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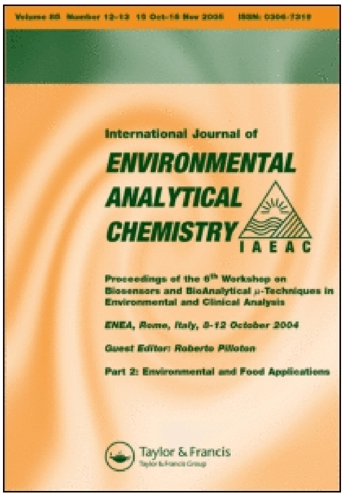

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DETERMINATION OF PARTICULATE IODINE IN AEROSOLS FROM DIFFERENT REGIONS BY SIZE FRACTIONATING IMPACTOR SAMPLING AND IDMS

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Concentrations of particulate iodine in aerosols depending on the particle size were determined after sampling with an impactor system by isotope dilution mass spectrometry (IDMS) using the production of negative I^- thermal ions. The collection efficiency of the impactor system was compared with a filter system by parallel samplings and agreed well. By different leaching processes, using sodium sulfite solution and distilled water, it was shown that various iodine species are incorporated in the aerosol particles. Determinations were carried out with samples from different areas, two continental places in Germany, which are more or less anthropogenically influenced, one location with marine and anthropogenic influences (North Sea) and one in the Weddell Sea, Antarctica, not anthropogenically influenced. In all cases we found the major part of the total iodine in the smallest aerosol particles with an aerodynamic diameter of <0.49μm. Investigations of the continental iodine in aerosols over a two-year period resulted in an average of (2.1±1.2) ng m^{-3} with significantly higher spots during winter only. The total iodine concentration of a sample from Antarctica is about one order of magnitude lower than the mean of the continental samples from Germany, whereas the contents of the North Sea samples are little higher. In an anthropogenically influenced area of Germany the proportion of the total iodine, which was not iodide but iodate and organoiodine leached by sulfite solution, was determined to be 15%, whereas in an Antarctic sample this portion was about 77%. Detection limits down to 1.8 pg m^{-3} for the impactor system and down to 6 pg m^{-3} for the other filter systems were obtained. Natural and anthropogenic sources, which can contribute to the inorganic and organic iodine compounds in the aerosol particles, are discussed.

KEY WORDS: Iodine, aerosol concentrations, impactor system, isotope dilution mass spectrometry, Europe, Antarctica.

INTRODUCTION

Iodine is described as an atmophil element,[1] because it is enriched in the atmosphere compared with other elements in the Earth's crust. The enrichment of iodine compared with chlorine in marine aerosols is well known,[2-4] and different theories concerning the

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ocean as the primary source of iodine exist, which explain this phenomenon.[2–6]

Since the nuclear reactor accidents at Windscale (October 1957) and Chernobyl (May 1986) the interest in the natural iodine cycle strongly increased because of the emission of radioactive iodine compounds into the atmosphere. The natural iodine exchange reactions and the natural iodine cycle must be known in order to estimate probable effects of radioactive iodine emissions for the environment. In this connection the different iodine compounds and forms, which exist in the atmosphere, play an important role.

Up to now, no exact knowledge on the natural iodine cycle has been available, because all the different iodine species in the atmosphere have not been identified due to their very low concentration level. Methyl iodide (CH_3I) is known as one of the gaseous organic compounds, especially in the marine atmosphere.[6–8]

We determined iodine in aerosol particles depending on the particle size at four different places, two of them with no direct marine influence and two others with marine influences. We also tried to differentiate between the different iodine compounds bound at the aerosol particles by using various leaching processes. Isotope dilution mass spectrometry (IDMS) was applied, which also enabled a reliable determination of iodine in the extremely low concentration level of Antarctica.

EXPERIMENTAL

Sampling places

Most of the samples were collected on the roof of the chemistry building of the University of Regensburg about 2 km south of the city of Regensburg, FRG. Other samples, which could also be anthropogenically influenced, were those collected in Bitterfeld, an industrial area about 25 km north of the city of Leipzig, FRG. Samples directly influenced by the ocean were collected at the North Sea in Spieka-Neufeld, a small village about 30 km north of Bremerhaven, FRG, and on board the German polar research ship "Polarstern" approximately 20 m above sea level in the Weddell Sea, Antarctica, from 70°31'S 7°42'W to 62°51'S 2°18'W during an expedition in March 1990.

Sampling procedure

Sampling was carried out with a six stage slot cascade impactor (Sierra 235) in connection with a 10 μm pre-separator or with a normal filter system consisting of one or two filter holders in series. The impactor system consists of five slotted plates covered with the corresponding slotted filters and one back-up filter. The 50% cut-off diameters according to the five stages are given by the manufacturer to be 7.2μm, 3.0μm, 1.5μm, 0.95μm and 0.49μm aerodynamic diameter. On the impactor plates slotted cellulose filters (Whatman Grade 41, No. 144 1980) were used and on the back-up filter a 8×10 square inch cellulose filter (Whatman Grade 41, No. 144 1866). A more detailed description of a cascade impactor is given elsewhere.[9] Possible sources of error during impactor sampling were discussed by

Dzubay et al.[10] and Markowski.[11] However, we did not use silicon oil or other substances on the filter material for reduction of bounce-off and blow-off effects to prevent any additional contamination.

Collections with the normal (single- or double-) filter system were carried out using different filter diameters, pore sizes and filter materials (see Table 1). After sampling all filters were removed from the impactor plates or filter holders and were stored in a PE foil in the dark until their preparation.

The relevant data for all samples together with the total iodine concentration (sum of all stages in the case of impactor sampling) are listed in Table 1. The given air volumes are corrected for 25°C and a pressure of 1 atm.

