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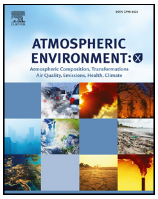

Influence of collection substrate and extraction method on the speciation of soluble iodine in atmospheric aerosols

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HIGHLIGHTS

- Aerosol iodine speciation determined by commonly used methods found to be unreliable.
- Optimum method tested used glass fibre filters and 30 min of mechanical agitation.
- Optimum method was applied to samples collected over the northwest Pacific Ocean.

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ABSTRACT

The extraction into aqueous solution of total soluble iodine (TSI), iodide and iodate were examined as a function of extraction times between 5 and 60 min for two different extraction methods and from two types of commonly used aerosol collection substrates. The extraction methods tested were ultrasonic agitation and mechanical shaking, while the substrates were cellulose fibre (CF) and glass fibre (GF). Tests were carried on substrates spiked with known amounts of iodide and iodate and on a pair of ambient aerosol samples collected at the University of East Anglia on both substrates over the same time period. The combination of ultrasonic agitation and CF substrates (which has been used in many published studies of aerosol iodine speciation) was shown to lead to variable recovery of iodine species and changes in speciation over extraction time. Mechanical shaking of GF substrates gave good recoveries of iodide and iodate from spiked experiments and stable speciation with time for the ambient aerosol sample. This combination is recommended for future use in the determination of aerosol iodine speciation. Mechanical shaking also appeared to be preferable to ultrasonic agitation for samples that were collected on CF substrates. The optimised conditions (mechanical shaking of GF substrates for 30 min) were applied to the analysis of samples collected during the Stratospheric ozone: Halogen Impacts in a Varying Atmosphere (SHIVA) cruise in the South China and Sulu Seas in November 2011. The results obtained showed variable proportions of iodide, iodate and soluble organic iodine species in these samples, with iodide concentrations possibly related to airmass history and background chemistry.

1. Introduction

The emission of volatile iodine-containing species from the sea surface is the primary route by which iodine enters the atmosphere (Saiz-Lopez et al., 2012; Carpenter et al., 2013). Once in the atmosphere, iodine plays a key role in the destruction of ozone in the lower troposphere (Davis et al., 1996; Saiz-Lopez et al., 2012) and under some conditions the products of iodine – ozone interactions can lead to the formation of new atmospheric aerosol particles (O'Dowd et al., 2002; Whitehead et al., 2010). Transport through the atmosphere is also an important pathway by which relatively abundant marine iodine can reach iodine-poor terrestrial environments (Fuge and Johnson, 1986), a pathway which can be a significant factor in determining the prevalence of iodine deficiency disorders (Fuge and Johnson, 2015). The incorporation of iodine into atmospheric aerosols is a significant step in all of these processes. The determination of the speciation of aerosol iodine is particularly important because it can provide information on the potential for aerosol iodine to re-enter the gas phase and hence contribute to further ozone destruction (Vogt et al., 1999; Pechtl et al., 2007). Knowledge of aerosol iodine speciation may also offer insights into the mechanisms of iodine-containing aerosol particle formation and suggest the likely fate and availability of iodine once deposited

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onto the land surface (Fuge and Johnson, 2015).

To date, there have been relatively few studies of the speciation of iodine in marine aerosol. In part this is due to the difficulties in determining iodine speciation at the low concentrations at which iodine in aerosol occurs in the atmosphere, typically $< 200\ \text{pmol m}^{-3}$ (Saiz-Lopez et al., 2012). However, within these studies, several different methods for collecting aerosol samples and determining the abundance of the various iodine fractions contained within them have been used (e.g. Baker et al., 2000; Baker, 2005; Gilfedder et al., 2008; Lai et al., 2008; Xu et al., 2010a; Zhang et al., 2015; Xu et al., 2015). There have been very few attempts to compare these various methods, and there are currently no standardised methods for the determination of aerosol iodine speciation. Ultrasonic agitation, which has been used in several studies (Baker et al., 2000, 2001; Baker, 2004, 2005; Gilfedder et al., 2008; Lai et al., 2008; Allan et al., 2009; Xu et al., 2010a, 2010b), has been suggested to cause changes in aerosol iodine speciation (Baker et al., 2000; Xu et al., 2010a) and such changes have been shown to be dependent on the aerosol collection substrate used (Xu et al., 2010a).

This manuscript describes experiments in which aerosol samples collected in parallel using two commonly-used collection substrates were extracted using different protocols for the recovery of soluble iodine species. Experiments were performed using cellulose fibre (CF) and glass fibre (GF) filters that were spiked with known amounts of iodide and iodate, and on a pair of (CF– and GF- collected) aerosol samples acquired from the roof of the University of East Anglia (UEA), UK. Optimum collection and extraction methods were then applied to a set of aerosol samples obtained during the Stratospheric ozone: Halogen Impacts in a Varying Atmosphere (SHIVA) cruise in the South China and Sulu Seas.

