Atmos. Chem. Phys., 8, 6069–6084, 2008
www.atmos-chem-phys.net/8/6069/2008/

Atmospheric
Chemistry
and Physics

Iodine speciation in rain, snow and aerosols

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Received: 29 January 2008 – Published in Atmos. Chem. Phys. Discuss.: 22 April 2008
Revised: 8 August 2008 – Accepted: 27 August 2008 – Published: 21 October 2008

Abstract. Iodine oxides, such as iodate, should be the only thermodynamically stable sink species for iodine in the troposphere. However, field observations have increasingly found very little iodate and significant amounts of iodide and soluble organically bound iodine (SOI) in precipitation and aerosols. The aim of this study was to investigate iodine speciation, including the organic fraction, in rain, snow, and aerosols in an attempt to further clarify aqueous phase iodine chemistry. Diurnal aerosol samples were taken with a 5 stage cascade impactor and a virtual impactor ($PM_{2.5}$) from the Mace Head research station, Ireland, during summer 2006. Rain was collected from Australia, New Zealand, Patagonia, Germany, Ireland, and Switzerland and snow was obtained from Greenland, Germany, Switzerland, and New Zealand. Aerosols were extracted from the filters with water and all samples were analysed for total soluble iodine (TSI) by inductively coupled plasma mass spectrometry (ICP-MS) and iodine speciation was determined by coupling an ion chromatography unit to the ICP-MS. The median concentration of TSI in aerosols from Mace Head was 222 pmol m^{-3} (summed over all impactor stages) of which the majority was associated with the SOI fraction (median day: 90±4%, night: 94±2% of total iodine). Iodide exhibited higher concentrations than iodate (median 6% vs. 1.2% of total iodine), and displayed significant enrichment during the day compared to the night. Interestingly, up to 5 additional, presumably anionic iodo-organic peaks were observed in all IC-ICP-MS chromatograms, composing up to 15% of the TSI. Soluble organically bound iodine was also the dominant fraction in all rain and snow samples, with lesser amounts of iodide and iodate (iodate was particularly low in snow). Two of the same unidentified peaks found in aerosols were also observed in precipitation from both Southern and Northern Hemispheres. This suggests that these species are transferred from the aerosols into precipitation and that they have either a relatively long lifetime or are rapidly recycled. It is thought that SOI is formed by reactions between HOI or I_2 and organic matter derived from the ocean surface layer. SOI may then photolytically decompose to yield iodide and the unidentified species. The data in this study show that iodine oxides are the least abundant species in rain, snow, and aerosols and therefore considerably more effort is required on aqueous phase iodine chemistry for a holistic understanding of the iodine cycle.

1 Introduction

Iodine speciation in aerosols and precipitation has been of interest recently in both atmospheric research and more applied environmental geochemistry and health. For example, release and photolysis of gaseous iodine species such as I_2 and CH_2I_2 followed by homogeneous nucleation of iodine oxides has been suggested as a novel process leading to new particle formation in the marine/coastal boundary layer (O'Dowd et al., 2002; McFiggans et al., 2004; Saiz-Lopez and Plane, 2004; O'Dowd and Hoffmann, 2005; Sellegri et al., 2005; Whalley et al., 2007). It has been suggested that these particles may grow large enough to form cloud condensation nuclei, and thus lead to enhanced droplet number concentrations (Cainey, 2007). Indeed, plumes of iodine derived aerosols have been observed extending a few hundred metres into the coastal boundary layer at Mace Head,