Sample treatment

Filters from the impactor samplings (slotted filters as well as the back-up filters) were halved. The slotted filters were always halved perpendicular to the slots before sample treatment took place to balance possible differences of the impactation on the filters. The first half of the filter was used for the determination of the total iodine content, the second half for additional investigations, e.g. of Cl^-, NO_3^- and SO_4^{2-}, or for a second parallel analysis of iodine.

The determination of the total particulate iodine concentration on impactor filters by IDMS was always carried out by the same method, described as follows: One half of the filters were transferred into a 100 ml Erlenmeyer flask and 0.2–0.5 g of an exactly known amount of a ^{129}I spike solution (1.5×10^{16} atoms iodine per g of solution), 40 ml of bidistilled water and 0.4 ml of a 0.5 mol l^{-1} Na_2SO_3 solution were added. This mixture was then heated at the boiling point for 1 h. After cooling down the solution was filtered by a 5 μm PTFE filter and acidified by 10 μl of concentrated H_2SO_4. Silver iodide (and also other silver halides) were precipitated by adding (10–400) μl of a 0.4% (by weight) silver nitrate solution. The higher the expected chloride content of the filter sample was, the smaller the added amount of silver nitrate was in order to prevent an excess of AgCl in the isolated sample. Such an excess of AgCl influences the ionization process in the mass spectrometer. After 30 min the silver halide precipitation was separated by a 5 μm PTFE filter and dried at 60°C.

Filters from samplings with only one filter or with filters in series (single-filter or double-filter systems in Table 1) were treated depending on the filter material. The treatment for the cellulose, cellulose nitrate and PTFE filters was exactly the same as for the impactor filters. Using cellulose filters (Whatman Grade 41, 8×10 square inches) the back-up filter system of the impactor was applied as double-filter arrangement for sampling, whereas for all other types of filters separate filter holders were used. When using glass microfibre filters, after the addition of the ^{129}I spike, of 30 ml bidistilled water and of 0.4 ml 0.5 mol l^1 Na_2SO_3 solution, 10 ml 10% (by weight) NaOH solution was also added and this mixture was then heated at the boiling temperature for 1 h. By NaOH the glass microfibre filters were cauterized which enables a more complete analysis of the air-borne particles impacted on the glass microfibre filter surface. The subsequent procedure was identical with the impactor filter treatment except for the use of 4.5 ml concentrated HNO_3 instead of H_2SO_4 for

Table 1 Sampling data and total particulate iodine concentrations

Date	*Air volume (m^3)*	*Sampling system*[1]	*Iodine concentration (ng m^{-3})*
Regensburg			
03/07/89	307.2	Impactor	1.30
05/07/89	265.3	Impactor	1.89
14/07/89	334.3	Impactor	1.67
21/07/89	373.2	Impactor	1.67
	55.9	Single-filter, cellulose nitrate (10cm/8 μm)	1.82
26/07/89	438.4	Impactor	1.60
10/08/89	330.3	Impactor	2.10
05/09/89	366.3	Impactor	2.18
	32.2	Single-filter, cellulose nitrate (5cm/0.8 μm)	1.86
25/09/89	431.2	Impactor	1.34
31/10/89	550.3	Impactor	2.01
28/11/89	619.5	Impactor	4.22
18/12/89	460.2	Impactor	2.13
29/12/89	475.7	Impactor	3.52
26/01/89	331.3	Impactor	0.61
04/02/89	412.9	Impactor	1.59
05/03/90	407.2	Impactor	2.52
04/04/90	687.2	Impactor	1.22
04/05/90	409.7	Impactor	1.23
06/06/90	1757.1	Impactor	1.29
29/06/90	635.7	Impactor	0.96
23/11/90	349.2	Double-filter, cellulose (8 × 10 square inches, Whatman Grade 41)	
		Filter 1	1.47
		Filter 2	0.08
29/11/90	1278.3	Double-filter, cellulose (8 × 10 square inches, Whatman Grade 41)	
		Filter 1	2.61
		Filter 2	0.13
	77.7	Double-filter, cellulose nitrate	
		Filter 1 (10cm/8 μm)	2.31
		Filter 2 (5cm/0.8 m)	0.10
11/01/91	195.6	Double-filter, cellulose nitrate	
		Filter 1 (10cm/8 μm)	1.32
		Filter 2 (5cm/0.8 μm)	0.08
18/01/91	99.4	Single-filter, cellulose nitrate (10cm/8 μm)	7.37
25/01/91	110.6	Single-filter, cellulose nitrate (10cm/8 μm)	2.65
01/02/91	95.6	Double-filter, PTFE (5cm/1.2 μm)	
		Filter 1	3.96

Table 1 Continued

Date	*Air volume* (m^3)	*Sampling system*[1]	*Iodine concentration* $(ng\ m^{-3})$
		Filter 2	≤0.03
05/03/91	25.1	Double-filter, PTFE (5cm/1.2 μm)	
		Filter 1	1.96
		Filter 2	≤0.10
18/03/91	75.8	Double-filter, PTFE (5cm/1.2 μm)	
		Filter 1	1.09
		Filter 2	≤0.03
04/04/91	115.9	Double-filter,	
		Filter 1 glass microfibre GF/A (6cm/1.6 μm)	1.40
		Filter 2 PTFE (5cm/1.2 μm)	≤0.02
12/04/91	102.9	Double-filter, glass microfibre GF/B (6 cm/1.0 μm)	
		Filter 1	0.87
		Filter 2	0.14
19/04/91	118.2	Double-filter, glass microfibre GF/B (6 cm/1.0 μm)	
		Filter 1	1.29
		Filter 2	0.14
23/04/91	118.8	Double-filter, glass microfibre GF/B (6 cm/1.0 μm)	
		Filter 1	1.33
		Filter 2	0.13
01/07/91	570.0	Impactor	1.24
26/10/91	76.4	Double-filter, glass microfibre GF/B (6 cm/1.0 μm)	
		Filter 1	2.94
		Filter 2	0.12
Bitterfeld			
03/05/91	1633.8	Impactor	1.31
	46.0	Double-filter, glass microfibre GF/B (6 cm/1.0 μm)	
		Filter 1	1.34
		Filter 2	0.14
North Sea (Spieka-Neufeld)			
14/09/89	201.0	Impactor	4.61
	189.7	Impactor	3.81
Antarctica (Weddell Sea)			
01/03/90	2755.5	Impactor	0.18

[1] The first number in brackets indicates the diameter of the filter used, the second one the width.

acidification. The NaOH solution used could effectively be purified with respect to iodide contaminations by ion exchange in an anion exchanger column filled with the strongly basic anion exchanger Dowex 1–X8 in the OH^- form. In this case a significant amount of Cl^- was introduced in the solution used for precipitation of iodide. Therefore only 10 µl of the silver nitrate solution were added in this case.