2. Materials and methods

2.1. Reagents

Reagent solutions and aerosol extraction solutions were made up in $18.2\ \text{M}\Omega\ \text{cm}$ ultrapure water (UPW; Elga Purelab Ultra). Calibration solutions and spikes added to extraction experiments were prepared from Aristar grade potassium iodide (KI: BDH) and 99.97% purity potassium iodate (KIO_3: Fisher). Instrument rinse solutions during ICP-MS analysis for total soluble iodine (TSI) were prepared from 25% tetramethyl ammonium hydroxide (TMAH: ACROS Organics).

Aerosol collection and simulated aerosol sample extraction experiments were done using Whatman 41 cellulose fibre (CF) and Whatman Grade G653 glass fibre (GF) substrates (both obtained from Air Monitors Ltd, UK). CF substrates were used without pre-treatment, while all GF substrates were washed by immersion in two separate UPW baths for periods of 1 h, with copious rinsing with UPW after each immersion. Following washing, GF substrates were dried overnight under a laminar flow hood, wrapped individually in aluminium foil and ashed at 450 °C for 4 h.

2.2. Aerosol collection procedures

Aerosol samples were collected using Tisch Hi-Vol collectors equipped with total suspended particulate (TSP) sampling heads, and operating at flow rates of $\sim 1\ \text{m}^3\ \text{min}^{-1}$. For initial work testing collection and extraction protocols, two samplers (one containing CF and one GF substrates) were deployed simultaneously on the roof of the UEA, Norwich, UK (52.62°N, 1.24°E) over the period 7th - 10th January 2011. The air volume filtered for each sample was $\sim 4200\ \text{m}^3$. During the SHIVA cruise, a single Hi-Vol aerosol collector was used, equipped with GF substrates in a TSP sampling head. The cruise took place in the South China and Sulu Seas in November 2011 (Fig. 1) and sample collection times varied between 13 and 25 h (Table 1). After collection, all samples were transferred to individual zip-locked polyethylene bags (after first being wrapped in aluminium foil, in the case of GF substrates) and stored at $-16\ ^\circ\text{C}$ until analysed.

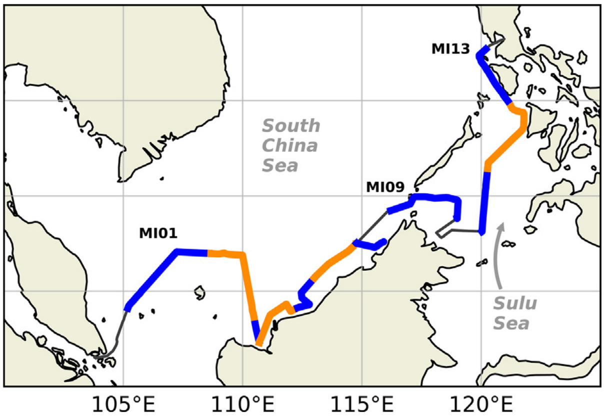

Fig. 1. Map of the SHIVA study area, showing the track of the FS *Sonne* between Singapore and Manila. Aerosol sample collection periods are shown as alternating thick blue and orange lines. Samples MI08 and MI10 (thin lines) were blanks.

2.3. Simulated aerosol samples

Extraction methods were tested on simulated aerosol samples, which were produced by spiking portions of unused (CF and washed and ashed GF) filters with known quantities of KI and KIO_3 solutions and then adding UPW, so that the final concentrations of added I^- and IO_3^- were both 100 nM. Spiked substrates suspensions were then subjected to the extraction protocols described below.

2.4. Soluble iodine extraction protocols

The performance of two methods for the extraction of soluble iodine species from collected aerosol samples were compared. In each case, a known portion of the aerosol sample was suspended in UHP water. For the simulated and UEA aerosol samples filter portions were 1/16 or 1/32 of its total exposed area and the water volume was 20 mL, while for SHIVA 1/4 of each filter was used and the water volume was 25 mL. Extraction of the UEA sample was performed on two separate occasions.

The first method used ultrasonic agitation (Decon model FS100B, 75 W, 35–45 kHz) to release iodine species from the aerosol material. This method was similar to those used in a number of previous studies (Baker et al., 2000, 2001; Baker, 2004, 2005; Gilfedder et al., 2008; Lai et al., 2008; Allan et al., 2009; Xu et al., 2010a, 2010b). Exposure to ultrasonic agitation was varied from 5 to 60 min. The second extraction method used a rotary shaking table to continuously agitate the extraction solutions at room temperature, also for periods of 5–60 min. This method was similar to the extraction method employed by Xu et al. (2015) and Zhang et al. (2015), but avoided the potential for grinding of the aerosol sample and substrate by a magnetic stirrer.

