Iodine speciation in aerosol particle samples collected over the sea between offshore China and the Arctic Ocean

KANG Hui¹, XU Siqi², YU Xiawei¹, LI Bing³, LIU Wei³, YANG Hongxia³
& XIE Zhouqing¹*

¹ Institute of Polar Environment, University of Science and Technology of China, Hefei 230026, China;
² Shenzhen Futian Environmental Monitoring Center, Shenzhen 518048, China;
³ National Research Center for Geoanalysis, Beijing 100037, China

Received 19 June 2015; accepted 17 September 2015

Abstract Iodine species collected by an onboard PM10 particle sampling system during the Second Chinese National Arctic Research Expedition (July–September 2003) were measured using inductively coupled plasma mass spectrometry and ion chromatography-inductively coupled plasma mass spectrometry. Iodine (I⁻) was detected in all samples over the Arctic Ocean, whereas additional iodine species including insoluble iodine, soluble organic iodine plus I⁻ were detected over the northwestern Pacific Ocean. The results suggest that the main form of iodine is different within the Arctic Ocean than it is outside. Enrichment factor values showed moderate enrichment of iodine in the northwestern Pacific, whereas a high enrichment factor was found in polar regions, implying sources other than sea salt. A potential explanation was ascribed to the role of sea ice melt in the Arctic and rapid growth of algae in seawater, which enhances the production of iodocarbon and air-sea exchange. This was confirmed by the larger values of total iodine in 2008 than in 2003, with greater sea ice melt in the former year. In comparison with earlier reports, ratios of iodate to iodide (IO₃⁻/I⁻) were much smaller than 1.0. These ratios were also different from modeling results, implying more complicated cycles of atmospheric iodine than are presently understood.

Keywords iodine, iodine speciation, sea-ice, EF factors, chlorophyll


1 Introduction

Atmospheric iodine participates in a variety of photochemical reactions in the troposphere. The concentration and speciation of iodine has received much attention because of the effect of the polar hole in the ozone layer in spring⁷. Iodine can also be directly involved in new particle formation, release and form marine boundary layer cloud condensation nuclei, which indirectly influence the earth’s albedo and global climate⁸. Atmospheric iodine can have marine, continental, and anthropogenic sources⁹, with the marine component considered the principal one⁹. The concentration of gaseous and particulate iodine in the atmosphere is very low. Because determination is difficult, there are few reports on the concentration and speciation of gaseous and particulate iodine. Because of differences in sampling points and analytical methods used, the composition and content of iodine in aerosols vary in the literature⁶,⁸,¹¹. Therefore, a wide range of samples monitored over a long period will contribute to understanding of the geochemical cycles of iodine in the atmosphere. In previous reports, samples were collected mainly from the Atlantic Ocean, East Antarctica and the Indian Ocean, but results for atmospheric iodine have rarely been reported. Lai et al.¹² treated the distribution of iodine species during an Antarctic expedition route, finding that soluble organic iodine (SOI) was the important component of aerosols. In the Northern Hemisphere, Xu et
al. described iodine speciation in the marine boundary layer over the Arctic Ocean and northwestern Pacific Ocean in 2008. Here, we present the concentration and speciation of iodine in PM10 (particulate matter with aerodynamic diameter < 10 μm) samples collected in the marine boundary layer (MBL) over the northwestern Pacific Ocean and Arctic Ocean, aboard the Chinese R/V XUE LONG icebreaker during the Second Chinese National Arctic Research Expedition (July–September 2003, CHINARE2003). Total iodine (TI) and total soluble iodine (TSI) were determined by inductively coupled plasma mass spectrometry (ICP-MS). Iodide and iodate (IO$_3^-$) were simultaneously determined by ion chromatography–inductively coupled plasma mass spectrometry (IC-ICP-MS). The results were compared with data obtained during the CHINARE2008 (July-September 2008).

2 Experimental details

2.1 Sampling

During the Second Chinese National Arctic Research Expedition, a total of 44 valid PM10 particulate samples and 5 field blanks were collected in the MBL from July to September 2003 (Figure 1). A high-volume PM10 air sampler was placed on the uppermost deck of the ship. Particulates were collected by drawing air through a cellulose filter (Whatman 41, Maidstone, UK, 20 cm×25 cm) at flow rate ~1.0 m$^3$·min$^{-1}$, with sampling durations of 24 h or 48 h. After sampling, the filters were packed in separate plastic bags, sealed, and placed in cold storage for later analyses.

