Iodine containing species in the remote marine boundary layer:
A link to oceanic phytoplankton

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[1] Iodine containing species have been measured in the particle phase (PM₃₅) and the gas phase during a ship campaign between January and February 2007 in the South Atlantic marine boundary layer (MBL). Methyl iodide (CH₃I) in the gas phase and soluble iodine species, i.e. iodide, iodate and an unidentified organic iodine species (UOI), in PM₂₅ were measured. Temporal variations of gaseous and particulate iodine species were investigated. The exposure of the sampled air masses to phytoplankton along the back-trajectories was studied using a lagrangian transport model and satellite observations of oceanic chlorophyll-a concentration. Significant correlations were found between the concentrations of iodine species and the average chlorophyll exposure along back-trajectories, indicating an emission from phytoplankton in the open ocean. Good correlations were found when the ship approached or crossed the active biological region in the West-southern Atlantic. These results strongly suggest a connection between iodine species and the phytoplankton in the ocean. This study was extended to examine the relation of the iodine measurements to satellite derived phytoplankton distributions. We show that specific phytoplankton species may have impact on different iodine containing species.


1. Introduction

[2] The importance of iodine chemistry in the marine boundary layer (MBL) has been established in the past decades due to its role in tropospheric ozone depletion events and new particle formation. Research in coastal areas e.g. Mace Head, observed that iodine was important for new particle formation [O’Dowd and Hoffmann, 2005]. Although some iodine speciation in open ocean regions has been reported [Baker, 2005; Lai et al., 2008] most studies to date have been coastal. Volatile iodine species such as I₂, CH₃I, CH₂I₂, CH₃Cl, etc. are thought to be precursors for atmospheric iodine reactions [Carpenter, 2003]. They are mainly emitted from the marine biotic and abiotic sources although terrestrial sources and/or influence could not be excluded [Carpenter, 2003; Sive et al., 2007; Williams et al., 2007]. However, also loss processes in sea-water can influence their concentrations in the MBL [Wingenter et al., 2004]. These volatile iodine species have lifetimes ranging from several days (CH₃I, C₂H₅I, C₃H₇I), several hours (CH₂ClI), an hour or less (CH₂IBr), several minutes at midday (CH₂I₂), to several seconds (I₂). Marine organisms including macroalgae (seaweeds) and microalgae (phytoplankton) are supposed to be the most important sources of these compounds, though the exact mechanisms of synthesis and release are still unclear [Carpenter, 2003; Küpper et al., 1998]. In the atmosphere, volatile iodine species are photolyzed under UV-visible light following their release and form iodine atoms [Carpenter, 2003]. The iodine atoms trigger a series of gas phase reactions, resulting in ozone destruction and, under certain conditions, may contribute to particle formation [O’Dowd and Hoffmann, 2005]. The latter could have a strong impact on climate if it occurs on a global scale. Recently, several studies have been conducted on the source of iodine containing compounds from macroalgae [Küpper et al., 2002; Küpper et al., 1998]. However, investigations of iodine chemistry in the gas and particle phases over the open ocean and its connection with phytoplankton type and activity are still scarce [Jones et al., 2010].

[3] Here we present the results of measurements of gaseous and particulate iodine containing species during a shipborne campaign travelling between South Africa and South America in January and February, 2007. This cruise crossed the atmospherically pristine open ocean area of the South Atlantic in order to investigate the relevance of oceanic phytoplankton to iodine containing species.

2. Experiment

[4] The cruise campaign was conducted onboard the scientific research vessel Marion Dufresne whilst crossing the South Atlantic Ocean from Cape Town, South Africa to Punta Arenas, Chile between January and February, 2007. The campaign was supported by the EU-research project ‘Organics over the Ocean Modifying Particles in both Hemispheres’ (OOMPH) [Williams et al., 2010].

[5] Methyl iodide (CH₃I) was measured by an offline and an online gas chromatograph–mass spectrometer (GC–MS) system [Gebhardt, 2008]. The offline GC–MS was used to measure gas samples collected in stainless-steel canisters. The air was drawn from the foremost of the ship at a flow rate of 12 l/min resulting in a residence time of ~30 s. Seventy samples were collected from 20th January to 4th February. The online GC–MS system was connected to a separate inlet also located atop a 10 m mast on the fore-
mast (18 m above sea level) and measured CH$_3$I from 27th January to 4th February every 40 minutes. The airflow rate was ~6–8 l/min and the air residence time was on the order of 1 minute. Both online and offline GC-MS systems were calibrated based on the same primary standards. The standard was calibrated against a high pressure halocarbon mixture [Schauffler et al., 1999]. The online and offline results of CH$_3$I samples showed a good agreement ($R^2 = 0.76$) in this campaign.