At the end of the extraction period, leachates were filtered through 0.2 µm cellulose acetate cartridge filters (Sartorius minisart) and were stored at 4 °C in the dark until analysis. Iodine concentrations measured in aerosol sample aqueous extracts (C^{ext}) were converted into atmospheric concentrations (C^{air}) taking into account the fraction of the total aerosol sample (f^{aero}) used, the volume of UHP water (V^{UHP}) and the volume of air (V^{air}) filtered during aerosol sample collection (Eqn. (1)).

$$C^{air} = C^{ext}\ f^{aero} / (V^{UHP}\ V^{air}) \tag{1}$$

2.5. Iodine speciation analysis

Filtered aqueous extracts were analysed for TSI content using ICP-MS (Thermo X-Series). Conditions were: RF power 1200 W, sampling

Table 1
Details of aerosol samples collected during the SHIVA cruise.

Sample	Start Date	Start Location	End Date	End Location	Sampling Time (hrs)	Air Volume (m^3)
MI01	16/11/2011	3.3°N 105.2°E	17/11/2011	5.6°N 108.6°E	23.5	1682.5
MI02	17/11/2011	5.6°N 108.6°E	17/11/2011	2.7°N 110.5°E	21.8	1563.5
MI03	18/11/2011	2.6°N 110.5°E	19/11/2011	1.9°N 110.7°E	22.8	1633.0
MI04	19/11/2011	1.8°N 110.7°E	20/11/2011	3.3°N 112.3°E	23.9	1714.0
MI05	20/11/2011	3.3°N 112.3°E	21/11/2011	4.5°N 113.0°E	23.5	1682.5
MI06	21/11/2011	4.6°N 113.0°E	22/11/2011	6.0°N 114.8°E	25.2	1807.2
MI07	22/11/2011	6.0°N 114.8°E	23/11/2011	6.0°N 115.7°E	24.7	1772.8
MI09	24/11/2011	7.4°N 116.2°E	25/11/2011	7.1°N 119.0°E	24.2	1737.7
MI11	26/11/2011	6.5°N 120.0°E	27/11/2011	9.1°N 120.3°E	24.0	1720.5
MI12	27/11/2011	9.2°N 120.2°E	28/11/2011	11.9°N 121.2°E	22.3	1598.6
MI13	28/11/2011	12.0°N 121.1°E	28/11/2011	14.2°N 120.2°E	13.0	933.4

depth 120 mm, 0.4 mL min^{-1} Micromist concentric nebulizer, carrier gas flow 0.87 mL min^{-1}, high resolution acquisition mode, acquisition time 900 s. TMAH (0.011 M) was used as a rinse solution between each analysis, in order reduce carry-over of iodine between samples. Chromatographic separation of iodide and iodate was achieved using a Dionex AS16 ion exchange column 2*250 mm, with Dionex AG16 guard column 2*50 mm. The eluant was 35 mM sodium hydroxide (NaOH) at a flow rate of 1.0 mL min^{-1} and the injection volume was 100 µL. The effluent of the chromatography column was interfaced directly to the ICP-MS and elution of iodine species was monitored using the same conditions as for TSI determination. The instrument was calibrated using standard solutions prepared by dilution of KIO_3 (TSI) or KI and KIO_3 (speciation) on a daily basis. TSI concentrations in marine aerosol have often been observed to exceed total inorganic iodine (TII, i.e. iodide plus iodate) concentrations, with the excess iodine being ascribed to the presence of soluble organic iodine (SOI) species (Baker, 2005).

2.6. Major ion analysis

Major ions (Na^+, $NH_4{}^+$, Mg^{2+}, K^+, Ca^{2+}, Cl^-, $NO_3{}^-$, $SO_4{}^{2-}$, Br^-, $C_2O_4{}^{2-}$) were determined in aqueous extracts of the SHIVA samples by ion chromatography (Dionex ICS-5000), using CS12A (cations) and AS18 (anions) columns. Concentrations of ions derived from seaspray (X_{ss}) were calculated from the measured Na^+ concentration for each sample and the ratio of that ion's concentration in seawater to that of Na^+ (ss-X = $Na_{aerosol}$ X_{sw}/Na_{sw}). Non-seasalt concentrations were calculated as the difference between measured concentrations and calculated seasalt concentrations (nss-X = $X_{aerosol}$ – ss-X).