Some of the filters from impactor samplings were determined for their I^- and IO_3^- contents by means of a procedure described by Reifenhäuser and Heumann for aqueous systems.[12] For this purpose ^{129}I enriched I^- and IO_3^- spike solutions are necessary. The used $^{129}I^-$ and $^{129}IO_3^-$ spike solutions are identical to those described by Reifenhäuser and Heumann containing an ^{129}I enrichment of 86.06%.[12] Exactly known amounts of the $^{129}I^-$ and the $^{129}IO_3^-$ spike solution were added to the filter together with 40 ml bidistilled water. After heating for 1 h at the boiling point and cooling down, the solution was filtered using a 5 µm PTFE filter and then I^- and IO_3^- were separated in an anion exchanger column (diameter 1 cm, height 6 cm) filled with the strongly basic anion exchanger resin Dowex 1–X8 (200–400 mesh) in the NO_3^- form. Because of very fast exchange reactions, e.g. between adsorbed iodide on the filter material and the iodide spike solution, an equilibrium between the spike iodine species and the corresponding iodine species with natural isotopic composition in the sample must be assumed for the leaching step. One of the advantages of the isotope dilution technique is that it is not necessary to isolate the isotope diluted I^- and IO_3^- species quantitatively. However, the two species must be completely separated from each other by the anion exchange process. Further details of the separation of I^- from IO_3^- are described elsewhere.[12]

Cl^-,NO_3^- and SO_4^{2-} contents of some of the filters were determined by ion chromatography using an ion chromatograph, type IC 1000 (Biotronik), and a conductivity detector. The filters were extracted with bidistilled water and the concentration of these extracts were determined by calibrating with standard solutions.

Mass spectrometric measurement

The isolated silver iodide (halide) samples were dissolved in a 25% (by weight) NH_3 solution and deposited on the evaporation filament of a double-filament (rhenium) thermal ionization ion source for mass spectrometric $^{129}I/^{127}I$ isotope ratio measurements. The principle of IDMS and further details are described elsewhere.[13,14] In this work a compact, cost-efficient and easy-to-use thermal quadrupole mass spectrometer, type THQ (Finnigan MAT), was applied.[14] For the mass spectrometric measurements 10 µg La as $La(NO_3)_3$ solution were deposited on the ionization filament to enhance the negative thermal ion current of I^-.[13,14] The isotope ratio determinations were carried out at an ionization filament temperature of (1200–1250)°C (controlled by an optical pyrometer); the evaporation filament was not heated by an electrical current.

Blank values and detection limits

Parallel to all sample treatments blanks were determined in the same manner by depositing the corresponding filters in the filter holders or in the impactor system (without sucking through any air), followed by the same chemical procedure as described before. In Table 2 the blank values are listed for the different sampling systems and types of filters. Differences

Table 2 Blank values for the sample treatment by using different filter materials and leaching processes

Filter system	*Leaching solvent*	*Number of determinations*	*Blank value (ng)*
Impactor sampling:			
—Slotted filters (1989) (cellulose filters)	$H_2O + Na_2SO_3$	4	6.4 ± 0.7
—Slotted filters (1989)	H_2O	4	5.4 ± 0.7
—Slotted filters (1990 and 1991)	$H_2O + Na_2SO_3$	5	8.6 ± 0.6
—Back-up filters (cellulose filters, Whatman Grade 41)	$H_2O + Na_2SO_3$	4	9.0 ± 1.0
—Back-up filters (cellulose filters, Whatman Grade 41)	H_2O	4	7.8 ± 1.1
Filter sampling:			
—Cellulose nitrate (5 cm/0.8 μm)[1]	$H_2O + Na_2SO_3$	3	7.0 ± 1.5
—Cellulose nitrate (10 cm/8 μm)	$H_2O + Na_2SO_3$	4	9.0 ± 1.3
—PTFE (5 cm/1.2 μm)	$H_2O + Na_2SO_3$	3	2.9 ± 0.8
—Glass microfibre GF/A (6 cm/1.6 μm)	$H_2O + Na_2SO_3 + NaOH$	4	4.4 ± 0.2
—Glass microfibre GF/B (6 cm/1.0 μm)	$H_2O + Na_2SO_3 + NaOH$	3	11.3 ± 2.0

[1] The first number in brackets indicates the diameter of the filter used, the second one the pore width.

for various time periods of the sample treatment and the different leaching processes for the filters are also listed.

The blank values and the variations of the blank lie significantly under those determined by Kritz and Rancher with the instrumental neutron activation analysis (INAA) using Nucleopore filters (diameter 4.7 cm, pore width 0.8 μm) to be (35±10) ng iodine per filter.[15] Other authors determined iodine contents in similar types of filter materials which are comparable with our results.[16,17]

The detection limit of the IDMS method for the iodine determination in filter samples is limited by the variation of the blank and not by the precision of the isotope ratio measurement. The detection limit can therefore be defined as three times the standard deviation of the blank determination. When approximately 100 m^3 of air were sucked through the single- and double-filter systems and about 1000 m^3 through the impactor system per sampling, detection limits in the range of (6–60) pg m^{-3} and of (1.8–3.0) pg m^{-3}, respectively, were obtained. These detection limits for the determination of particulate iodine in the atmosphere by IDMS are significantly lower than those obtained with INAA by Barrie and Barrie to be in the range of (70–100) pg m^{-3}.[18] The comparison of these results show that isotope dilution mass spectrometry can be applied as one of the very few sensitive methods which is able to detect extremely low particulate iodine concentrations in the atmosphere.

