an EF(Fe) value of ten in the South and North Atlantic only in a few cases, whereas the corresponding enrichment factors for Pb are always distinctly above ten. The highest enrichment factors, however, were found for Cd and Zn (Table 6). It is also interesting to point out that comparable EF(Fe) values were found in the same area during different years, as it is shown for Ni in Figure 4 measured in March and April, 1988 and 1989, respectively.

In average, the highest enrichment factors for all elements were found in Antarctica (Table 5). This clearly indicates that other sources than crustal material must be responsible for the heavy metal contributions in Antarctic atmosphere.

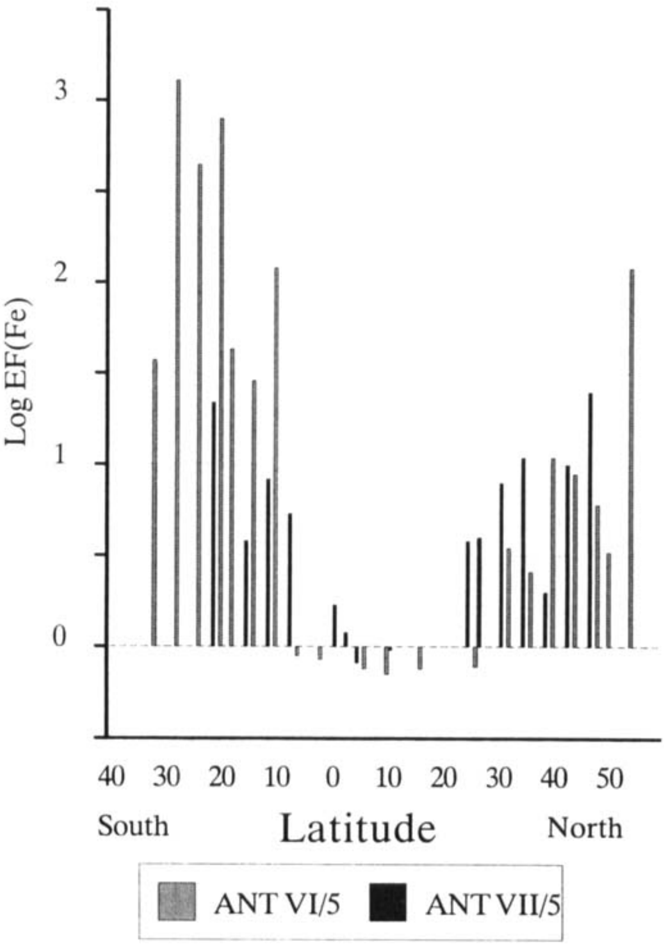

Figure 4 EF(Fe) values of Ni for the marine aerosol over the Atlantic Ocean from 33°S to 54°N determined during ANT VI/5 and ANT VII/5 (March–April 1988 and 1989).

Area influenced by Saharan mineral dust

During the expedition legs ANT VI/5 and ANT VII/5 the influence of the Saharan mineral dust on the aerosol concentration of heavy metals was determined between the equator and about 20°N. The iron concentrations represented in Figure 5 clearly show the influence of this crustal material (concentration in ng m^{-3} in a logarithmic scale!). The iron concentrations in this area were always determined to be higher during ANT VI/5, which reflects the smaller distance to the African Continent of the ship's course during this expedition compared with ANT VII/5 (see Figure 1). The distance between both courses was about 300 km at latitudes between 10°N and 20°N. Thus the iron concentrations in the end of March, 1988 and 1989, respectively,