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Ireland (Sellegri et al., 2005 and refs therein). To date, the new particles are thought to form through polymerization of IO_2 dimers and to initially consist of purely oxidized forms of iodine such as I_2O_4 or I_2O_5 (McFiggans, 2005; Saunders and Plane, 2005; Pechtl et al., 2006). These species should decay to IO_3^- shortly after formation or may even be taken up as HIO_3 from the gas phase (Pechtl et al., 2007). Most models predict that iodate is the only stable iodine species in aerosols, rain and snow and that any reduced iodine species, such as iodide, should be oxidized (by ICl, O_3 and other highly oxidizing species) at diffusion controlled rates to I_2, HOI and then further to IO_3^- (Vogt et al., 1999; McFiggans et al., 2000; Baker, 2005; Saiz-Lopez et al., 2006; Enami et al., 2007; Pechtl et al., 2007). Alternatively, models predict that the intermediate species such as I_2 or IBr may degas to the gas phase leaving the aerosol progressively depleted in halide ions during ageing. However, field studies and more recent modelling attempts have suggested that organic iodine species in aerosols and precipitation are important, and have also found iodine enrichment factors (relative to ocean water) in excess of 1000 (e.g. Duce et al., 1965; Rancher and Kritz, 1980; Gilfedder et al., 2007a; Pechtl et al., 2007). Moreover, Rosinski and Parungo (1966) have shown data from both field and laboratory experiments that suggest reactions between gaseous iodine (I_2) and vegetation derived VOCs (e.g. terpenes) to form ice nuclei on exposure to UV radiation and natural sunlight. Both camphor-I compounds and CH_3I were identified by mass spectrometry; although due to the rather rudimentary experimental setup it is impossible to tell if the iodine was bound to the organics in the gas phase or within the aerosols after nucleation of the organic precursors. Indeed, despite many laboratory studies showing the formation of IO_2-IO_2 derived aerosols, little direct field evidence exists for the presence of oxidized iodine species in the particle phase. This is mostly hampered by the lack of reliable methods for speciation at low iodine concentrations and a method for sampling nucleation size aerosols.

On a more applied level, 30% of the world's population suffers from insufficient iodine intake (de Benoist et al., 2004). This is not unilaterally confined to less developed countries either; many of the more industrialized countries (e.g. Ireland) also have insufficient iodine intake despite the iodine supplements added to salt (de Benoist et al., 2004; Andersson et al., 2007). As such, the sources and species of natural iodine in precipitation (which is the dominant iodine contributor to soils, e.g. Fuge and Johnson (1986) and Schnell and Aumann (1999) are of concern to the wider population.

The aim of this communication is to demonstrate that 1) Soluble Organically bound Iodine (SOI) is the dominant iodine species in size segregated and $PM_{2.5}$ aerosols sampled at Mace Head, on the west coast of Ireland, and that iodate is the least abundant species and; 2) SOI in precipitation occurs globally and that at least one iodo-organic species is transferred from marine aerosols into rain and snow.

2 Methods

2.0.1 Aerosol sampling

During the 2006 MAP (Marine Aerosol Production from natural sources) campaign aerosols were sampled at the Mace Head atmospheric research station using a Berner 5 stage cascade impact sampler fitted with cellulose nitrate filter paper and housed in a protective shelter. The samples were taken on the 15, 17–20, 25, 26, and 29 of June and 4 of July and were segregated into day (8:00–20:00) and night (20:00–8:00) in the size ranges: stage 5 5.9–10 μm, stage 4 2–5.9 μm, stage 3 0.71–2 μm, stage 2 0.25–0.71 μm and stage 1 0.085–0.25 μm. Typically about 50 m^3 of air were sampled per 12 hour sampling period at a flow rate of 4.5 m^3 h^{-1}. To ensure that the results were not sampler dependent and to gain a better idea of short term temporal changes (morning, 8:00–14:00, afternoon, 14:00–20:00 and night, 20:00–8:00) we also employed a virtual impactor ($PM_{2.5}$ μm) for the 15, 17–20, 25, 26 and 29 of June and 6 of July. This was operated at a flow rate of 1.5 m^3 h^{-1}. In addition, to test whether the filter material was influencing the concentrations and proportion of organic iodine we also took one sample from a high volume sampler (PM_{10} μm) fitted with a quartz filter that had been precombusted at 500°C for 24 h. It was operated at a nominal flow rate of 1.13 m^3 min^{-1}. One day (15/6/06) of $PM_{2.5}$ samples were also taken offshore (North Atlantic Ocean) aboard the *Celtic Explorer* with a virtual impactor ($PM_{2.5}$ μm) during the day (8:00–20:00) and night (20:00–8:00). Back trajectories for these dates using the NOAA-HYSPLIT model (Sup. Figs. 1–9) http://www.atmos-chem-phys.net/8/6069/2008/acp-8-6069-2008-supplement.pdf and black carbon data from the Mace Head station (http://macehead.nuigalway.ie/map/g_database.html) indicated that on the 15, 17, 19, 20, and 29 of June clean marine air was arriving at the site. Samples on the 18 and particularly the 25, 26 of June and 4 July were polluted. All aerosol samples were extracted with milli-Q water by ultrasonification for 20 minutes and the liquid was subsequently filtered (0.45 μm) and analysed by the methods outlined in Sect. 2.3.