RESULTS AND DISCUSSION

Efficiency and reproducibility of the particulate iodine sampling

The efficiency of the impactor sampling was checked within three different samplings

(21/07/89 and 05/09/89 in Regensburg, 03/05/91 in Bitterfeld) by applying a single- or double-filter system at the same time and at the same location as the impactor system. The results of these parallel experiments can be seen from Table 1. Using the impactor system we applied Whatman 41 filters. The usage of Whatman 41 filters for aerosol sampling is little disputed in the literature.[19,20] However, no significant differences in the results between the impactor system (Whatman 41 filters) and the other filter systems (glass microfibre filters or cellulose nitrate filters) were found. The efficiency for collecting particulate iodine in the atmosphere is therefore comparable for both systems.

The use of two filters in series within one sampling should answer the question of how efficiently the filter system works due to the completeness of the collection of particulate iodine. Double-filter systems were therefore applied in several cases (see Table 1) for different types of filters. Using cellulose, cellulose nitrate and PTFE filters only a small portion of the total particulate iodine in the range of (0.8–5.7)% was found on the second filter, even if 0.8 μm pore size filters were used as a second cellulose nitrate filter instead of a 8 μm filter at the first collection stage. When using glass microfibre filters the portion of the iodine on the second filter is little higher (about 10%).

It is well-known that besides particulate iodine gaseous iodine compounds are also present in the atmosphere.[4,6–8,21] In this case methyl iodide (CH_3I), other organoiodine compounds, HI, I_2 and HOI are discussed. It was tested if glass microfibre filters are able to adsorb gaseous iodine compounds such as CH_3, HI and I_2. It could be shown that none of these substances was adsorbed on these filters, so that these gaseous compounds cannot essentially influence the particulate iodine determination. These investigations on gaseous iodine compounds in the atmosphere are described in more detail elsewhere.[22]

The reproducibility of the analytical procedure for the iodine determination by using the impactor system was checked with sample 29/12/89. In this case all filters of the different impactor stages were halved and then both halves (analysis 1 and 2) were independently treated and analysed. Table 3 summarizes the results. The differences in the analysed iodine concentrations for the corresponding halved filters are in the range of (1.3–15.6)%. Here, inhomogeneities during the particle collection on both filter halves may be responsible for the major part of these differences. However, the difference in the total iodine concentration of all impactor stages is only 1.2%.

Wershofen and Aumann determined particulate ^{127}I and ^{129}I in the atmosphere of Bonn, Germany, via a combination of neutron activation and γ-ray coincidence counting.[16] They

Table 3 Reproducibility of the analytical results for halved impactor filters (sample 29/12/89)

Impactor stage	*Iodine concentration (ng m^{-3})* *Analysis 1*	 *Analysis 2*
1	0.027	0.024
2	0.154	0.130
3	0.506	0.483
4	1.213	1.229
5	0.927	1.026
6 (Back-up)	0.670	0.648
Total	3.497	3.540

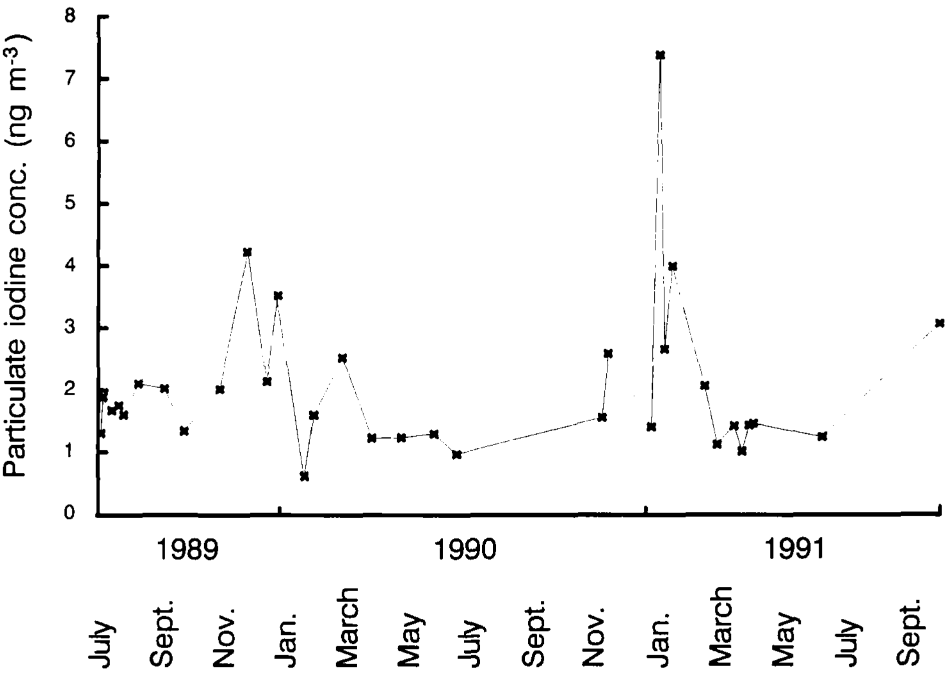

Figure 1 Total particulate iodine concentrations in the atmosphere of Regensburg over a two-year period (July 1989—October 1991)

found an $^{127}I/^{129}I$ ratio of 3×10^6. This result clearly shows that the background contribution of ^{129}I in natural aerosol samples can be neglected compared with the amount of ^{129}I spike added to the samples for the isotope dilution analysis.