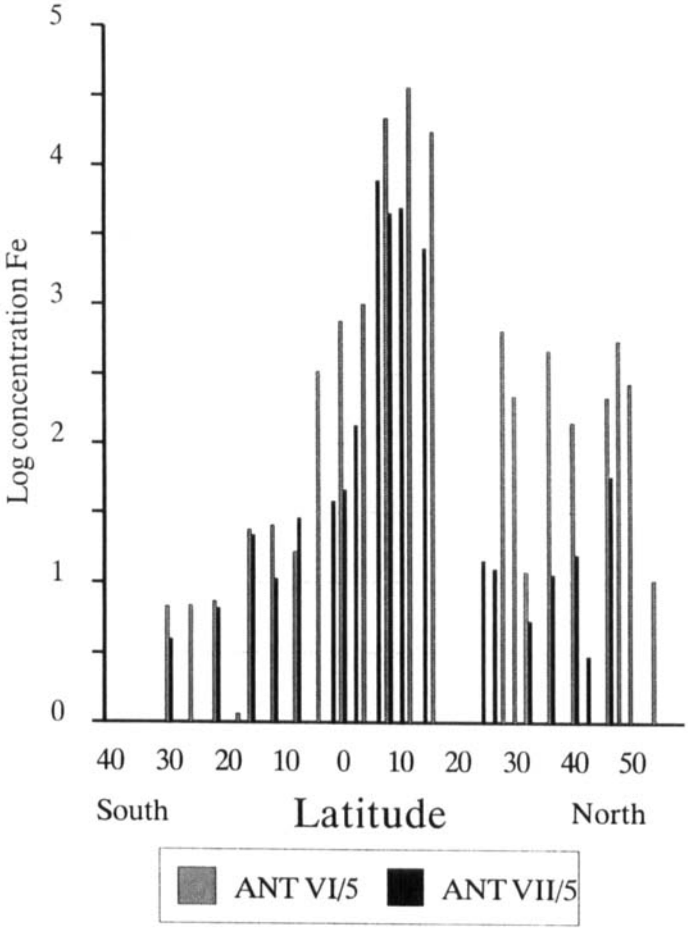

Figure 5 Fe concentration (ng m^{-3}) in the marine aerosol over the Atlantic Ocean from 33°S to 54°N determined during ANT VI/5 and ANT VII/5 (March–April 1988 and 1989).

differ by one to two orders of magnitude, which agrees well with the knowledge that desposition of large particles (like sand particles) takes place quickly.

In general, the influence of Saharan mineral dust described above is also found for the other heavy metals. For example, relatively high concentrations were also analysed for Tl and Pb (Figures 6 and 7). In contrast to the behaviour of Fe the Tl and Pb concentrations increase drastically when approaching the industrialized European Continent. Normally the contents of these elements in this area exceed those in the region influenced by Saharan sand. This demonstrates the anthropogenic contribution of Pb and Tl in aerosols of the continent.

The increase of concentrations by Saharan mineral dust is more intense regarding the elements Fe, Cr, and Ni dominated by the Earth's crust than for Cd, Pb, and Zn. For the last three elements the distance from the African Continent does not have

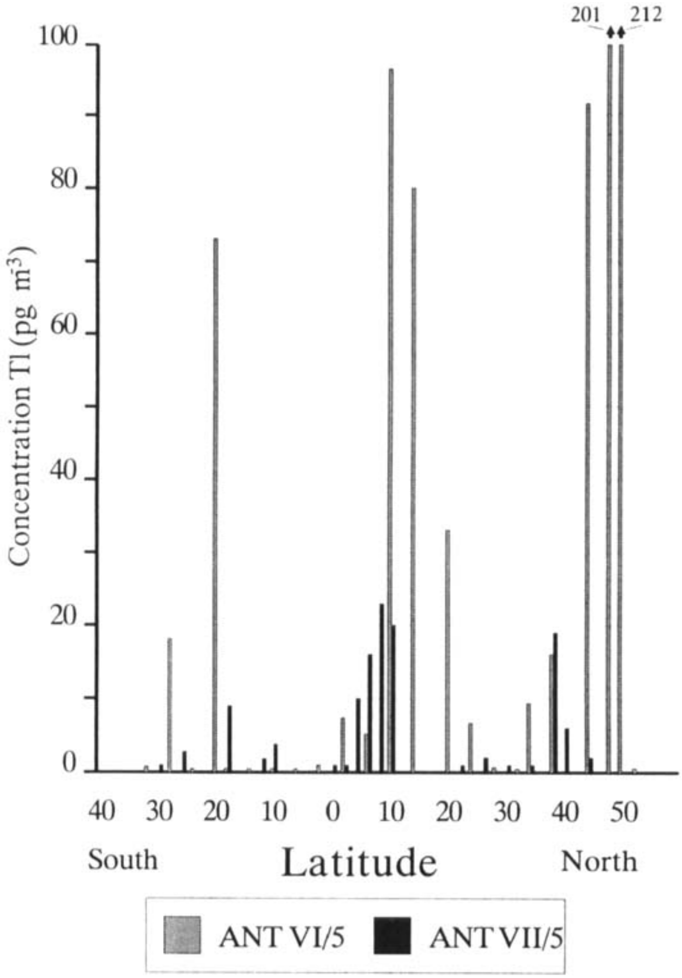

Figure 6 Tl concentration in the marine aerosol over the Atlantic Ocean from 33°S to 54°N determined during ANT VI/5 and ANT VII/5 (March–April 1988 and 1989).