2.1 Precipitation sampling

Rain samples were obtained from various locations from the Southern and Northern Hemispheres: 2 samples from a rural location in Australia (late summer, Barkers Vale, N.S.W.), 1 sample from a costal rural location on the North Island of New Zealand (early autumn, Oakura), 4 samples from Patagonia Chile (from Biester et al. 2004 as given in Gilfedder et al. 2007a), 8 samples from Mace Head, Ireland (collected on the same dates as aerosol samples to allow a comparison between aerosol and droplet phases), 1 sample from rural East Germany (summer, Lauchhammer), 1 sample from the Black Forest Germany (spring), 26 samples from Lake Constance,

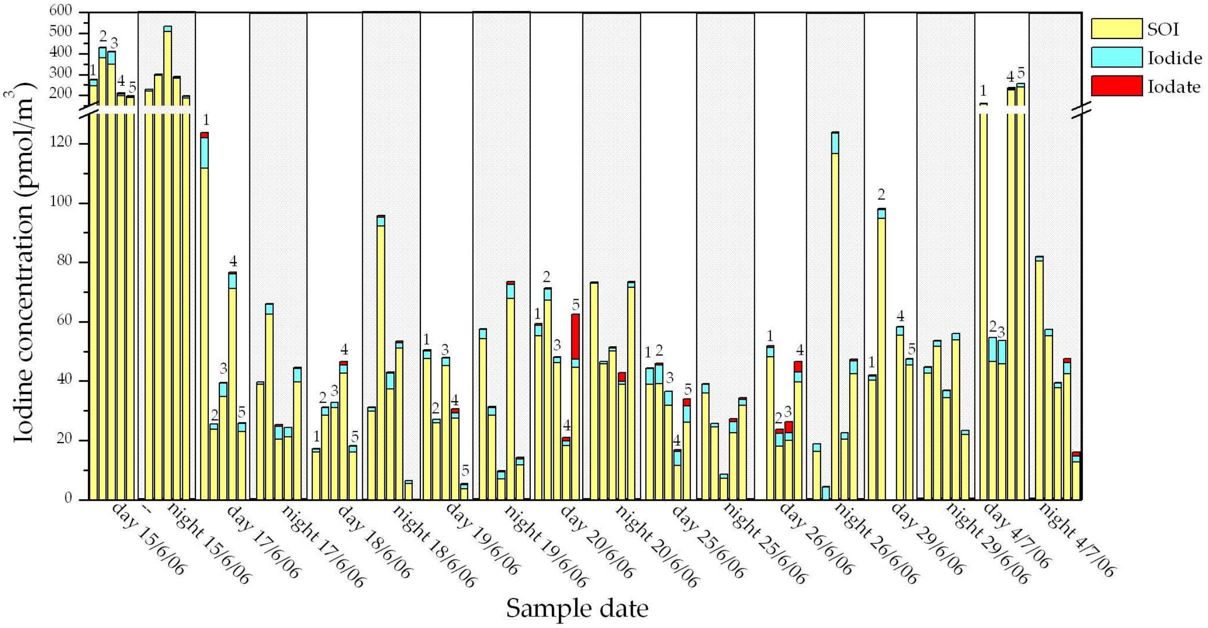

Fig. 1. Total soluble iodine (TSI), soluble organically bound iodine (SOI), iodide, and iodate concentrations in size-segregated aerosols from Mace Head research station. Numbers in the graph represent the different impactor stages and the grey shading shows nighttime sampling.