Total iodine concentrations

Figure 1 represents the total particulate iodine concentrations which were determined over a two-year period in Regensburg. The average is (2.1±1.2) ng m^{-3} with clearly higher values during winter. During the rest of the year (April-September) the particulate iodine concentration is nearly constant with (1.5±0.3) ng m^{-3}. In Regensburg westerly winds are dominant. However, no significant dependence of the iodine concentration on the wind direction was found.

Table 4 summarizes particulate atmospheric iodine concentrations which are given in the literature for different locations in the world. Our results for Regensburg, Bitterfeld, the North Sea coast and Antarctica agree well with data from other comparable regions obtained by other authors, mostly using INAA. Besides being an extension of the relatively poor knowledge on the global atmospheric iodine distribution, our measurements show that IDMS is a reliable method for particulate iodine determinations. Because INAA has, up to now, been one of the very few methods, which is able to analyse the low atmospheric iodine

Table 4 Concentrations of particulate iodine at different locations

Location		*Iodine concentration (ng m^{-3})*	*Reference*
USA			
—Various locations		0.63–5.67	23
—New York City		3.5	24
—Cambridge, Mass.		2–10	25
—College Park, Maryland		3.8 ± 4.6	26
—Northwest Territories		0.2	24
—Kansas		2.6	24
—Arizona		1.3	24
Pacific			
—Various locations		5.3–17.6	23
—Hawaii		1.3–5.7	3
		1.4–5.2	4
—Enewetak Atoll		2.7 ± 2.0	27
—American Samoa		1.6 ± 2.0	28
Gulf of Guinea		4	15
Tokyo		1.7–12.7	29
Poland, Katowice	(summer)	9–1740	30
	(winter)	18–90	30
Germany			
—Hamburg		3.4	17
—Deutsche Bucht (North Sea)		2.0	17
—Spieka Neufeld (North Sea)		4.2 ± 0.4	This work
—Bonn		2.0 ± 1.9	16
—Regensburg		2.1 ± 1.2	This work
—Bitterfeld		1.3	This work
Bermuda		3.8	24
Antarctica			
—McMurdo		0.93 ± 0.39	31
—South Pole		0.49 ± 0.12	31
	(Antarctic summer)	0.26 ± 0.06	32
	(Antarctic winter)	0.13 ± 0.04	32
—Weddell Sea	(Antarctic fall)	0.18	This work

contents, IDMS can now be used as an interesting alternative. However, IDMS is more sensitive which makes this method especially preferable when extremely low concentrations must be analysed, e.g. in Antarctica or other remote areas.

Impactor results

Figure 2 represents the results of the impactor samplings in Regensburg during the one-year period July 1989 to June 1990. The highest portion of the total particulate iodine was always found — with only one exception — on the 5th and 6th (back-up filter) stage of the impactor where the smallest particles with an aerodynamic diameter AD of <0.95 μm are collected. On average in all determinations 75.3% of the total iodine was collected on these two impactor stages. Such an iodine distribution was also found by other authors for marine regions.[24,25]

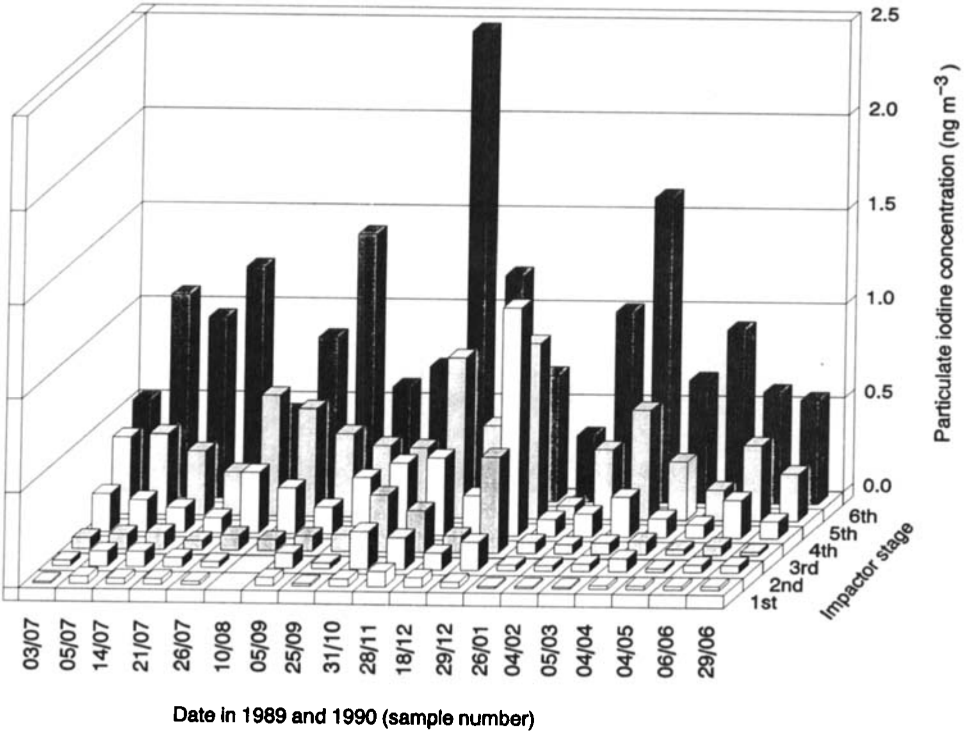

Figure 2 Size fractionated iodine concentrations in the atmosphere of Regensburg over a one-year period

If we compare the results of the different impactor stages for the various locations, a similar distribution pattern was found (Figure 3) independent on the total iodine concentration. The highest portion of the total iodine was analysed for the smallest particles collected on the back-up filter, except for Bitterfeld. However, it has to be taken into account that the distribution pattern for Regensburg is the mean of 19 different samples, whereas for the other locations only one or two samples were taken. Chloride, sulfate and nitrate in the atmosphere of Regensburg (sample 01/07/91) show a similar distribution pattern on the impactor stages as compared with iodine (Figure 4). In this case the other anions were leached by bidistilled water from the filters and have been analysed by ion chromatography, so that only water soluble compounds have been detected.