an effect comparable with the first elements mentioned indicating that the Saharan mineral dust is not the only important source in this area. This can be seen more clearly by the EF(Fe) values, which are up to ten for Pb but mostly below one for Cr and Ni, respectively (Figures 3 and 4).

South Atlantic

The heavy metal concentrations determined in samples of the expedition ANT VII/5 best reflect the real situation over the open sea in the South Atlantic (samples A/B1–A/B6 of ANT VII/5 in Table 4). These concentrations are very often below the

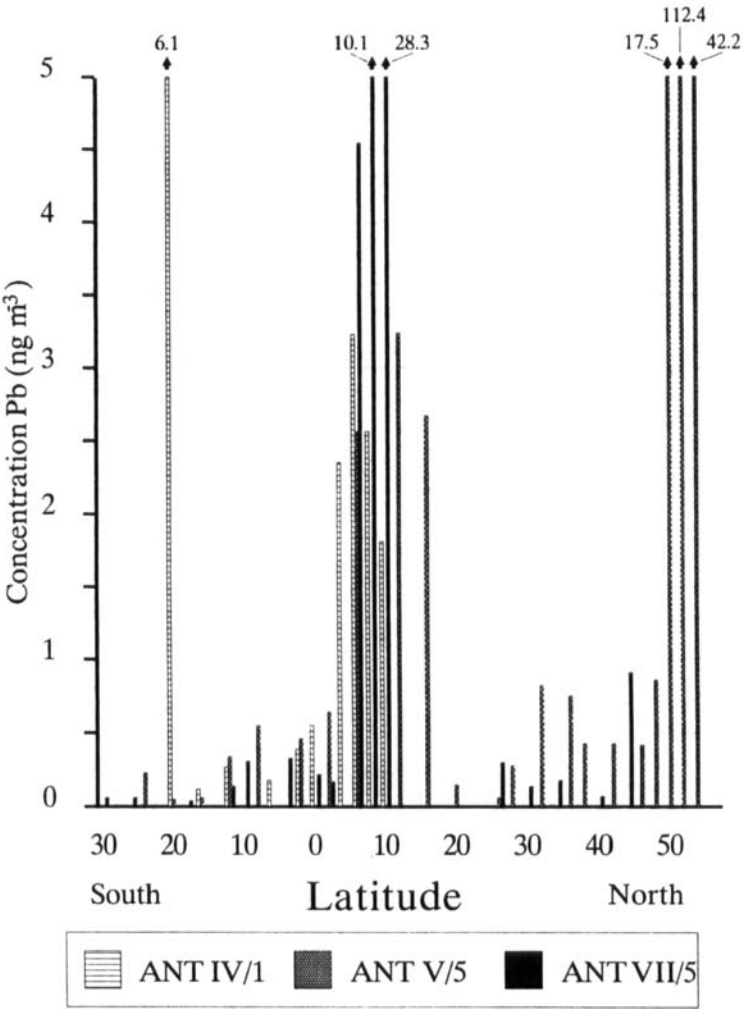

Figure 7 Pb concentration in the marine aerosol over the Atlantic Ocean from 30°S to 54°N determined during ANT IV/1[20], ANT V/5[21] and ANT VII/5 (October-November 1985, March-April 1987, March-April 1989).

detection limit or in the lowest ng m^{-3} range for most of the elements and in the pg m^{-3} range for Tl and Cd, respectively. Figure 7 represents a comparison of Pb results from expedition ANT VII/5 with those obtained during previous expeditions[20,21] (ANT IV/1 during October-November 1985 from Dakar to Punta Arenas (Chile); ANT V/5 during March-April 1987 from Puerto Madryn (Argentina) to Bremerhaven). The samples of all expeditions show comparably low Pb concentrations in aerosols over the South Atlantic although the ship's courses were different. The only relatively high Pb concentration of 6.1 ng m^{-3} was measured at the coast line near the industrialized area of Rio de Janeiro, which again clearly shows the anthropogenic origin of this element.