Germany (Gilfedder et al., 2007a), and 2 samples from different parts of the Alps (autumn, Sedrun and summer, Interlaken), Switzerland. Note that the samples from Mace Head were collected at two locations; firstly from the atmospheric research station located near the shore and secondly from a small cottage about 200 m inland from the station. Samples were collected either directly into LDPE bottles or with a polypropylene funnel (that had previously been cleaned with Milli-Q water) draining into the sample bottle. Snow samples were collected in LDPE bottles from: Greenland (clean sector, Summit camp taken from a snow pit at the surface, 25 cm, 50 cm and 100 cm depth during June and July 2007); Lake Constance (all surface snow), and the Black Forest (surface snow as given in Gilfedder et al. 2007b), both Germany; the Alps (Fiescherhorn Glacier ice core samples as given in Jenk et al. 2002) and hail from the mountains around Interlaken (taken in June 2006), Switzerland; and Mt. Taranaki (also known as Mt. Egmont, surface samples taken in August 2006, note that these samples were quite old and could therefore be subject to unknown changes), New Zealand. Most samples from Europe were analysed within a few weeks and all samples were analysed within 2 months.

2.2 Analytics

All rain, snow and aerosol samples were filtered through 0.45 μm filters and iodine species were analysed by ion chromatography-inductively coupled plasma mass spectrometry (IC-ICP-MS) by the methods outlined in Gilfedder et al. (2007b). Total iodine was measured by normal mode ICP-MS. Due to the high total iodine concentrations in aerosol samples total iodine was diluted by a factor of 10 prior to analysis. Soluble organically bound iodine was calculated as TSI-$\sum$ inorganic species. Unknown species identified in IC-ICP-MS chromatograms were quantified using the iodide calibration curve. This should not present a problem as all iodine is ionized to I^+ in the plasma prior to being quantified by the MS system. Total iodine and iodide calibrations were checked periodically with standard reference material BCR611, which has a recommended total iodine concentration of 9.3±1.3 μg l^{-1} and an iodide level of 9.0±1.1 μg l^{-1}. Unfortunately, there is currently no standard reference material for iodate. Concentrations were always within the standard deviation given in the certificate and deviated from the average value by less than 10%. Replicate analysis for three consecutive aerosol samples gave a relative standard deviation (RSD) of 2.2% for total iodine. The precision of the speciation measurement was calculated based on 15 replicates of the standard reference material over 2 months, which gave a RSD value of 4.1%.

3 Results

3.1 Iodine speciation in aerosols and rain from Mace Head

Total soluble iodine (TSI) levels in size-segregated aerosols were relatively consistent over the sampling period (median 222 pmol m^{-3}, $\sum$0.085-10 μm), except for the 15 of June, when concentrations were considerably higher (e.g. night