Sources of iodine

The fact that in most of the experiments the highest portion of the total iodine was associated with the smallest particles means that indications of the primary sources of iodine can be obtained. Two different aerosol fractions are often discussed, the coarse particles and the fine particles.[33] The coarse particles are those with an AD value of >2.5 μm and they are

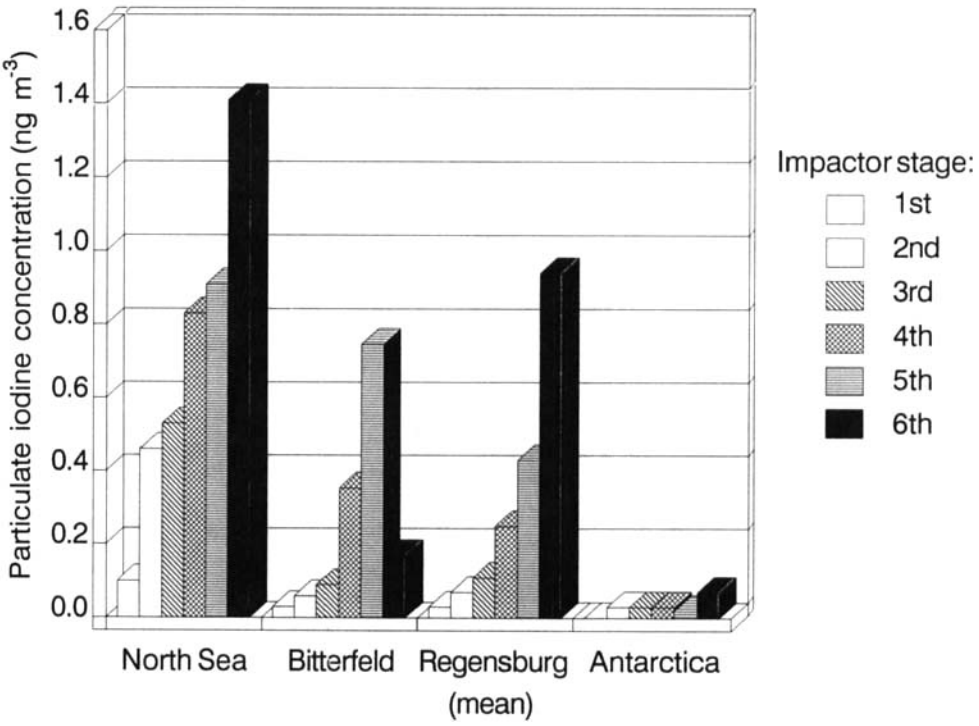

Figure 3 Size fractionated iodine concentrations in the atmosphere of Spieka-Neufeld (North-Sea), Bitterfeld, Regensburg and Antarctica

normally created by mechanical processes such as abrasion, raising dust, vulcanic activities or sea-spray effect.

The small particle fraction can be again divided into particles of the Aitken range (AD<0.08 μm) and into those of the accumulation range (0.08 μm<AD<2.5 μm). Particles of the Aitken range are produced by homogeneous and heterogeneous nucleation.[33] Particles of the accumulation range arise from the growing of Aitken particles by coagulation. Because of a fast coagulation, the life-time of Aitken particles is relatively short. During combustion processes aerosol particles of the accumulation range can also be produced by condensation of low volatile vapors. Particles of the accumulation range are not big enough to be deposited quickly by gravitation or precipitation.

Our investigation from Regensburg and from the other different regions clearly show that in all cases the iodine associated with coarse particles of AD values >2.5 μm (that is the iodine content on impactor stages 1 and 2) plays only a minor role compared with the fine particles. This is valid even in marine areas (North Sea, Antarctica), so it can be concluded from these results that most of the iodine originated from the ocean is not transported by sea-spray into the atmosphere. The high portion we found for iodine associated with the small particles can therefore be of anthropogenic origin, especially from combustion processes, and of natural origin, e.g. by emission of volatile iodine compounds from the ocean.

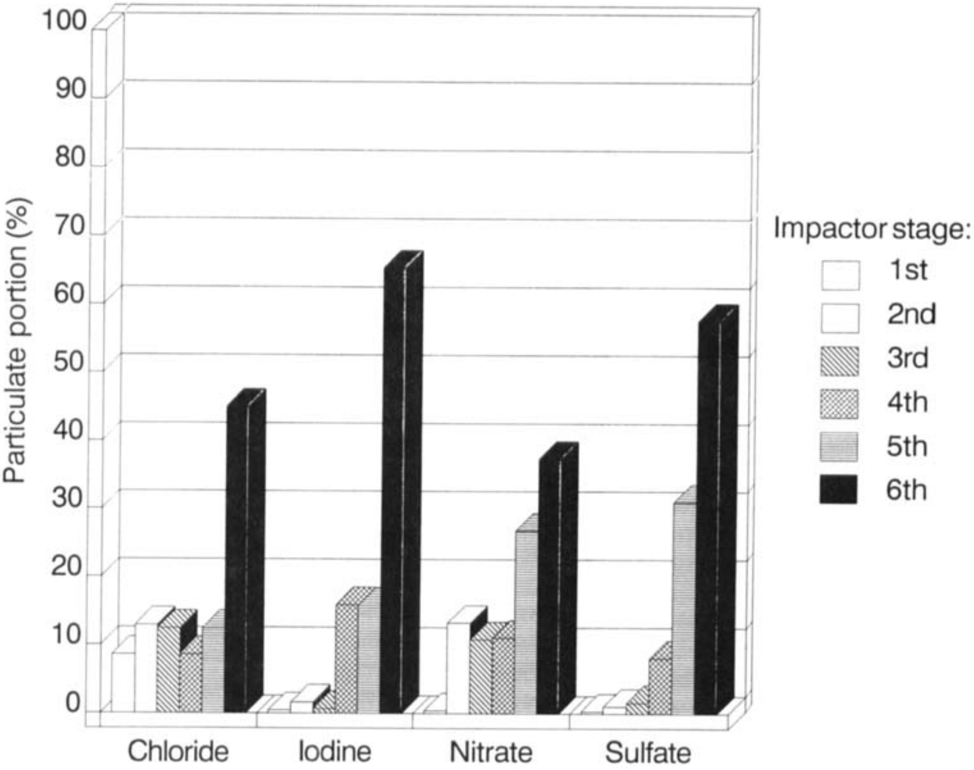

Figure 4 Size fractionated concentrations of chloride, iodine, nitrate and sulfate in the atmosphere of Regensburg (sample 01/07/91)

