



Iodine concentration and availability in atmospheric aerosol

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Abstract

Iodine has been determined in aerosol samples collected at a coastal site in southeast England using instrumental neutron activation analysis (INAA) and by an electrochemical technique, after aqueous extraction. Size distribution and enrichment factor data for the samples are consistent with a non-sea-salt source of iodine, presumably gas-to-particle conversion of volatile iodocarbons. On average, only ~ 70% of INAA (i.e. total) iodine could be released from the aerosols as inorganic iodine by aqueous extraction at 95°C. Extraction at a more environmentally realistic temperature (20°C) decreased this yield to ~ 25%. Through the use of high-energy UV light, which is known to destroy organic matter, the yield of aqueous extractable iodine at the lower temperature was increased for some samples. Thus, it appears likely that iodine is present in aerosol in varying proportions as soluble inorganic iodine, soluble organic iodine and insoluble, or unextractable, iodine. The different characteristics of these fractions are likely to have significant impacts on the cycling and reactivity of iodine in the atmosphere. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Cycling of iodine in the atmosphere may be an important route for ozone destruction in the marine troposphere (Davis et al., 1996) and lower stratosphere (Solomon et al., 1994), where the primary source of iodine is the emissions of biogenic iodine from seawater (Moore and Tokarczyk, 1993; Klick and Abrahamsson, 1992; Schall et al., 1997). Although the detailed mechanisms of iodine cycling are currently uncertain (e.g. Sturges and Barrie, 1988; Chatfield and Crutzen, 1990; Chameides and Davis, 1980; Sander and Crutzen, 1996; Campos et al., 1996; Vogt et al., 1999), ultimately it is removed from the atmosphere via aerosol and rain. While there is some data available on the speciation of iodine in rain

(Campos et al., 1996; Truesdale and Jones, 1996), there is comparatively little on the chemical form of iodine in aerosol. The majority of published aerosol iodine data has been acquired by instrumental neutron activation analysis (INAA; e.g. Duce et al., 1983; Barrie and Barrie, 1990; Anderson et al., 1996). While this method is an excellent means of determining total iodine, it cannot provide any information on iodine speciation. This is important, as it appears that some forms of aerosol iodine (e.g. iodide) are labile and may be returned to the reactive atmospheric pool by photochemical reaction, while others (e.g. iodate) are not and are believed to act as sinks to the reactive pool (Chatfield and Crutzen, 1990; Solomon et al., 1994; Vogt et al., 1999). The literature on field determination of iodine speciation in aerosol is rather scarce, with iodide reported to dominate the speciation in samples from the North Sea coast (Gäbler and Heumann, 1993), while iodate was determined to be the major species in samples from the tropical Atlantic (Wimschneider and Heumann, 1995). Iodate has been reported to comprise < 10% of aerosol iodine in samples collected at Tokyo, Japan (Tsukada et al., 1987).

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Gäbler and Heumann (1993) used an extraction method including the reducing agent Na_2SO_3 to increase the extractable yield of iodine from an Antarctic aerosol sample. This method may have resulted in the reduction (and extraction) of organic iodine, as well as iodate, from their samples although it was not possible to differentiate between these two forms. By contrast, Campos et al. (1996) and Truesdale and Jones (1996) reported the ratio of iodate to iodide in rain to be ~ 1 , despite using very different analytical techniques.

In this paper we report aerosol iodine concentrations for a coastal site in the southeast of England. Iodine has been determined using INAA and electrochemically after different aqueous extractions; a relatively aggressive, hot method and a more environmentally realistic, cold method. We have concentrated on non-volatile iodine species, as we are interested in the rates and mechanism of iodine removal from the atmosphere. The implications of our results for the availability and cycling of iodine in the atmosphere are discussed.

2. Materials and methods

Reagents used for electrochemical iodine analysis were of BDH-AnalaR grade (ascorbic acid (AA), KI, Triton X-100) or Aristar grade (HCl). KIO_3 was certified to 0.01 N (Wako Pure Chemicals Industries Ltd.). Ultra-pure water (Milli-Q, Millipore) was used to make up these solutions and for extraction of aerosol iodine.