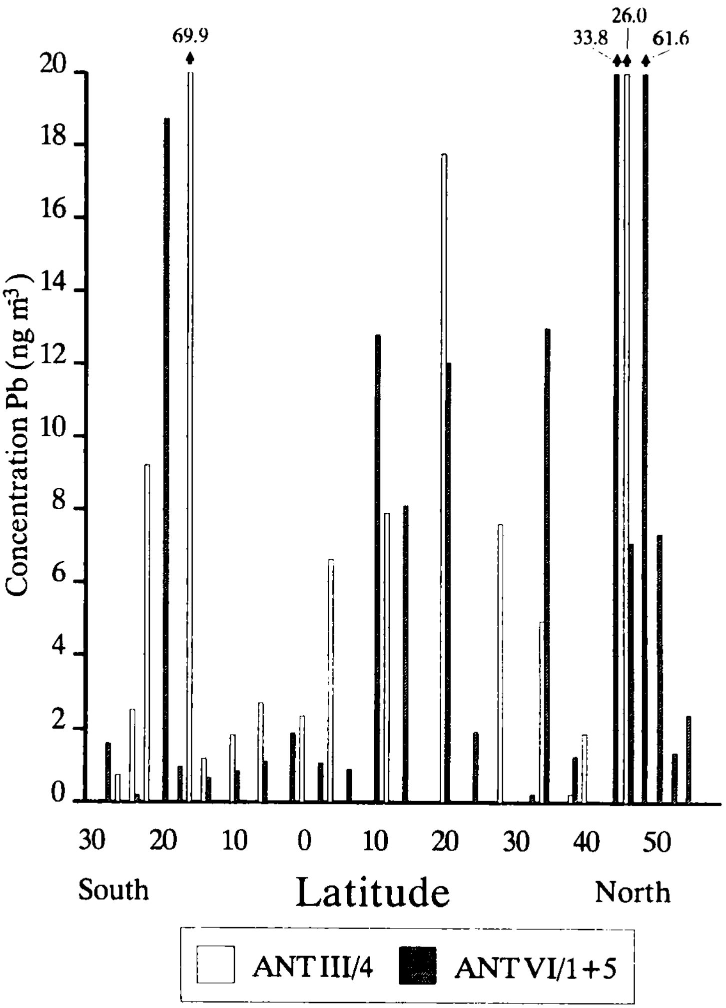

Figure 8 Pb concentration in the marine aerosol over the Atlantic Ocean from 30°S to 54°N determined during ANT III/4[20], ANT VI/1 and ANT VI/5 (March–April 1985, September 1987, March–April 1988).

Whereas during the above mentioned expeditions the non-anthropogenically influenced aerosol samples from the South Atlantic always showed Pb concentrations of distinctly below 1 ng m^{-3}, some samples of expedition ANT VI/5 in the South Atlantic exceed the 1 ng m^{-3} level (Table 4). During this part of the expedition departing from Cape Town with a north-westerly course a continuous south-eastern trade wind was blowing. Because we did not use the automatic wind control system during this expedition (only during ANT VII and ANT VIII) contamination by the ship's exhaust gases could occur. Especially sample A4 (Table 4) seemed to be contaminated, which is also indicated by the EF(Fe) data for Pb (Figure 3).

Because of its enrichment in fossil combustibles,[4,5,40] Ni can be used as an indicator for contaminations from the ship's exhaust gases. The EF(Fe) enrichment factor for Ni in the South Atlantic of expedition ANT VI/5 (Figure 4), therefore, always shows higher values than that one of expedition ANT VII/5. Because enrichment factors for Ni of more than 100 only occur in aerosols strongly influenced by combustion processes, we could conclude from the Ni results that some of the ANT VI/5 samples from the South Atlantic were contaminated by the ship's exhaust gases. This illustrates the appropriate use of Ni determinations for contamination control on board the ship.

North Atlantic

Sampling over the North Atlantic was characterized by two different meteorological situations during ANT VI/5 and ANT VII/5, respectively. During ANT VI/5 the air masses were mainly transported from northern or north-eastern directions (samples A/B20–A/B22). These air masses had passed the European Continent before sampling took place. The concentrations increased for nearly all elements in the given order of samples. However, this effect is more obvious for elements with an anthropogenic source like Pb, Cd, Zn, and Tl than for a typical crustal element like Cr (Table 4). The Fe concentrations remain relatively constant in the range of 200–500 ng m^{-3}.