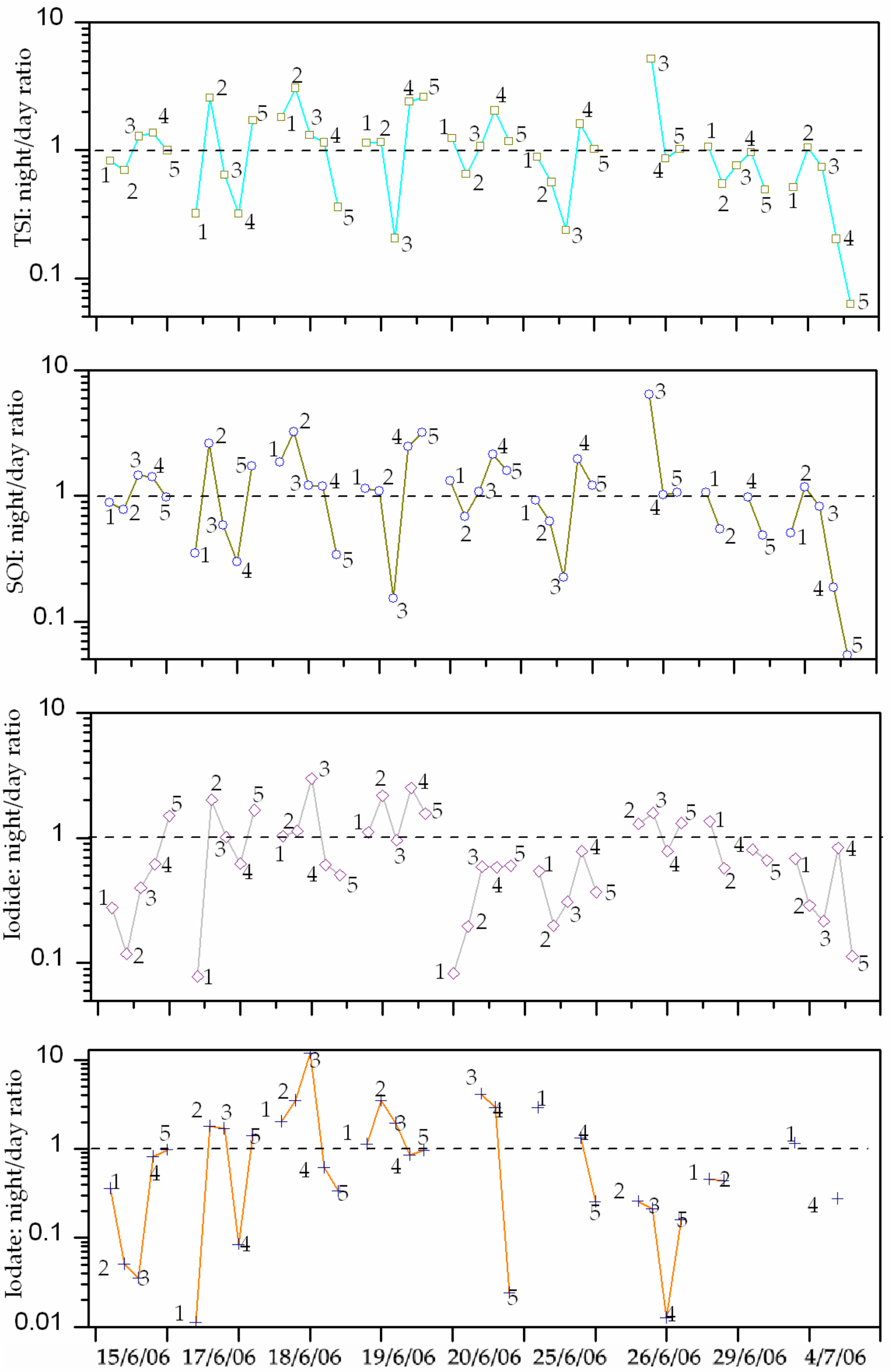

Fig. 2. Size segregated iodine concentrations from nighttime samples divided by iodine concentrations in samples from the previous day. Numbers indicate impactor stage (i.e. aerosol size fraction) and the dashed line shows 1:1 relationship between day and night. Note that where no data exists either measurement was not possible or concentrations were below the detection limit.