Bulk and size-segregated aerosol samples were collected at the Weybourne Atmospheric Observatory (WAO) on the north Norfolk coast between August 1996 and October 1997 (Table 1). The site ($52^\circ 57' 25''\text{N}$, $1^\circ 7' 40''\text{E}$) is situated on a north-facing coast at an elevation of 15 m above sea level, ~ 75 m from a gently shelving pebble beach (see Penkett et al., 1999). There are no significant populations of flora that might provide a source of volatile iodine species (e.g. macroalgae) near the site. Samples were collected using Graseby–Anderson high-volume samplers at a flow rate of $\sim 1 \text{ m}^3 \text{ min}^{-1}$. Bulk samples were collected on 20×25 cm cellulose filters, cascade impactor samples were collected on slotted cellulose filters with a 20×25 cm cellulose paper as backup (all Whatman Grade 41). The air masses sampled were examined using 5-day back trajectories, and were divided into three main groups (see Table 1): westerly (W) – the air mass originated in the Atlantic and passed over the UK mainland before arrival at WAO; easterly, marine (E/M) – arrival at WAO directly from the North Sea, without significant passage over land; easterly, continental (E/C) – arrival from continental Europe. One sample (designated M/C) was collected from a mixture of E/M and E/C air mass types.

Iodine was determined on portions of the filter papers directly using INAA. Samples were activated in a pneu-

Table 1

Aerosol sample types, start dates, and sampling times and air mass types (based on 5-day back trajectories)^a

Sample	Type	Start date	Total time (h)	Air mass type
L2	D	8/8/96	24.1	W
C3	D	9/8/96	27.0	W
C8	D	14/8/96	48.5	E/M
L13	D	20/8/96	26.2	E/C
C17	D	24/8/96	21.8	W
C19	D	26/8/96	46.1	W
L48	C	4/11/96	28.0	W
L54	C	5/12/96	16.0	M/C
L57	C	23/12/96	45.9	E/C
L73	C	13/3/97	28.3	W
L75	C	27/3/97	28.0	W
C29	C	11/7/97	20.0	W
C31	C	4/8/97	28.0	E/C
C33	C	20/8/97	24.6	W
C38	C	22/9/97	28.0	E/M
C51	D	21/10/97	22.8	E/M

^a(Samples types: D — daily sample, continuous collection; C — composite sample, collection for 4 h per day, around local noon. Air mass types are defined in the text.)

matic irradiation system with a 1 mm cadmium liner to remove thermal neutrons. This significantly reduced the interfering background in the γ -ray spectrum due to activation of sodium and chlorine present on the filter paper. Samples were irradiated for 20 min in an epithermal neutron flux of $9.5 \times 10^{14} \text{ m}^{-2} \text{ s}^{-1}$, allowed to decay for 2 min and then counted for 25 min on a high-resolution γ -ray spectrometry system.

Two extraction methods were employed to release iodine (e.g. iodide, iodate) from the filter papers. In the more vigorous, “hot” method, portions of filter were suspended in Milli-Q water in sealed polyethylene tubes and continuously stirred at 95°C for 3 h. The tubes were then cooled rapidly and the extract was immediately filtered ($0.45 \mu\text{m}$, cellulose acetate). Iodine was also extracted from each filter using ultrasonification for 5 min at 20°C (“cold” method), in a similar manner to the method used by Yaqub et al. (1991) to extract major ions from aerosol samples. These extracts were filtered in the same manner as for hot extracts.

Analysis (duplicate or triplicate) of inorganic iodine in filter extracts was carried out using the method of Campos (1997). The voltammetric system consisted of a hanging mercury drop electrode (Metrohm VA 663), interfaced to a personal computer via a voltammeter (μ -Autolab, Ecochemie bv). Extracts were diluted 2-fold or 4-fold with Milli-Q in the voltammetric cell (total volume ~ 10 ml) and $50 \mu\text{l}$ 0.1 mol l^{-1} AA and $75 \mu\text{l}$ 0.2% v/v Triton X-100 added. The solution was then

purged with ultrapure argon for 5 min and then acidified by addition of 50 μl 6 mol l⁻¹ HCl. Total reducible iodine (i.e. iodide and AA-reducible iodine) was then determined as iodide, by square-wave cathodic stripping voltammetry using the following conditions: deposition potential 0 V, deposition time 30 s, step potential 2 mV, wave amplitude 20 mV, frequency 75 Hz, equilibration time 5 s, scan -0.1–0.7 V. The reduction step has been shown to be 100% efficient for the reduction of iodate (Campos, 1997), and is likely to be so also for other non-iodide inorganic iodine species (if present). We therefore believe that all the inorganic iodine present in the filter extracts is detected by this method.