Besides samples with high concentrations two samples were also found at about 32°N (A/B17) and 53°N (A/B23), which showed relatively low heavy metal levels. These low concentrations could be explained by the influence of Arctic air masses deduced from meteorological data and satellite pictures. A strong dependence of heavy metal concentrations over the North Atlantic on Arctic air masses was also observed during a previous expedition (ANT V/5 in April 1987).[21]

The continuous increase of mainly anthropogenic elements like Pb, Cd, Tl, and Zn from 20°N onward to the north is reflected by a distinct increase of the corresponding EF(Fe) values by about two orders of magnitude compared with the data of the area influenced by Saharan mineral dust (see Table 6 and Figure 3). The increase concerning Cu is only one order of magnitude and no significant increase was found for the crustal element Cr. Compared with crustal material, Pb is generally enriched in the atmosphere over the North Atlantic from 26°N to 54°N (Figure 3), which does not apply for Cr (except sample A/B23).

As already mentioned a different meteorological situation existed during ANT VII/5 with main wind directions from the north-west to the north, which transported marine air masses to our sampling sites (samples A/B16–A/B20). The concentrations of Cu, Cd, Tl, and Cr often remained below the detection limit. The more marine character of the analysed aerosols became especially obvious for the Fe concentrations, which were found to be about a factor of 20 lower when compared with samples from ANT VI/5. The Zn and Ni level was also found to be one order of magnitude lower, Pb and Tl about two orders of magnitude lower.

The EF(Fe) data during this part of the expedition very often could only be given as maximum or minimum value because of the detection limits, which were reached (Table 6). However, the corresponding Ni and Cr data, which were mostly not far away from unity, clearly indicate the origin from crustal material for these heavy metals. The enrichment factors for Pb and Zn were about one order of magnitude higher than those from the South Atlantic. Because the excess Pb and excess Zn may very probably be of anthropogenic origin even if marine air masses of the North Atlantic have been detected. This is in conformance with the general situation showing the Northern Hemisphere to be more anthropogenically contaminated than the Southern Hemisphere.

The samples collected during ANT VI/1 in the English Channel and in the Biscaya show very similar concentrations for the same element at different locations except sample A6 (Table 4). From this it follows that the air masses should be of similar origin, which agrees with the meteorological situation that the air masses of samples A1–A5 had passed the British Islands before collection. The difference of concentrations in sample A6 is due to air masses, which came from the middle of Europe and had passed the highly industrialized areas of North-Western Germany, Belgium, The Netherlands, and parts of France. The measured concentrations can be compared with those during ANT VI/5 where air masses also dominated, which had passed the European Continent.

Comparison of Pb results from different expeditions

Figure 8 represents the Pb results of two expeditions (ANT III/4[20], ANT VI/1 and ANT VI/5) with nearly the same course and comparable meteorological conditions. The concentrations are in good agreement and differ hardly by a factor of two. As discussed before, the samples around 20°S may be contaminated by the ship's exhaust gases caused by the south-eastern trade winds. However, the results of the other samples between 30°S and the equator are similar for both expeditions and represent the real Pb level in aerosols over the South Atlantic. Also the influences of the Sahara and of the anthropogenic emissions of the European Continent were in the same order of magnitude during the different expeditions.

Figure 7 illustrates the situation where preferably marine air masses were collected during three expeditions (ANT IV/1, ANT V/5, ANT VII/5). ANT IV/1 represents an Atlantic crossing from Dakar to Rio de Janeiro[20] and ANT V/5 a course on the longitude at 30°W.[21] The Pb levels of these two expeditions are again in the same concentration range for similar latitudes but they are distinctly lower compared with the results represented in Figure 8, where the anthropogenic influence of the continents became more noticeable.

From the results discussed above, it can be concluded on a more global scale that the heavy metal concentration in the marine aerosol does not vary very much with time at the same location under comparable meteorological conditions. Or, vice-versa, the heavy metal concentration in the atmosphere over the Atlantic Ocean should be predictable at least within a factor of about two for different meteorological conditions.