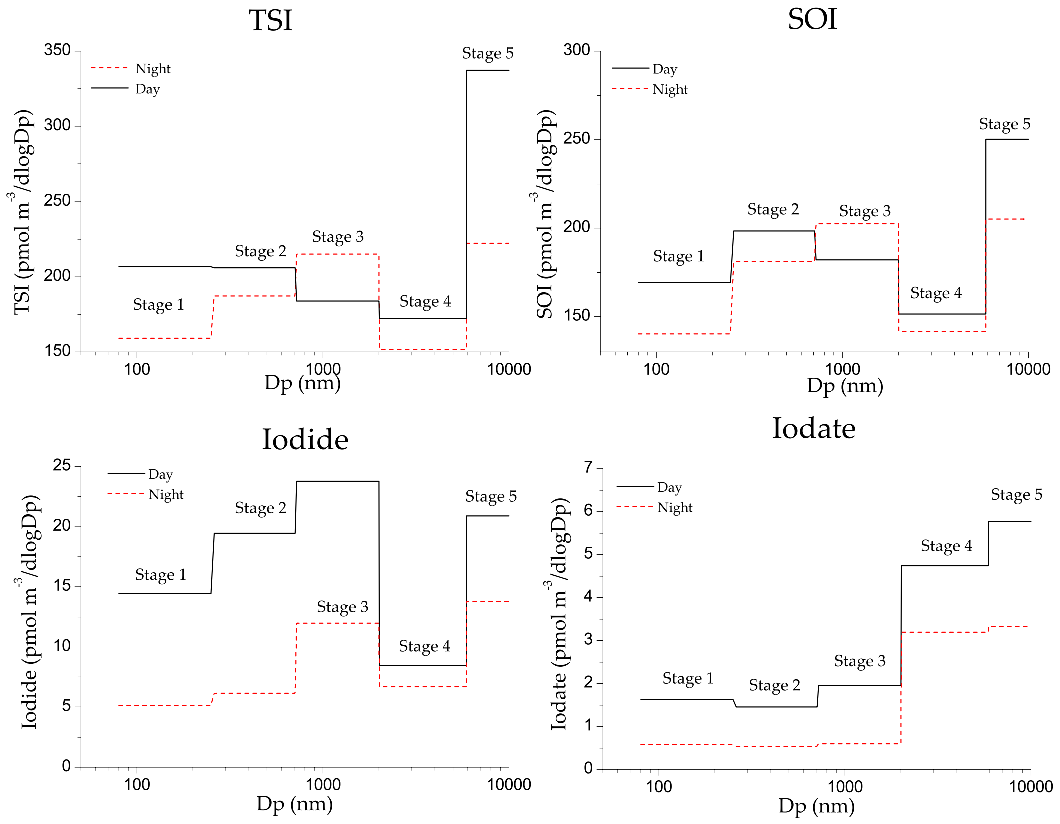

Fig. 3. Normalized (dlogDp) average iodine speciation in size segregated aerosols. TSI-total soluble iodine, SOI – soluble organically bound iodine. Each stage is averaged over the respective impactor stages and the study period.

1554 pmol m^{-3}) than on all other sampling dates (Fig. 1). Soluble organically bound iodine (SOI) was the dominant species in the aerosol samples from Mace Head (median 210 pmol m^{-3}, range 122–1490 pmol m^{-3}, $\sum$0.085–10μm), accounting for 83–96% (median 90±4%) of TSI during the day and 90–97% (median 94±2%) during the night (Fig. 1). Iodide was the most abundant inorganic aerosol species (median 13 pmol m^{-3}, range 4.7–135 pmol m^{-3}), except for a few isolated cases in the largest size modes, where iodate and iodide concentrations were about equal. Iodate concentrations ranged from below detection to 17 pmol m^{-3}, with a median of 2.7 pmol m^{-3} (1.2%) and maximum of 6.4% of the total iodine. Figure 2 presents the night to day ratio of iodine concentrations in the size-segregated aerosols to highlight diurnal trends in the data. Values above one indicate enrichment during the night relative to the previous day, whereas values below one demonstrate enrichment during the day relative to the night. Each iodine species in Fig. 2 was subject to a Chi-square (χ^2) statistical test with Yates correction for continuity in an attempt to ascertain whether day-night differences in iodine speciation were significant. This test ignores the magnitude of the enrichments, and treats the data nominally, being either "day" or "night" enriched. Data that showed neither enrichment during the day or night (i.e. fell onto the "1" line) was excluded from the test. These calculations demonstrate that there was no significant difference between the numbers of observations being enriched during the night compared to the day for all species except for iodide ($p>0.05$). For iodide the number of observations of daytime enrichment was significantly higher than the number of observations falling into the night enriched category ($p<0.05$). There was no noticeable dependence of iodine species on aerosol size classes unless the data was normalized by the logarithm of impactor size ranges (i.e. by channel size; concentration/dlogDp). Such transformations allow a more representative comparison between the impactor stages and, as shown in Fig. 3, is given here as the average for each aerosol size class over the study period. After normalization, there was still very little difference between the different aerosol size classes for TSI, SOI, and iodide (Fig. 3). Iodate appeared to be concentrated in the largest size fractions during both the day (67% of iodate in the >2 μm fraction) and night (79% of iodate in the >2 μm fraction) in agreement with the data in Baker (2005). Figure 3 also shows that, on average, iodide and iodate levels were higher during the day than during the night over all impactor stages.