Aerosol iodine concentrations were calculated after correcting for reagent blanks, dilution and the iodine content of unexposed filter papers. The detection limit of the technique under these conditions was ~ 0.4 nmol l⁻¹, which corresponds to an aerosol iodine concentration of < 0.1 pmol m⁻³ under the conditions typically used to collect and measure these samples. Major ion concentrations on the filter papers were determined by ion chromatography (Cl⁻, NO₃⁻ and SO₄²⁻) or inductively coupled plasma — atomic emission spectroscopy (Na⁺, Mg²⁺ and Ca²⁺) using methods similar to those of Yaqub et al. (1991). Enrichment factors (EF) for aerosol iodine, relative to seawater composition, were calculated using the following relationship ($I_{\text{seawater}} = 0.45 \mu\text{mol l}^{-1}$ (Truesdale, 1995)):

$$\text{EF} = \frac{(I/\text{Na})_{\text{aerosol}}}{(I/\text{Na})_{\text{seawater}}}$$

Aqueous aerosol extracts were photolysed using a 500 W Hg-vapour lamp (Metrohm, 705 UV Digestor). During photolysis samples were contained in quartz tubes with PTFE stoppers and maintained at 70°C for 30 min.

3. Results

Mean and standard deviation enrichment factors of INAA iodine in these samples were 350 ± 270 ($n = 20$, median 250), and clearly indicate that aerosol iodine originates from sources other than sea spray. This was confirmed by analysis of size-segregated aerosol samples, where enrichment factors were found to be orders of magnitude higher in the fine fractions, than the coarse (sea spray, $> 1.5 \mu\text{m}$) fraction, and most of the iodine is on the finest fraction of the aerosol (Table 2). This is consistent with the results of Gäbler and Heumann (1993) and Wimschneider and Heumann (1995), although somewhat different to those of Duce et al. (1983). Our observations support the hypothesis of formation of aerosol iodine by gas-to-particle conversion from volatile iodocarbons such as methyl iodide, either directly or via

Table 2
INAA iodine concentrations (pmol m⁻³) and enrichment factors (EF) in two size-segregated aerosol samples

Size (μm)	Sample L2		Sample L13	
	Conc	EF	Conc	EF
> 1.5	0.9 ± 0.3	35	2.3 ± 0.3	78
1.0–1.5	1.0 ± 0.4	440	4.0 ± 0.4	230
< 1.0	3.6 ± 0.5	2900	15.5 ± 1.1	33000

other gaseous precursors (Chatfield and Crutzen, 1990). This aerosol iodine is associated preferentially with the smaller sulphate particles (Vogt et al., 1999).