![Figure 1](image1.png)  
**Figure 1** Map showing cruise routes of the Second Chinese National Arctic Research Expedition (CHINARE2003) (blue line for departing trip and red line for return trip; black dots represent sampling points).

2.2 Analyses of iodine species

A piece (3 cm$^2$) was cut from each sample filter and dissolved in screw-top PTFE-lined stainless steel bombs, using a 10% ammonia solution at 185°C for 15 h. The solution was then filtered quantitatively using filter paper and TI was measured using an Agilent 7500a ICP-MS (Agilent Technologies, Santa Clara, CA, USA). The detection limit for TI was 0.1 μg·L$^{-1}$ for the aqueous solution. For soluble species, aerosol filter samples (3–9 cm$^3$) were extracted in water by ultrasonic-assisted extraction for 5 min. The extract was filtered through 0.45-mm filters and TSI was measured with the aforementioned ICP-MS. Iodide and iodate were separated and quantified using an IC-ICP-MS system. An Agilent 1100 HPLC and ICS-A23 IC column with an ICS-A2G guard column (Yokogawa Analytical Systems, Tokyo) were used. The mobile phase consisted of 0.03 mol·L$^{-1}$ (NH$_4$)$_2$CO$_3$ (pH=8.0) and the flow rate was 0.8 mL·min$^{-1}$. The Agilent 7500a ICP-MS was used as the detector to scan the isotope $^{127}$I (Figure 2).

![Figure 2](image2.png)  
**Figure 2** Typical ion chromatography-inductively coupled plasma mass spectrometry chromatograms of iodine species in aerosol samples (sample 12).

Iodide and iodate were successfully separated and then quantified with an external calibration curve. Detection limits were 0.012 and 0.008 mg·L$^{-1}$ for iodide and iodate, respectively, based on an injection volume of 1.0 mL. Standard deviations at the 0.127 mg·L$^{-1}$ level for iodide and iodate were 3.15% and 2.23% ($n=7$), respectively. For a typical air volume of 1500 m$^3$, a 3-cm$^2$ piece of cut filter and 10-mL extract, corresponding atmospheric detection limits for TI, I$^-$ and IO$_3^-$ were 0.72, 0.087 and 0.058 pmol·m$^{-3}$, respectively. Insoluble iodine (ISI) was calculated as TI minus TSI (ISI $=$ TI $-$ TSI). SOI was calculated as TSI minus the inorganic iodine species (SOI $=$ TSI $-$ iodide $-$ iodate). Total Br (TBr) and Br speciation were also determined together with TI and iodine speciation, using the same extract.

2.3 Relevant data

Air mass back trajectories were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (reanalysis dataset) from the National Oceanic and Atmospheric Administration’s (NOAA) Air Resources Laboratory (www.arl.noaa.gov/ready.php). Monthly global distributions of chlorophyll were downloaded from the MODIS website, National Aeronautics and Space Administration (http://modis.gsfc.nasa.gov). Arctic sea ice distributions were downloaded from a National Snow and Ice Data Center website (http://nsidc.org/index.html).
3 Results and discussion

3.1 Iodine species in the Arctic Ocean

The distribution of iodine and its species in PM10 particles within the marine boundary layer during the Second Arctic Expedition is shown in Table 1, and by a bar chart in Figure 3. Iodate was detected in only 12 of 29 samples, with a maximum 0.29 pmol·m⁻³. ISI was not detected in 2 samples, SOI was not detected in 1 sample, and iodide ion (I⁻) was detected in all samples. The concentration of TI was 19–88 pmol·m⁻³ with average 42±15 pmol·m⁻³. The concentration of TSI was 4–88 pmol·m⁻³. The concentration of I⁻ was 0.4–36.9 pmol·m⁻³. The results show that iodide was the common form in the PM10 samples of the marine boundary layer over the Arctic Ocean. The contribution of iodide to TI ranged from 1% to 93% (average 31%) and that of TSI from 6% to 100% (average 43%). The contribution of ISI to TI was 0%–74% (average 41%), SOI was detected in almost all samples. The contribution of SOI to TI was 0%–74% (average 28%) and that of TSI was 0%–94% (average 57%). The proportion of IO₃⁻ was the smallest among the iodine species, <1%. These results indicate the main form of iodine was not identical across the various samples.