A pre-separator PM$_{2.5}$ (aerosol with aerodynamic diameter <2.5 μm) sampler equipped with cellulose fibre filters (diameter 70 mm, Grade 41, Whatman, UK) was placed on the upper-most deck of the ship to collect aerosol samples from 20th January to 4th February. A constant flow of 4.5 m$^3$ h$^{-1}$ with a duration of ~23.5 h for each sample (except for the last sample for ~47 h) was maintained for sampling. A total of 14 PM$_{2.5}$ samples were collected. After water extraction, inductively coupled plasma – mass spectrometry (ICP-MS) and ion chromatography (IC) - ICP-MS were used for total soluble iodine (TSI) measurement and soluble iodine speciation, respectively. Iodide (I$^-$), iodate (IO$_3^-$) and an unidentified iodine signal which was quantified using iodide standard and named unidentified organic iodine (UOI), were detected by IC-ICP-MS measurement (described by Lai et al., 2008).

During the cruise, dimethyl sulfide (DMS) was measured by a proton transfer reaction mass spectrometer (PTR-MS) [Lindering et al., 1998] and Chlorophyll-a (Chl-a) was determined in-situ by HPLC pigment analysis of 3-hourly collected water samples from the ship’s seawater line (7 m below the sea surface). Marine Chl-a concentrations taken from the satellite borne measurement of SeaWiFS (http://seawifs.gsfc.nasa.gov/) were used to produce mean Chl-a concentration of CH$_3$I was also measured by online GC-MS system in the range of 0.6–3.0 pmol/mol. Sources of CH$_3$I are believed to be mainly from oceanic emissions but it is also released by some terrestrial biomes and anthropogenic activities (e.g. biomass burning) [Andreae & Feely, 1994].

### Table 1. Concentrations of Iodine Species in PM$_{2.5}$ and in Gaseous Phase During OOMPH

<table>
<thead>
<tr>
<th>Phase</th>
<th>Iodine Species</th>
<th>Range</th>
<th>Average</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{2.5}$ (pmol/m$^3$)</td>
<td>Soluble iodine</td>
<td>2.9–9.9</td>
<td>5.8 ± 1.9</td>
<td>3.7%</td>
</tr>
<tr>
<td></td>
<td>Iodate</td>
<td>0.2–1.1</td>
<td>0.6 ± 0.3</td>
<td>9.2 ± 3.7%</td>
</tr>
<tr>
<td></td>
<td>Iodide</td>
<td>0.1–2.1</td>
<td>1.1 ± 0.6</td>
<td>18.1 ± 7.1%</td>
</tr>
<tr>
<td></td>
<td>Unidentified organic iodine (UOI)</td>
<td>1.5–3.6</td>
<td>2.0 ± 0.6</td>
<td>37.2 ± 10.6%</td>
</tr>
<tr>
<td></td>
<td>Soluble organic iodine (SOI)</td>
<td>2.6–7.1</td>
<td>4.2 ± 1.3</td>
<td>72.7 ± 9.3%</td>
</tr>
<tr>
<td>Gas (pmol/mol)</td>
<td>CH$_3$I (offline measurement)$^a$</td>
<td>0.4–2.6</td>
<td>1.4 ± 0.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH$_3$I (online measurement)$^b$</td>
<td>0.6–3.0</td>
<td>1.4 ± 0.6</td>
<td></td>
</tr>
</tbody>
</table>


3. Results and Discussion

During the OOMPH cruise, TSI ranged from 2.9 to 9.9 pmol/m$^3$ with an average of 5.8 ± 1.9 pmol/m$^3$ (Table 1). Iodide (I$^-$) concentrations were higher than iodate (IO$_3^-$) in 13 of 14 samples, and iodide and iodate accounted for 9.2 ± 3.7% and 18.1 ± 7.1% of TSI respectively. The ratios of IO$_3$/I$^-$ ranged from 0.16 to 1.52 with a median of 0.55. The concentration of soluble organic iodine (SOI) was obtained by calculating the difference between TSI and the sum of I$^-$ and IO$_3^-$(i.e. [SOI] = [TSI] − ([I$^-$] + [IO$_3^-$])). As observed in the previous studies, SOI was the most abundant iodine species, accounting for 72.7 ± 9.3% of TSI, showing that a large fraction of the iodine content in particle phase remains to be identified [Baker, 2005]. Nevertheless, applying the speciation technique used in this work, the SOI fraction could be further characterized. Beside the iodide and iodate signals in the ion chromatogram an unidentified iodine signal (UOI) was clearly separated and was quantified using ICP-MS. The same unidentified iodine content was also observed in a previous ship campaign [Lai et al., 2008]. UOI accounted for 23.2–52.2% in TSI and 31.1–69.5% in SOI during this campaign, in fact larger than the inorganic iodine species.