An intercomparison of aerosol iodine measured directly on the filters using neutron activation analysis and electrochemical measurement of iodine after extraction using hot and cold water is shown in Fig. 1. Meteorological influences on aerosol iodine concentrations in these samples are not discussed as there was found to be no statistical difference between the iodine concentrations of samples from different air mass types. The INAA technique is assumed to measure the total iodine contained on the filter paper. The hot and cold extractions yield lower concentrations of iodine, presumably due to the presence of other iodine species (e.g. organics – see below) that are not detected by the electrochemical method, and also possibly due to inefficient extraction of iodine from the filter paper before measurement. However, extractions of unexposed filters which had been loaded with iodine (KI & KIO₃) gave recoveries of $100 \pm 2\%$ and make the possibility of inefficient extraction, of inorganic iodine at least, unlikely. The proportions of total (INAA) iodine extracted by the hot and cold methods are shown in Table 3. There were no trends in extractable iodine with size distribution for the fractionated samples discussed above (data not shown). Similar extraction behaviour has been reported for iodine in aerosol samples collected at Tokyo, in which only 42–73% was water soluble (Tsukada et al., 1987), and for bromine in Arctic aerosols (Sturges and Barrie, 1988), where the mean ratio of Br⁻ (measured by ion chromatography) to Br (INAA) was 0.68. Tsukada et al. (1987) were able to confirm the insoluble nature of a fraction of aerosol iodine through INAA analysis of filters after ultrasonic extraction. Thus in our study only $\sim 23\%$ of aerosol iodine is soluble in cold water in forms detectable by electrochemistry (i.e. iodide, iodate and AA-reducible organic iodine). These conditions are those most relevant to atmospheric iodine cycling. A further $\sim 46\%$ of aerosol iodine is made available to electrochemical analysis by heating to 95°C.

Experiments were conducted in which the duration of ultrasonification for cold extraction was extended in an

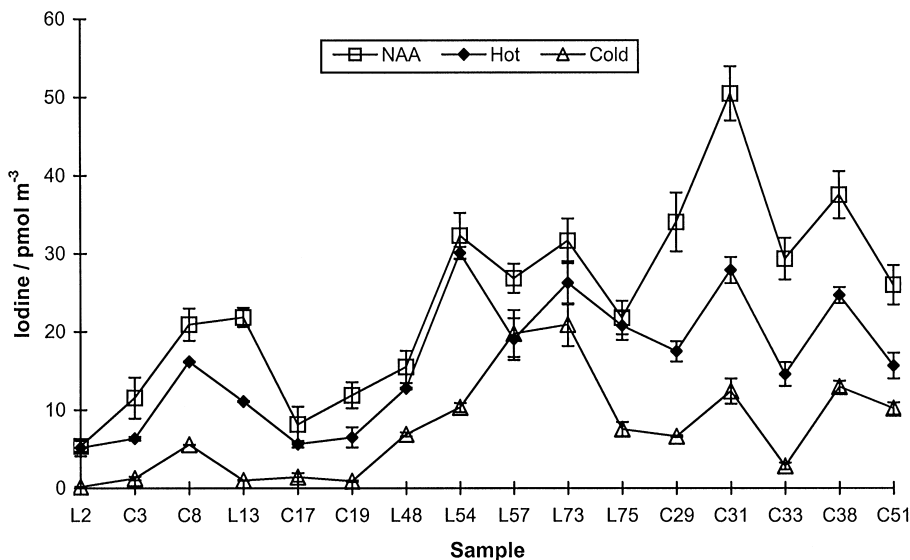


Fig. 1. Aerosol iodine concentrations determined using neutron activation analysis (INAA) and electrochemically after extraction in water at 95°C (Hot) and 20°C (Cold).

Table 3

Mean, standard deviation and median ratios of hot- and cold-extracted aerosol iodine to neutron activation iodine for the data shown in Fig. 1 ($n = 16$)

Method	Mean	SD	Median
Hot	0.69	0.19	0.66
Cold	0.23	0.21	0.18

attempt to increase the yield of extractable iodine. Contrary to expectation, yields decreased with increasing ultrasonification time (Fig. 2). However, subsequent exposure of the extracts to high-energy ultra-violet light designed to destroy organic matter (Wong and Cheng, 1998) apparently converted the 'lost' iodine to (detectable) inorganic iodine so that the total yield was unchanged. These results indicate that ultrasonification may result in the formation of organic iodine species, which are not detected by the electrochemical method. An alternative explanation for this behaviour could be that extended periods of ultrasonification lead to the extraction of interferents from the filter, which mask the electrochemical iodine peak. If exposure to UV light destroyed these interferents, the original iodine signal would be restored and results similar to those of Fig. 2 would be observed. However, the release and destruction of such interfering substances would be expected to cause changes in the sensitivity of the method with increasing extraction time and after UV exposure. No changes in sensitivity were observed during these experiments and