Table 1 Concentrations (± standard deviation) of iodine species in aerosols over the Arctic Ocean (n = 29)

<table>
<thead>
<tr>
<th>Species</th>
<th>Range/ (pmol·m⁻³)</th>
<th>Average/ (pmol·m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total iodine (TI)</td>
<td>19–88</td>
<td>42±15</td>
</tr>
<tr>
<td>Total soluble iodine (TSI)</td>
<td>4–88</td>
<td>27±20</td>
</tr>
<tr>
<td>Insoluble iodine (ISI)</td>
<td>N.D. –44</td>
<td>15±11</td>
</tr>
<tr>
<td>Iodide (I⁻)</td>
<td>0.4–37.0</td>
<td>13.8±12.7</td>
</tr>
<tr>
<td>Iodate (IO₃⁻)</td>
<td>N.D.–0.29</td>
<td>0.04±0.07</td>
</tr>
<tr>
<td>Soluble organic iodine (SOI)</td>
<td>N.D.–60</td>
<td>13±13</td>
</tr>
</tbody>
</table>

Note: N.D., Not detected.

Figure 3 Bar chart of concentrations of iodine species in aerosol over Arctic Ocean (n=29).

The main source of I in the aerosols in the marine boundary layer is direct release by sea wave droplets and reaction products of gaseous substances (including I), and oxidizing substances such as ozone, which are released from marine organisms. However, it has been reported that IO is released through melting of the front edge of ice cover and the sea ice zone in polar regions. The enrichment factor (EF) of I, calculated as the ratio of I in aerosol to I in seawater, can be used to distinguish sources. Because of a lack of data on Na concentration of the samples, we used the Br concentration in calculation. According to the literature, significant depletion or enrichment of the total Br of suspended particles cannot occur relative to Br in seawater, and the EF of Br in PM10 particles is at least 0.5. This means that < 50% of the Br in sea salt aerosol no longer exists in aerosol particles because of sedimentation or atmospheric chemical reactions. The calculation is

\[ EF(I) = \frac{(I_{\text{air}}/Br_{\text{air}})}{(I_{\text{seawater}}/Br_{\text{seawater}})} \]

An EF of 1–10 usually indicates that the source of I is ocean or soil; 100–500 indicates moderate enrichment and > 500 extreme enrichment. The EF(TI) was 468–8810 (average 2676±2180), EF(TSI) was 370–6839 (average 2055±1698), and EF(I⁻) was 26–4784 (average 1069±1281). Even though a 50% depletion of Br in PM10 aerosols was used in the calculation, an extreme enrichment of I was present in most samples, indicating that direct release by sea wave droplets was not the primary source. The average concentration of TI was 42±15 pmol·m⁻³, and the rate of the TI concentration change in 29 samples was a mere 35%. This suggests a homogeneous distribution of iodine in PM10 particles within polar regions.

As suggested by other works, change in sea ice will impact atmospheric iodine. Thus, we investigated this relationship. The results of typical back trajectories demonstrated that most of the air mass traversed the front edge of the ice cover or sea ice area during the prior 48 h. From Figure 4, the temperature for sample BB-20 (the highest TI in the Arctic) during collection was 8.7°C, the highest measured during the Arctic voyage. Sea ice melt is apparent at the receding ice edge. Ice diatoms have been shown to be a potential direct source of HOI and I₂ to the Arctic atmosphere. More recently, observations suggest that the source of iodine is related to processes associated with coastal sea ice. Arctic sea ice melt may enhance the growth of algae and thereby increase the production of iodocarbon, which is a potential source of I precursors in aerosols. Abundant growth of chlorophyll a, indicating considerable growth of algae, has been discovered in Arctic Circle seas such as the Bering Strait (Figure 6).
3.2 Iodine species in northwestern Pacific Ocean

The distribution of iodine and its species in PM10 particles within the marine boundary layer over the northwestern Pacific during the Second Arctic Expedition is shown in Table 2, and by a bar chart in Figure 7. Iodate was detected in 2 of 15 samples; maximum concentration was 0.06 pmol·m$^{-3}$. ISI, SOI and $\Gamma^-$ were detected in all samples with widely existing forms. Concentrations of TI, TSI, and $\Gamma^-$ were 15–73, 5–63, and 0.9–63.1 pmol·m$^{-3}$, respectively. These results show that soluble iodine is a major form of iodine. $\Gamma^-$ had the largest proportion among all iodine species, accounting for 3%–86% (39%) of TI and 13%–100% (55%) of TSI. The concentration of ISI was a slightly higher than that of SOI, accounting for 6%–77% (34%) of TI. SOI constituted 0.3%–60% (26%) of TI, and 0.3%–8% (45%) of TSI. Iodate (IO$_3^-$) had the smallest proportion among all iodine species, accounting for < 0.1%. There was no apparent correlation between $\Gamma^-$, ISI or SOI.
Table 2  Concentrations of iodine species a in aerosols over sea areas outside the Arctic Ocean