Due to these two possibilities the sources of the particulate iodine measured in Regensburg, about 800 km away from the coast of the North Sea, can be discussed as follows:

(1) Volatile iodine compounds, emitted from the ocean, accumulate with small aerosol particles of a relatively long atmospheric life-time and are transported over long distances from the ocean to the inner of the continent. If only iodine, emitted by the marine ocean, influences the particulate concentration over the continent, a decrease of the concentration by a first order kinetics must be expected with the distance from the ocean:

$$N = N_0 e^{-kt} \quad (1)$$

with N and N_0 as the concentration of particulate iodine at any point away from the ocean and beside the coast, respectively.

Uematsu et al. have calculated the constant k for aerosol-bound iodine in connection with investigations during the Chernobyl nuclear reactor accident in 1986 to be (0.22–0.33) d^{-1}.[34] Using this k value, the average of our two determinations at the North Sea coast (September 1989) of 4.2 ng m^{-3} and the given wind velocity of 2.6 m s^{-1} during the time of these samplings, we can calculate the expected particulate iodine concentration in Regensburg by equation (1) to be (1.3–1.9) ng m^{-3}. This agrees well with the measured average in

Regensburg during the period April-September of (1.5 ± 0.3) ng m^{-3}. Although the little data we have from the North Sea in correlation with that from Regensburg are not adequate for an exact statement, the results suggest that iodine of marine origin influences the atmospheric iodine concentration over the continent, especially during the summer. The continuous input of iodine from the ocean into the continental atmosphere also would explain the relatively constant aerosol iodine content in Regensburg during summer.

(2) The second possible source of particulate iodine in the atmosphere of Regensburg may be due to anthropogenic combustion processes. That this process also contributes to the iodine concentration is proved by higher iodine values measured during winter (Figure 1) when higher amounts of fossil substances are burned. Exceptions to this higher level can be explained by meteorological conditions, e.g. for sample 26/01/90 by a storm which quickly dilutes anthropogenic influences in the city. The higher particulate iodine concentration in winter agrees well with the increase of the vanadium content in aerosol particles of Regensburg from 6.1 ng m^{-3} measured by Köppe from July to November 1988.[35] Vanadium is an indicator element for the combustion of fossil substances.[36]

The results of our investigations indicate that both processes, (1) and (2), contribute to the particulate iodine over the continent and that, as expected, iodine from the combustion of fossil substances plays a more important role in winter than it does in summer. However, an exact specification of how much of the total particulate iodine originates from process (1) or (2) is not made possible by the impactor results.

The highest portion of chloride, nitrate and sulfate in aerosols of Regensburg was also found associated with the smallest particles (Figure 4). In the atmosphere over the European Continent these anions originate mainly from anthropogenic combustion processes by the formation of, e.g. NO_x and SO_2, respectively, followed by gas-to-particle conversion processes.[33] Similar processes are therefore possible for volatile iodine compounds, e.g. HI, I_2 and organoiodine species after photolytic decomposition.

Particulate iodine in an Antarctic sample

The total particulate iodine measured in one sample of the Weddell Sea, Antarctica, shows that the concentration is about one order of magnitude lower than that we determined for Regensburg and that was also found for most of the other places in the Northern Hemisphere (Table 4). On the other hand, our result agrees well with the same tendency found for other places in Antarctica (Table 4).

It is well known that the atmosphere in clean room compartments contains significantly lower particle concentrations, especially of the small particles, compared with urban regions.[33] Therefore the low particulate iodine content in the atmosphere of Antarctica is probably due to the low concentration of small particles in the air of this remote region, although it was recently found that essential amounts of biogenically produced methyl iodide are emitted from the south polar sea (concentration range (0.2–7.5) ng l^{-1}) into the Antarctic atmosphere (concentration range (0.6–7.9) pptv).[37] The emission of elementary iodine from the ocean was also suggested.[4] Chameides and Davis indicate aerosol particles as possible sinks for inorganic gaseous iodine compounds.[21] They assume that from methyl iodide inorganic iodine species are produced by photolytic reactions in the atmosphere. Duce

Table 5 Enrichment factors EF on the different impactor stages of the Antarctic aerosol sample 01/03/90

Impactor stage	*Concentration* *Iodine (pg m^{m-3})*	*Chloride (μg m^{-3})*	*EF value*
1	≤2.0	0.05	≤15
2	28.2	0.88	12
3	31.6	0.39	31
4	29.3	0.16	70
5	22.5	0.09	96
6 (Back-up)	70.7	0.07	388

et al. also explained the reduction of the particulate iodine concentration from Hawaii to the South Pole by a factor of about five with the long distance of particle sources to Antarctica.[31] However, the exact mechanism of the formation of marine particulate iodine is still unknown.