2.7. Airmass back trajectories

Airmass origins during the SHIVA cruise were assessed using 5-day airmass back trajectories obtained from the NOAA HYSPLIT model. Trajectories were calculated for heights of 10, 500 and 1000 m above the ship's position at the start of each sample collection period.

3. Results and discussion

3.1. Iodine recovery during extraction of simulated aerosol samples

Percentage recoveries of TSI, iodide and iodate for the two extraction methods and both filter types are shown in Fig. 2. For the GF substrate, recoveries were close to 100% for TSI and 82–95% for iodide and iodate and were relatively constant with extraction time. Similar recoveries of TSI (i.e. ~100%) were also achieved for CF substrates (except for the shaking experiment at 15 min). Recoveries for iodide and iodate from the CF substrates were much more variable and were particularly low for iodate. In the shaking experiments, recoveries for iodide were generally > 120%, which indicated that there may have been some reduction of iodate to iodide in this case. Similar experiments conducted by Xu et al. (2010a) also showed significant changes in iodine speciation with increasing exposure of CF substrates to ultrasonication. In that case, recoveries of iodide decreased from 87% after 5 min to 18% after 60 min. These authors also reported smaller decreases in recovery of iodide (100%–85%) from GF substrates, while the recoveries of iodate were not significantly different from 100% for either CF or GF substrates under these conditions.

3.2. Iodine speciation in aerosol samples from UEA

The variation in concentrations of TSI and iodide over time for the two experiments performed on the sample collected at UEA under the different extraction protocols is shown in Fig. 3. Iodate concentrations during these experiments are not shown because they were below the analytical detection limit (equivalent to 0.32 pmol m^{-3} for these samples) in all but two cases. The much lower concentrations of iodide than TSI and the absence of detectable iodate indicates that this sample contained a substantial proportion of SOI. For example, in the second experiment after 30 min of shaking the GF sample, the observed concentrations of TSI, iodide and iodate were 7.8 ± 0.2, 3.6 ± 0.6 and < 0.32 pmol m^{-3} respectively, implying a concentration of SOI of 3.8–4.1 pmol m^{-3}.

The results obtained generally show greater stability in speciation than was observed in the simulated extraction experiment. In particular, neither TSI nor iodide concentrations showed appreciable changes with extraction time under the shaking regime. In the ultrasonication experiments there were indications that the iodide concentration increased with increasing extraction time (especially for the CF substrate, Fig. 3c), while the TSI concentration was relatively stable. This implies that ultrasonication caused conversion of another species into iodide over time under these conditions. Since iodate concentrations were too low to account for the increase in iodide, its source was presumably SOI. Changes in iodine speciation (conversion of inorganic iodine into SOI) with increasing exposure to ultrasonication have been observed previously in a sample of aerosol collected on CF substrate at a coastal site in the UK (Baker et al., 2000).

3.3. Optimum conditions for aerosol iodine speciation determination

Although there were some inconsistencies between the results of the simulated extractions and those of the extraction of the aerosol samples from UEA, there were some clear trends which can be used to aid the selection of optimum conditions for the determination of aerosol iodine speciation. Both experiments showed that the combination of ultrasonic extraction and CF substrates resulted in speciation that was variable with extraction time and showed evidence of species interconversions. Similar variability under these conditions has been reported in other studies (Baker et al., 2000; Xu et al., 2010a). The likely cause of this effect is the generation of active oxygen species, such as hydrogen peroxide, caused by acoustic cavitation during ultrasonication (Kanthale et al., 2008), which has been demonstrated to oxidise iodide (Liu and Wu, 1934). This combination is therefore considered to be the