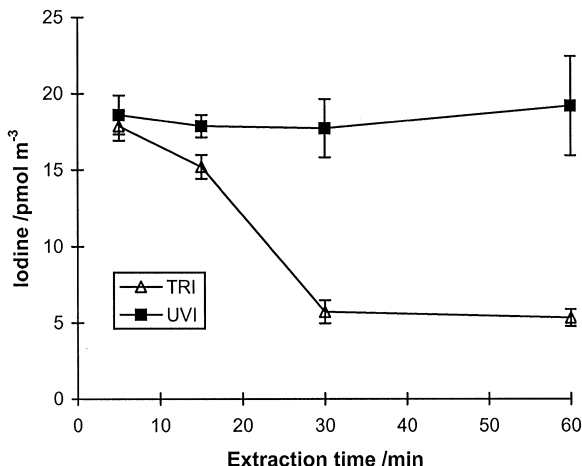


Fig. 2. Total reducible iodine (TRI) measured in aqueous extracts of sample L57 after various ultrasonification times and the same samples measured after the extracts had been UV irradiated (UVI).

we therefore believe that the formation of organic iodine species is the more likely explanation.

In the case of the sample illustrated in Fig. 2 (L57) there does not appear to be a significant organic iodine fraction present at very short extraction times. This was not always found to be the case. Table 4 shows iodine concentrations measured by the INAA, hot, cold and cold followed by UV treatment methods for L57 and another sample (C51). For C51 the cold + UV method

Table 4

Aerosol iodine concentrations (pmol m^{-3}) for samples L57 and C51 determined by INAA, hot extraction, cold extraction and cold extraction followed by UV photolysis

Sample	INAA	Hot	Cold	Cold + UV
L57	27 ± 2	19 ± 1	20 ± 1	19 ± 1
C51	26 ± 3	16 ± 1	10 ± 1	16 ± 2

recovered considerably more iodine than cold extraction alone and, in this case, yielded a very similar concentration to the hot method, indicating the presence of organic iodine in the sample and that this organic fraction was converted to detectable iodine after 3 h at 95°C . While we currently have too little data to ascribe the difference between the yields of the hot and cold methods to the presence of organic iodine compounds in all cases, it does appear that there is a variable fraction of water-extractable iodine in aerosol that is likely to be organic. Considering the sample collection and processing procedures used, this organic iodine is likely to be of higher molecular weight and less volatile than the iodocarbon precursors to the atmospheric iodine pool.

4. Conclusions

Our results suggest that only about a quarter of the total aerosol iodine is readily soluble at low temperature as inorganic iodine and that organic iodine species may form an important aerosol iodine reservoir. While low molecular weight gaseous iodine species are emitted from seawater (Moore and Tokarczyk, 1993; Klick and Abrahamsson, 1992; Schall et al., 1997), these cannot form the aerosol organic iodine without subsequent processing (Vogt et al., 1999). Mechanisms for the formation of (low volatility) organic iodine species have been discussed (Truesdale and Luther, 1995). Potential precursors for organic iodine formation might be provided by the presence in the marine atmosphere of I_2 and HOI (Gäbler and Heumann, 1993) and IO radicals (Alicke et al., 1999). Analogous reactions with OH, O_3 and NO_3 are believed to lead to the conversion of biogenic hydrocarbon gases to organic aerosol (Andreae and Crutzen, 1997). The important issue arising from this work is that only a fraction of the total aerosol iodine is likely to be available for recycling back into the gas phase, because a considerable portion appears to be insoluble. A further fraction appears to be soluble as organic iodine species and its potential to be recycled must be dependent on the character of the compounds involved. We have not attempted to characterise this fraction, although in general C–I bonds are relatively labile. Thus to assess the role of aerosol iodine, it is essential to undertake measurements

of soluble inorganic iodine, rather than the total aerosol iodine based on methods such as neutron activation. We are currently studying the speciation of inorganic aerosol iodine, as this has important implications for the cycling of atmospheric iodine (Chatfield and Crutzen, 1990; Solomon et al., 1994). Our results here add weight to the growing body of evidence pointing to the importance of organic matter in aerosols (Cornell et al., 1995; Spokes et al., 1996; Cornell and Jickells, 1999).

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