The concentrations of TSI and iodine species from the virtual impactor were comparable to the cascade impactor

Table 1. Total soluble iodine concentrations and speciation in rainfall from the Mace Head station and Mace Head cottage. All concentrations in nmol l^{-1} except where indicated.

Sample location	Sample date	Total iodine	Iodide	Iodate	SOI	% SOI
Mace Head station	17–18/6/06	19.7	3	3.4	13.3	67
Mace Head cottage	17–18/6/06	20.5	2.3	3.7	14.5	70
Mace Head station	19–20/6/06	24.4	5	3.7	15.8	64
Mace Head cottage	19–20/6/06	33.1	8.7	4.7	19.7	60
Mace Head station*	26/6/06	37	6.8	4.2	26	70
Mace Head cottage	29/6/06	30.7	5.8	3.9	20.9	68
Mace Head station	8/7/06	47.3	6.4	1.72	39.2	83
Mace Head cottage	8/7/06	18.1	4.3	1.8	12.0	66

* taken over a 4 h rain period.

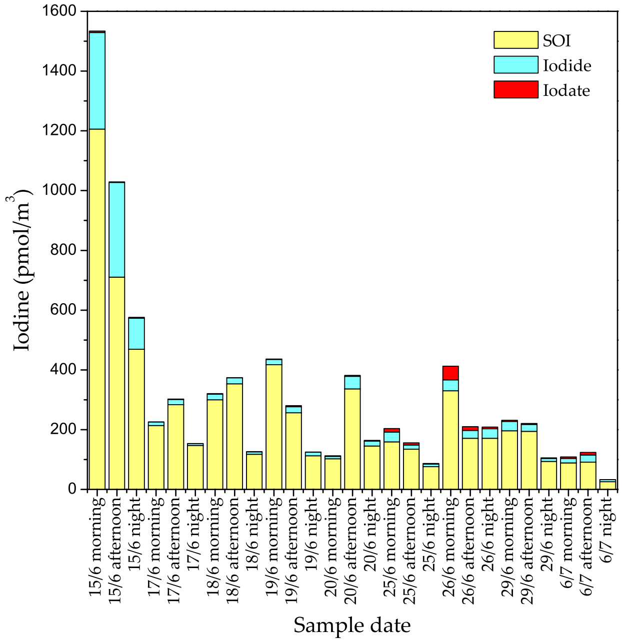

Fig. 4. Soluble organically bound iodine (SOI), iodide and iodate concentrations in aerosols collected with a virtual impactor ($PM_{2.5}$) during the morning (8:00–14:00), afternoon (14:00–20:00) and night (20:00–8:00).

values (median TSI-209 pmol m^{-3}, SOI-182 pmol m^{-3}, iodide-18 pmol m^{-3}, iodate-2.3 pmol m^{-3}). The $PM_{2.5}$ results displayed a pronounced minimum in total iodine levels during the night in most cases, while there were no notable systematic differences between morning and afternoon samples. SOI was the dominant species accounting for 69–96% of the total iodine and iodate was the least abundant, with a median and maximum of 1.24% and 6% respectively.

The offshore $PM_{2.5}$ samples from the 15 of June contained significantly lower iodine levels (day-410 pmol m^{-3}, night 561 pmol m^{-3}) compared to the Mace Head station samples collected on the same day (Fig. 4) but closely resembled the station data between 17–29 of July. This strongly suggests that the coastal environment was the source of the excess iodine in the station samples observed on the 15th in both $PM_{2.5}$ and cascade impactor samples and that the other samples more closely represented background marine conditions. SOI was again the dominant iodine component in both offshore samples (day 92%, night 91% of the total iodine) followed by iodide (day 28 pmol m^{-3}, night 49 pmol m^{-3}) and iodate (day 1.9 pmol m^{-3}, night 1.6 pmol m^{-3}).