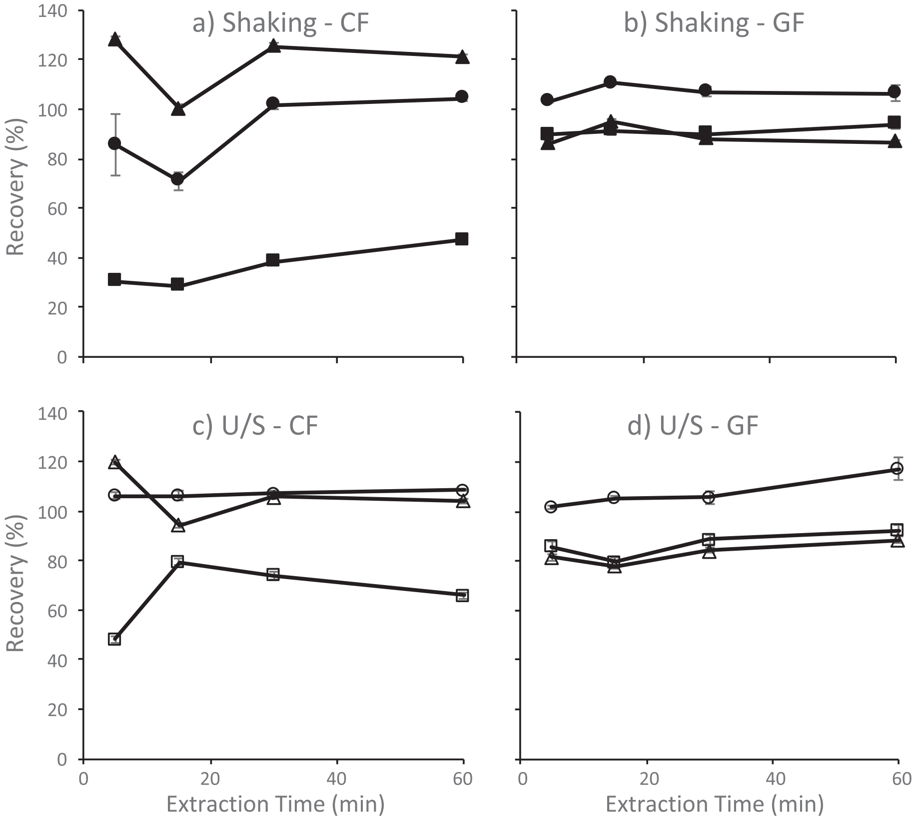

Fig. 2. Percentage recoveries obtained for TSI (circles), iodide (triangles) and iodate (squares) during extraction of portions of CF (a and c) and GF (b and d) substrates. Sample agitation during extraction was by mechanical shaking (a and b) or ultrasonication (c and d). Error bars show the spread of duplicate extractions – in most cases these are smaller than the symbols.

least reliable method of those tested.

In the simulated aerosol extraction experiment, the combination of GF substrates and mechanical shaking (Fig. 2b) yielded recoveries for TSI, iodide and iodate that were consistently close to 100% over the majority of extraction times. This combination also gave results for iodine concentrations that were relatively insensitive to extraction time for the sample collected at UEA (Fig. 3b). The results obtained by mechanical shaking of the CF substrates for the UEA sample (Fig. 3a)

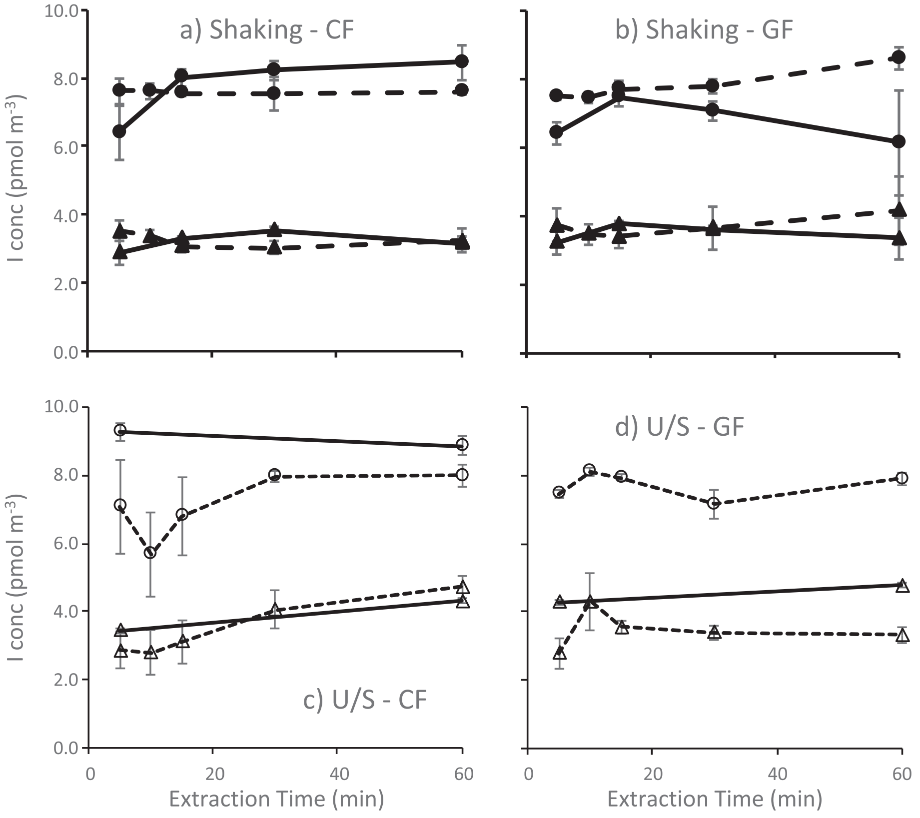

Fig. 3. Atmospheric concentrations of TSI (circles) and iodide (triangles) determined after extraction of the UEA aerosol sample from CF (a and c) and GF (b and d) substrates. Sample agitation during extraction was by mechanical shaking (a and b) or ultrasonication (c and d). Error bars show the spread of duplicate extractions. Extractions were conducted during two separate experiments, denoted by solid or dashed lines. TSI determinations for the first experiment in d) were lost due to instrument malfunction.