CH$_3$I is the only gaseous iodine species reported here. From canisters and offline GC-MS measurements, the concentration of CH$_3$I was in the range between 0.4 and 2.6 pmol/mol during the whole sampling period. From 27th January to 4th February, 2007, CH$_3$I was also measured by an online GC-MS system in the range of 0.6–3.0 pmol/mol. Sources of CH$_3$I are believed to be mainly from oceanic emissions but it is also released by some terrestrial biomes and anthropogenic activities (e.g. biomass burning) [Andreae & Feely, 1994].

![Figure 1. Temporal variation of iodine-containing species during the OOMPH cruise (20th January–4th February, 2007). The uncertainties of offline and online CH$_3$I measurements were lower than 5% and 3.4%. The uncertainties for soluble iodine speciation were 3.0%, 3.0% and 1.7% for TSI, iodide and iodate.](image-url)
Correlations between iodine species and oceanic chlorophyll-a: (a) Correlations between atmospheric iodine species concentrations and chlorophyll-a exposure along back-trajectories of increasing length; (b) Correlations between iodine species concentrations and average chlorophyll-a exposure to specific phytoplankton functional types along 2-day back-trajectories.

Figure 2. Correlations between iodine species and oceanic chlorophyll-a: (a) Correlations between atmospheric iodine species concentrations and chlorophyll-a exposure along back-trajectories of increasing length; (b) Correlations between iodine species concentrations and average chlorophyll-a exposure to specific phytoplankton functional types along 2-day back-trajectories.

A linear correlation was observed between online CH$_3$I and DMS ($R^2 = 0.50$) supporting a dominance of oceanic CH$_3$I sources (see auxiliary material). To further elucidate the potential source of the iodine species, the biological activity has been studied using both the in-situ Chl-a measurement along the cruise track and the satellite borne Chl-a measurements over the South Atlantic Ocean. Chl-a is used here as a biomass tracer to reflect the abundance of phytoplankton. The in-situ Chl-a concentration increased significantly from the South African coast to the Argentinean coast, ranging from 0.03 to 4.63 µg/l, in accordance with satellite observations from SeaWiFS. Lower Chl-a concentrations were measured during 20th–27th January, however, from 28th January, the ship approached a high Chl-a region with increased phytoplankton activity (bloom) near the Argentinean coast. The phytoplankton bloom is caused by the confluence of the warm Brazil and the cold Malvinas current and possibly by atmospheric iron deposition [Erickson et al., 2003]. The elevated iodine species concentrations at the end of the campaign are likely linked to this large scale biological bloom and suggest a marine biological source. However, poor correlations were found between the concentrations of iodine species and in-situ Chl-a. To understand the exact location and nature of the source over the open ocean, a method was therefore used to estimate the Chl-a exposure along air mass back-trajectories (1–7 days) using a Lagrangian transport model and satellite observations of oceanic Chl-a concentration [Arnold et al., 2010]. The correlations between iodine containing species and back-trajectory Chl-a averages are shown in Figure 2a. In the particle phase significant correlations were found between soluble iodine species and the Chl-a averages, except UOI. However, the correlations were also found to vary with the different exposure times. The poorest correlations were obtained with an exposure time of 7 days and the correlations are generally improved with shorter biological exposure time. The strongest correlations were found consistently between soluble iodine species and Chl-a averages over 2-day exposure, showing that oceanic biological activity 2 days upwind of the ships location had a strong influence on the particle iodine species. I$^-$ and IO$_3^-$ had stronger correlations with the Chl-a averages than CH$_3$I and SOI. However, from 28th January to 4th February, good correlations were found between the CH$_3$I (both online and offline measurements) and the Chl-a averages. This may suggest the presence of different sources (i.e. coastal and open ocean) during this cruise.