<table>
<thead>
<tr>
<th>Species</th>
<th>Range/ Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total iodine (TI)</td>
<td>15–73 / 34±18</td>
</tr>
<tr>
<td>Insoluble iodine (ISI)</td>
<td>0.9–34.5 / 11±8</td>
</tr>
<tr>
<td>Total soluble iodine (TSI)</td>
<td>5–63 / 23±16</td>
</tr>
<tr>
<td>Soluble organic iodine (SOI)</td>
<td>0.2–21.3 / 7.4±5.6</td>
</tr>
<tr>
<td>Iodate (IO₃⁻)</td>
<td>N.D. –0.06 / 0.01±0.02</td>
</tr>
<tr>
<td>Iodine (I⁻)</td>
<td>0.9–63.1 / 15.7±17.4</td>
</tr>
</tbody>
</table>

Figure 6 Global distribution of chlorophyll a in August 2003 and 48-h backward air mass trajectories for sample BB-19. Different color trajectories represent various air mass elevations.

EFs of TI were 188–2017 with average 751±514. The EF of TSI was 156–1299, with average 505±328, and the EF of I⁻ was 52–1093, with average 276±261. These results reveal moderate enrichment, which indicates that a small proportion originated from sea salt. Except for the BB-44 and BB-49 samples, iodine showed little seasonal variation from July–September in the marine boundary layer of the northwestern Pacific. There was no apparent correlation across 15 samples between the amount of iodine, distribution of chlorophyll a, and the various sources. These findings indicate that the influences on the species and levels of atmospheric iodine are very complex.

3.3 Comparison with CHINARE2008 in Arctic Ocean and the literature

There are very few reports on the concentration of iodine species in the marine boundary layer of the Arctic Ocean. Sturges et al. [25,32] reported on concentrations of iodine at three coastal locations in the Canadian Arctic and one site in central Alaska from 1979 to 1987. The maximum concentration of TI was only 32 pmol⋅m⁻³, much less than in the present study. However, TI concentration in CHINARE2008[13] was much higher than in CHINARE2003. A potential explanation may be linked to sea ice area decrease from climate warming in recent years. From Figure 8, Arctic sea ice area continuously declined from 1979 to 2008, and reached its second lowest point in the satellite
record during September 2008. In polar regions, sea ice area decline increases open sea, resulting in a large area of algae growth and enhancement of air-sea exchange\cite{33}. Algae such as ice diatoms have been proven a potential direct source of I precursors in the Arctic atmosphere\cite{15-16}. This creates more volatile iodine substances in the atmosphere and eventually affects levels of atmospheric iodine.

For the iodine species, some early atmospheric chemistry models of iodine suggested that iodate is the only EF (I) revealed extreme enrichment of I, indicating little obvious correlation among the other iodine species. A large $\text{EF}_{\text{ISI}}$ or $\text{SOI}$ indicated moderate enrichment of iodine. $\text{EF}_{\text{ISI}}$ or $\text{SOI}$ showed no apparent correlation between $\Gamma$, ISI or SOI. The $\text{EF}$ showed moderate enrichment of iodine.

Compared with the literature, levels of atmospheric iodine were found to increase in response to sea ice melt in the Arctic Ocean. However, $\text{IO}_3^-/\Gamma$ ratios were < 1.0, in contrast with modeling results, indicating more complicated cycles of atmospheric iodine.

**Acknowledgements** This research was supported by grants from the National Natural Science Foundation of China (Grant nos. 41176170 and 41025020), the Chinese Polar Environment Comprehensive Investigation & Assessment Programs (Grant no. CHINARE2011-2015) and China Polar Science and Strategic Research Fund Project, Chinese Arctic and Antarctic Administration (Grant no. 20140302).

**References**

Iodine speciation in aerosol particle samples collected over the sea between offshore China and the Arctic Ocean