Table 2
Measured concentrations of TSI, iodide and iodate and calculated SOI concentrations (all pmol m^{-3}) in SHIVA aerosol samples.

Sample	TSI	Iodide	Iodate	SOI[a]
MI01	11.1 ± 2.3	2.25 ± 0.04	6.8 ± 0.1	< 2.3
MI02	12.4 ± 2.4	3.40 ± 0.08	6.02 ± 0.07	3.0 ± 2.4
MI03	8.2 ± 1.3	4.4 ± 0.2	1.9 ± 0.8	1.8 ± 1.5
MI04	8.6 ± 1.0	3.3 ± 0.3	1.4 ± 0.1	3.9 ± 1.1
MI05	9.0 ± 1.1	3.6 ± 0.4	2.6 ± 0.2	2.9 ± 1.2
MI06	15.5 ± 2.2	3.8 ± 0.2	9.8 ± 0.6	< 2.3
MI07	9.2 ± 0.2	3.7 ± 0.6	4.2 ± 0.1	1.3 ± 0.7
MI09	8.1 ± 0.2	3.0 ± 0.1	5.0 ± 0.1	< 0.3
MI11	15.9 ± 1.4	5.5 ± 0.5	5.04 ± 0.07	5.4 ± 1.5
MI12	8.3 ± 1.2	5.2 ± 0.4	3.3 ± 0.3	< 1.3
MI13	7.0 ± 0.4	6.1 ± 0.2	1.6 ± 0.2	< 0.5

[a] Detection limits for SOI were estimated by propagating the uncertainties in the measured concentrations of TSI, iodide and iodate for each sample.

were very similar to those obtained with the GF substrates, although the CF/shaking combination did not appear to yield reliable results for iodate in the simulated aerosol experiment.

It was therefore concluded that the GF/shaking combination gave the most reliable iodine speciation results, and that a shaking time of 30 min was sufficient to quantitatively extract the soluble iodine fraction from ambient aerosol samples (Figs. 2b and 3b). Given the results obtained for the UEA sample collected on the CF substrate, it is cautiously suggested that similar extraction conditions might also result in reliable speciation analysis for samples collected on this substrate.

3.4. Iodine speciation in SHIVA aerosol samples

Results obtained for the analysis of the samples collected during the SHIVA cruise (TSI, iodide, iodate and SOI concentrations) using the optimised sampling and extraction methods are shown in Table 2. Full aerosol composition data from the cruise are available from Baker and Yodle (2018).

TSI, iodide and iodate were detectable in all of the SHIVA samples, with iodide accounting for 20–87% (median 39%) of the soluble iodine. SOI was detectable in 5 of the samples. The wide variation in the relative proportions of the soluble iodine species in these samples is in agreement with the results obtained from many other studies of marine aerosols (Baker, 2004, 2005; Lai et al., 2008, 2011; Allan et al., 2009; Xu et al., 2010b, 2015; Zhang et al., 2015). TSI concentrations reported here for the SHIVA samples (7.0–15.9 pmol m^{-3}; Table 2) were similar to the range (~13–20 pmol m^{-3}) previously reported in the South China and Sulu Seas (Lai et al., 2008). These authors reported that SOI and iodide dominated the speciation of the samples that they collected, with iodate contributing less than 10% to TSI. In the SHIVA samples iodate was found to be a more significant component (16–63% of TSI). The analysis methods used by Lai et al. (2008): CF substrates and 20 min ultrasonic extraction, were found to be the least reliable conditions for the determination of aerosol iodine speciation of those tested in the present work. This difference in methodology may contribute to the variation in iodine speciation between the two datasets, but the possibility that this was due to natural variability in speciation cannot be excluded.

The SHIVA samples show loss of Cl^- and Br^-, relative to seawater composition (Fig. 4 a & b), as has been previously reported in many other studies of aerosol composition (e.g. Keene et al., 1990; Sander et al., 2003). In contrast, the total inorganic iodine (TII, the sum of I^- and IO_3^-) concentrations in the SHIVA samples were significantly higher than expected from seaspray generation (Fig. 4c), with TSI concentrations being enriched over seawater iodine concentrations by factors of ~35–310. Iodine enrichment in marine aerosol has been reported in several previous studies, as a result of the dominance of marine gas-phase iodine emissions over those associated with seaspray generation (Saiz-Lopez et al., 2012).