Our results are also comparable with concentration ranges determined by other groups. For example, Chester *et al.*[7] analysed particulate lead in the marine aerosol in 1979–1981 during different cruises from England to Rio de Janeiro. They found—depending on the location and the meteorological condition—Pb concentrations in the range of (1.3–203) ng m^{-3} over the North Atlantic and of (0.27–7.5) ng m^{-3} over the South Atlantic. Our data obtained during the expeditions ANT VI/5 and ANT VII/5 during March-April 1988 and 1989 of (0.14–62) ng m^{-3} and (<0.04–19) ng m^{-3}, respectively, are in a similar order of magnitude. However, it is interesting to note that our values tend to be at a little lower level. Whether this small and, up to now, not significant decrease is a consequence of the more reduced use of leaded gasoline from 1979 to 1989 or only the influence of temporary local and meteorological events must be checked during the next years.

Antarctica

Results are presented for the first time in Table 5 for aerosol samples collected between 60°S and 77°S in Antarctica concerning eight heavy metals. Because 0.8 μm pore size filters were used in Antarctica, the results are not directly comparable with those of the other expeditions especially for Cd (see description under "filter treatment").

The extremely low Fe levels in the range of 0.2–9 ng m^{-3} as well as Ni and Cr concentrations mostly below the detection limit of about 0.04 ng m^{-3} demonstrate that crustal material cannot strongly contribute to heavy metals in Antarctica. This is understandable because of the great distance of Antarctica to other continents. The low Ni concentration also indicates that contamination by the ship's exhaust gases was not a problem during sampling in Antarctica, where the same wind direction control system was used as during the ANT VII/5 expedition. The Tl data of down to 0.2 pg m^{-3} is the absolutely lowest heavy metal concentration measured in the Antarctic atmosphere up to now.

Although the concentrations of Cu, Zn, Pb, and Cd in Antarctic aerosols are on the average lower than those measured more to the north, a significant amount of these metals could be collected on the filters in Antarctica. In this connection it is interesting to point out that the aerosol concentrations increased rapidly for most elements (especially for Pb and Zn) when the polar Antarctic circle was passed (between samples AB11 and AB12). The high EF(Fe) values especially for Zn, Pb, and Cd, which were also found in Antarctic ice samples,[32] indicate another origin of these elements than crustal material. Three different sources should be, above all, taken into consideration:

1) Contamination by man's activities in Antarctica,
2) Long range transportation of small particles in the troposphere,
3) Emission of metals from the polar Antarctic sea, e.g. by biogenic activities.

Boutron and Wolff calculated the contribution of man's activities in Antarctica on the Pb level up to 19%.[41] On the other hand, aerosol particles in the submicrometer range, which are subjected to long range transportations in the atmosphere, contain relatively high concentrations of Pb and especially of Cd.[26] From Cu it is known that this element has a high degree of marine origin in remote areas up to 50%.[9]

Although there is no exact evidence up to now, we believe that the polar sea is one of the major sources for Tl, Cu, Zn, Cd, and also in many cases for Pb in the Antarctic atmosphere. The extremely high EF(Fe) values measured only 20 m above the open polar sea are one of the reasons for this statement. Another indication for the evidence of this postulation is the fact that samples AB5–AB8 show lower EF(Fe) data especially for Pb, Cd, and Zn than those collected before or after these samples. The indicated samples were collected along the ice shelf border at the most southern sampling sites down to 77°S. In these cases the pack ice moved away just a short time before the ship passed. Therefore, biogenic activities in the surface layer of the polar sea, which should be responsible for an emission of heavy metals, were not already at their maximum. However, the heavy metals in the Antarctic atmosphere must intensively be investigated in the future for a better understanding of the real sources of these elements.

CONCLUSION

This work presents extensive data on the distribution of eight heavy metals in the near surface aerosol over the Atlantic Ocean from Europe (54°N) to Antarctica (77°S). The concentrations differ up to five orders of magnitude. High quality of the analytical data is obtained by using isotope dilution mass spectrometry and by extensive contamination control. Comparisons with data from previous expeditions show good agreement under similar meteorological conditions. This knowledge allows predictions of the heavy metal pattern over the Atlantic Ocean depending on the local conditions and also contributes to a better understanding of the global distribution of these elements. The investigations in Antarctica also indicate a possible contribution of the polar sea to the heavy metal concentration, especially of Cd, Pb, and Zn, in the Antarctic atmosphere.

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