The relationship between iodine species and Chl-a averages along back-trajectories in different regions have been examined in further detail. In the bloom region (28th January–4th February), much stronger correlations with Chl-a averages were observed in all iodine species in both particulate and gas phases. I$^-$ and IO$_3^-$ have stronger correlations ($R^2 > 0.45$) with Chl-average exposure $<3$ days while better correlations were also found between CH$_3$I and Chl-a with $2–3$ days of biological exposure ($R^2 > 0.20$). SOI had strong correlations with the Chl-a averages over 1–7 days biological exposure ($R^2 > 0.5$). Interestingly, correlations between UOI and Chl-a averages were found in this region and these improved with longer biological exposure times.

 auxiliary materials are available in the HTML. doi:10.1029/2011GL049035.
Since most of the samples were taken when the air masses were travelling over open ocean for several days, these results indicate phytoplankton as the major regional source of iodine. It also suggests that air mass transport originating from/passing over the biological source region play a dominant role in the variations of iodine containing species, which can be attributed to the transport of the investigated species and/or the transport of those gaseous precursors having suitable lifetimes (<7 days). Firstly, both gaseous and particulate species studied in this case have relatively long lifetime: CH₂I has a lifetime of ~7 days while I₂ and I both are relatively stable due to their high abundances in the particle phase [Baker et al., 2001]. These species can be transported after their formation. SOI species though unidentified have also been suggested to be stable due to its co-existence in particulate and precipitation [Gilfeder et al., 2008]. This is a possible explanation of the higher correlations of SOI/UOI with Chl-a averages over longer periods of biological exposure. Another possibility to explain maximum correlations over longer periods of biological exposure time is that long living precursors (e.g. CH₃I, C₂H₂I, CsH₃I) instead of short living species (I₂, CH₃J, CH₃Br, CH₃Cl etc.) dominate the iodine chemistry.

[12] The distribution of phytoplankton functional types (PFTs) in the ocean area was estimated and 4 PFTs were determined to have their dominance in different parts of the ocean area, i.e. haptophytes, prochlorococcus, synechococcus and diatom. “Dominance” indicates that a given PFT contributes more than 60% of the total pigment composition in the given area of surface ocean. The averages of Chl-a along the 2-day back-trajectories with exposure to these different PFTs were also estimated. Correlations between the concentrations of iodine species between 28th January and 4th February and PFT-specific Chl-a average are shown in Figure 2b. I and IO₃ had high correlations with haptophytes and diatom (R² > 0.7). CH₂I was found to be slightly related to the exposure of prochlorococcus, synechococcus and diatom (R² = 0.27, 0.26 and 0.23, respectively). This is in agreement with the previous studies showing that such phytoplankton species are capable of CH₂I production [Brownell et al., 2010; Hill and Manley, 2009]. SOI and UOI were both related to prochlorococcus, synechococcus and undetermined phytoplankton types. SOI also correlated well with the exposure to diatoms. Diatom species have been observed to be able to release reactive iodine species (e.g. HOI), which has been proposed to participate in SOI production [Baker, 2005; Hill and Manley, 2009]. Until now the concentration of SOI in marine aerosols is still unknown, which makes it challenging to investigate the mechanism of SOI production from specific PFTs.

[13] In contrast to the strong connection between iodine species and biological activity at the end of cruise, correlations between the elevated concentrations of iodine species and Chl-a averages at the beginning (20th to 27th January) were poor. This suggests that phytoplankton is not the only source of iodine over the open ocean. Abiotic sources might play a role in the less biologically affected regions or the coastal regions [Sive et al., 2007; Williams et al., 2007]. However, a previous study also showed that abiotic process (such as the addition of iron) may cause the loss of CH₂I, indicating the complexity of CH₂I production in the MBL [Wingenter et al., 2004]. Due to the limited data and information in this region, the source of iodine species over this period is not yet clear.

[14] The observed atmospheric variations in iodine species could be influenced not only by source location and abundance and type of biomass but also by other factors such as sea-air exchange, atmospheric mixing and reactivity, and meteorological conditions [Arnold et al., 2010; Jones et al., 2010; Mahajan et al., 2010]. Some efforts have been made to investigate the influence on iodine containing species of other such factors, such as sea surface temperature, wind direction and wind speed which can affect the sea-air exchange over sea surface (see auxiliary material). No further evident relation could be obtained, which may suggest less influence from these factors. However, to account for these other factors robustly would require knowledge of their variation along back-trajectories as air masses are advected in the MBL towards the ship. A lack of such information on suitable timescales during air mass advection currently negates a more rigorous analysis [Arnold et al., 2010]. All in all, the results in the biological blooming region strongly indicate a link between iodine chemistry and phytoplankton in the open ocean, which may improve the understanding of iodine chemistry in the MBL. In the future, more work including field monitoring and theoretical investigation are needed to reveal the contribution of phytoplankton to iodine chemistry in the MBL.

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