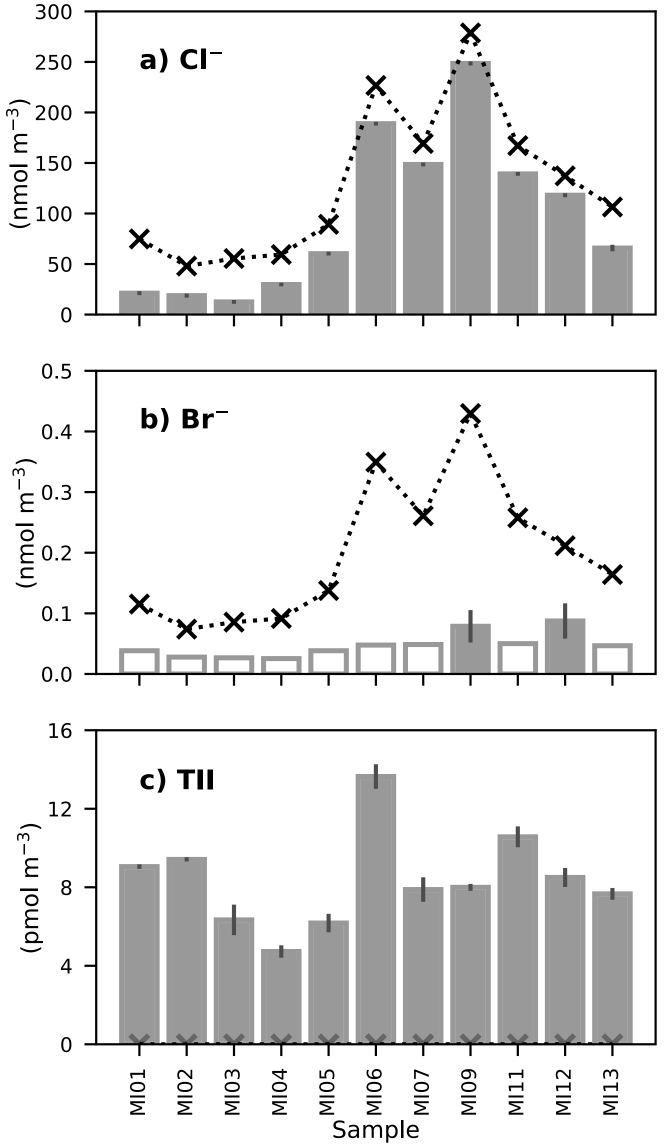

Fig. 4. Concentrations of a) chloride, b) bromide and c) total inorganic iodine in the SHIVA aerosol samples (bars). Each panel also shows the calculated concentrations of Cl^-, Br^- and inorganic iodine due to seasalt (crosses) in each sample. Empty bars in b) indicate that Br^- concentrations were below the limit of detection. Values plotted in those cases were 75% of the detection limit concentration.

Previous studies have indicated that aerosol iodine speciation varies with airmass origin (e.g. Baker et al., 2001). Since the dominant source of iodine to the atmosphere is the photolysis of precursor gases to produce iodine atoms (Saiz-Lopez et al., 2012), the variation in aerosol speciation is presumably due to differences gas- or aerosol-phase chemistry subsequent to this photolysis. It is therefore interesting to investigate whether there are influences of airmass origin on the speciation of iodine in the SHIVA samples, and whether aerosol background chemistry might play a part in this. Two distinct types of airmass back trajectory were encountered during the cruise (Fig. 5): samples MI01 – 05 were associated with circulation over the southern regions of the South China Sea (SCS), while the air sampled during the later period of the cruise originated in the western North Central Pacific (NCP) and passed over the Philippines before collection. The SCS group had significantly higher nss-SO_4^{2-} and lower nss-Ca^{2+} than the NCP group (two-tailed Mann Whitney *U* test, $p = 0.05$). Iodide

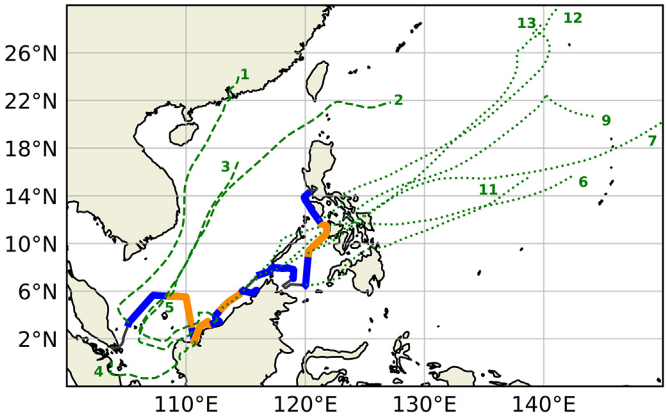

Fig. 5. Surface level (10 m) 5 day airmass back trajectories for the start of each of sample collection period during the SHIVA cruise. Dashed lines are for the South China Sea group and dotted for the North Central Pacific group. Numbers at the upwind end of each trajectory correspond to the sample numbers.