In the Antarctic sample the chloride concentration was also determined on all impactor stages. The results are listed in Table 5 together with the enrichment factor EF which is defined by

$$EF = \frac{(c_I/c_{Cl})_{sample}}{(c_I/c_{Cl})_{seawater}} \tag{2}$$

with $(c_{I,Cl})_{sample,\ seawater}$ as the concentration of iodine and chloride in the aerosol sample and seawater, respectively. For $(c_{I}c_{Cl})_{seawater}$ the value of 2.6×10^{-6} given by Wedepohl is used.[38]

A continuously increasing EF value is found with smaller particle sizes (with increasing number of impactor stages). This indicates that the major portions of the collected iodine and chloride are not from the same source or—more exactly—that they are emitted by different mechanisms from the polar sea into the Antarctic atmosphere. Whereas chloride is essentially transported by seaspray from the seawater surface into the atmosphere, which causes the decrease of the determined chloride concentration from impactor stage 2 to 6, iodine may be emitted as volatile inorganic and organic compounds into the atmosphere, which causes the higher iodine concentrations on the small particle side and the higher EF values. Our results agree well with previous investigations of Seto and Duce[39] trying to explain the iodine enrichment on marine aerosols.

Iodine speciation in aerosol particles

Because of the low iodine concentrations in aerosol particles and because of the limited number of sensitive analytical methods, only a little information is available on the iodine species. For example, by NAA small iodine amounts are, indeed, determinable, but this method does not detect iodine species. Particulate iodine can generally consist of the inorganic compounds, iodide and iodate, and of organoiodine substances. To differentiate the iodine species, we treated a selection of samples by three methods in connection with IDMS:

Table 6 Speciation of particulate iodine by leaching the filter with bidistilled water (method (a) and a sulfite solution (method (b))

Sample		*Concentration ($ng\ m^{-3}$)*		*Difference*[1]
		method (a)	*method (b)*	*(%)*
Regensburg (10/08/89)				
Impactor stage	4	0.24	0.28	17
	5	0.57	0.68	19
	6	0.86	1.04	21
Regensburg (25/09/89)				
Impactor stage	6	0.52	0.60	15
			Mean	18 ± 3
Antarctica (01/03/90)				
Impactor stage	1	$\leq 2.1 \times 10^{-3}$	$\leq 2.1 \times 10^{-3}$	—
	2	5.1×10^{-3}	28.2×10^{-3}	453
	3	7.6×10^{-3}	31.6×10^{-3}	316
	4	4.4×10^{-3}	29.2×10^{-3}	564
	5	3.4×10^{-3}	22.5×10^{-3}	562
	6	19.7×10^{-3}	70.7×10^{-3}	259
	Total	42.2×10^{-3}	184.3×10^{-3}	337

[1] Differences related to method (a).

(a) Leaching with bidistilled water and subsequent acidification to pH = 2.5. Lower pH values have to be avoided to prevent an iodine exchange between the I^- and IO_3^- ion.

(b) Leaching with bidistilled water under sulfite addition (this is the normal way to treat filter samples in this work) and

(c) Separation of I^- and IO_3^- by anion exchange chromatography.

Using method (a) only iodide is determined by the described analytical procedure. In the case of method (b), iodide, iodate and all organoiodine compounds, which can be converted into iodide by a sulfite solution, are included, whereas method (c) directly separates iodide from iodate.

In Table 6 the results of two samples from Regensburg and one from Antarctica are listed where one half of the filter was treated by method (a), the other half by method (b). Because of the low iodine concentrations on the first impactor stages, only some of the last impactor stages were analysed except in the high-volume Antarctic sample. In all cases the addition of a sulfite solution, which reduces iodate to iodide and is also able to transfer certain organoiodine compounds into iodide,[12] results in higher iodine data. This demonstrates that besides iodide, which is analysed by method (a), other iodine species (iodate and organoiodine) are also included in the aerosol particles. The difference between the two iodine determinations in the samples of Regensburg is 18% on average. The difference for the five last impactor stages of the Antarctic sample is essentially higher with a mean of 337% related to method (a). This result obviously shows that not only the total iodine concentration is distinctly different in aerosol particles of Europe compared with the remote area of Antarctica, but also the iodine species distribution. However, for a more detailed knowledge, additional investigations must be carried out in the future.

For a direct analysis of iodide and iodate an IDMS method was applied, which was developed by Reifenhäuser and Heumann using a ^{129}I and a $^{129}IO_3^-$ spike solution for the isotope dilution process (method (c)).[12] In each case one half of the two last impactor stages

Table 7 Iodide and iodate speciation of particulate iodine in the atmosphere of Spieka-Neufeld, North Sea (sample 14/09/89)

Impactor stage	*Method*[1]	*Iodine amount (ng)* I^-	*Iodine amount (ng)* IO_3^-[2]
5	(a)	110	—
	(c)	113	≤10
6	(a)	215	—
	(c)	225	≤10

[1] For description of methods see text.
[2] Detection limit of IO_3^- is 10 ng.

of an aerosol sample from the North Sea was analysed by method (a) and (c). The results are listed in Table 7. For the iodate determination the detection limit of 10 ng was reached. However, it can be seen that the iodate amount on impactor stage 5 is less than 9% of the amount of iodide, on impactor stage 6 less than 4%. This agrees well with preliminary results we obtained with a sample from Regensburg and with those of Tsukada et al., which have shown that in the water soluble part of aerosol particles of Tokyo the iodate portion is 10% or less.[29]

On the other hand, high-volume samplings with a significantly larger amount of the collected total iodine should be used in the future to determine the real portion of iodate in aerosol particles.

It is interesting to note that the iodine amounts determined by method (a) agree within the normal variation of two halves of a slotted filter from the same collection (see Table 3) with the amounts of iodide determined by method (c). This verifies the assumption that the iodine analysed by method (a) is mainly iodide and not another iodine compound.

CONCLUSION

This investigation has shown that IDMS is a reliable method for the determination of particulate iodine down to the lowest pg m^{-3} level. Thus IDMS is, to our knowledge, by far the most sensitive analytical method for the determination of iodine traces in aerosols. By using different leaching procedures and by the application of the corresponding spike species, iodine speciation is also possible.

It was generally found by impactor samplings that the iodine is usually associated with the smallest particles. The ocean as well as anthropogenic processes could be identified as sources for iodine. However, further investigations must be carried out in the future for a better knowledge of the mechanisms which convert the different possible iodine compounds of the primary sources into particulate iodine.

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