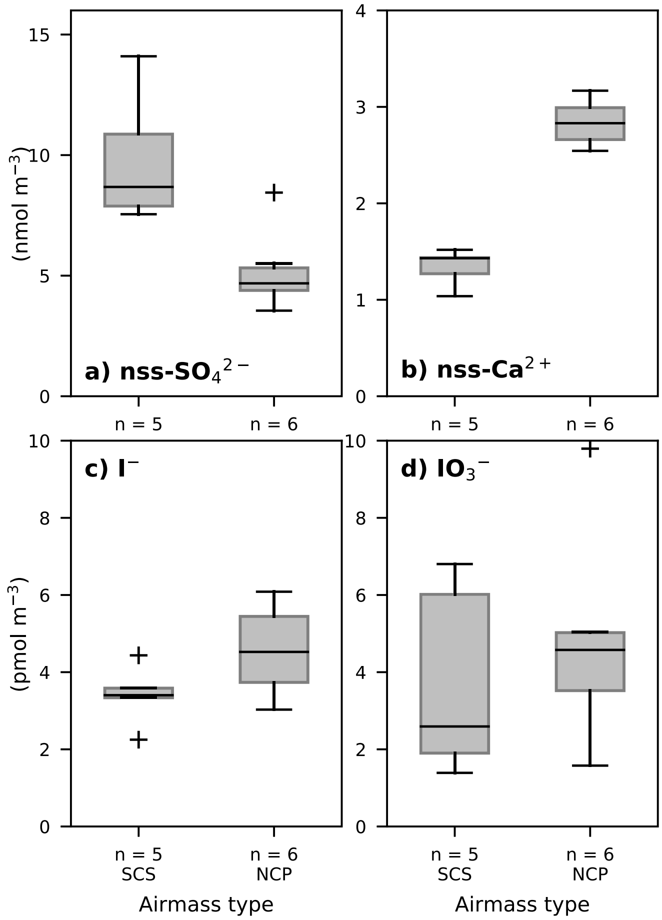

Fig. 6. Box and whisker plots showing the distribution of a) non-seasalt sulphate, b) non-seasalt calcium, c) iodide and d) iodate between the South China Sea (SCS) and North Central Pacific (NCP) airmasses encountered during the SHIVA cruise. Boxes show the inter-quartile range (IQR) of the data and whiskers include values up to 1.5 times the IQR beyond the box. Values outside this range are plotted as individual crosses. Median values are shown by horizontal lines within each box.

concentrations were also lower (but not significantly different) in the SCS group, while there was very little difference between the IO_3^- concentrations of the two groups (Fig. 6). The higher nss-SO_4^{2-} content of the SCS type might be due to fossil fuel combustion emissions from East Asia, while the higher nss-Ca^{2+} content in the NCP type may indicate a small source of mineral dust from the Philippines (although nss-Ca^{2+} concentrations were low in all samples). The differences in nss-SO_4^{2-} and nss-Ca^{2+} between the two groups may indicate that there are also differences between the acidity of the two airmass types, but there is insufficient evidence to confirm this, or whether such differences might contribute to the differences between their I^- concentrations.

4. Conclusions

The analysis of aerosol iodine speciation has been examined using two different aerosol collection substrates (CF and GF) and different extraction conditions (ultrasonication and mechanical shaking over periods of 5–60 min). In agreement with other studies, the combination of CF collection substrates and ultrasonic agitation appeared to cause changes in iodine speciation and it is recommended that these conditions are avoided in future work. Based on the results of extractions of both simulated aerosol samples spiked with inorganic iodine species and of an ambient aerosol sample, the optimum conditions for aerosol iodine speciation determination appear to involve the mechanical shaking of samples collected on GF substrates for a period of 30 min. For samples collected on CF substrates, mechanical shaking also appears to give more reliable results for iodine speciation determination than ultrasonic agitation.

Analysis of samples collected during the SHIVA cruise in the South China and Sulu Seas, using the optimised collection and extraction methods, yielded similar TSI concentrations to previous reports from the region, but rather different iodine speciation. These differences in speciation may have been due to the different sampling and extraction methods used.

Author contributions

ARB conceived the project and the experiments were designed by CY and ARB. All laboratory work was conducted by CY. The manuscript was drafted by ARB with contributions from CY.

Conflicts of interest

The authors declare that they have no conflict of interest.

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