In addition to the SOI calculated by the mass balance approach described above, the IC-ICP-MS chromatograms also contained up to 5 peaks in addition to the inorganic iodide and iodate species (Figs. 5 and 6). These peaks were observed in size-segregated samples, $PM_{2.5}$ samples from the station and offshore as well as the PM_{10} sample (Supplementary material Figs. 10 and 11 http://www.atmos-chem-phys.net/8/6069/2008/acp-8-6069-2008-supplement.pdf). Other than the peak eluting shortly after iodate (retention time ca. 4 min 40 s; note that the exact retention time depends on age of the column and to a lesser extent ambient conditions such as room temperature) which corresponded to an iodoacetic acid standard, all of these additional peaks remain unidentified. Note that even the iodoacetic acid assignment is only provisional at present, as ion chromatography is not a definitive method for organic anion identification, and it is possible that two or more molecules elute at very similar times, obscuring an exact identification. The iodoacetic acid (provisional) concentrations had a median value of 0.4 pmol m^{-3} (<0.03–2.3 pmol m^{-3}; n=9) during the day and 0.3 pmol m^{-3} (<0.03–0.9 pmol m^{-3}; n=8) during the night. Unfortunately there were not enough consecutive data points to allow any thorough investigation of diurnal or aerosol size related trends. To date we have injected all commercially available standards such as iodoacetic acid, diiodoacetic acid, I_3^-, iodopropionic acid, and a range of aromatic iodine compounds into the IC-ICP-MS system. None of these standard compounds matched the unidentified peaks. However, these unidentified species must be organic (due to the instability of all inorganic species other than iodide and iodate), and anionic as they are efficiently separated by the anion exchange column. The largest of these unknown species (termed peak (p) 4; elution time ca. 7–8 min.) was often even more abundant than iodate. There were also significant correlations between the unknown peaks and iodide during the day, although this tended to collapse during the night. Correlations with TSI, SOI and iodate were much weaker (Fig. 7).

Soluble organically bound iodine was also the major fraction in the rain samples from Mace Head station and the cottage (Table 1). However, the SOI in rain consistently represented a lower proportion of the TSI compared to the aerosol samples and generally had a larger proportion of iodate. In fact, in some of the rain samples iodate was at a similar, or slightly higher, concentration than iodide. This is consistent with inorganic iodine speciation measurements in rainfall from the North Sea region, analysed by electrochemical methods (Campos et al., 1996), and rainfall from west England measured by photometry (Truesdale and Jones, 1996). This is further conformation that our speciation technique is accurately recording the iodide and iodate levels. Interestingly, the largest of the unknown compounds (p4) observed in the aerosol chromatograms were also consistently found in the Mace Head rain chromatograms (Fig. 8).

3.2 Iodine speciation in rain and snow samples

Iodine concentrations in rain and snow samples from both the Northern and Southern Hemispheres were surprisingly similar given the different environments from which they were taken (Tables 2 and 3). As would be expected, the highest average concentrations were observed near the coast (e.g. Mace Head and Oakura). However, total iodine levels further inland, such as at Lake Constance, often displayed similar concentrations to locations directly adjacent to the coast. As such, there is no evidence for a strong (if any) iodine concentration gradient between the ocean and the terrestrial environment. Recent work has found significant fluxes of methyl iodide from a number of terrestrial environments, which could be a possible solution to the lack of an obvious iodine gradient inland (Keppler et al., 2000; Manley et al., 2007; Sive et al., 2007). Alternatively, the relative uniformity in iodine levels observed in rainfall between locations (see also Krupp and Aumann, 1999) could be related to iodine cycling between the gas phase and droplets. Note that Moyers and Duce (1972) and Rancher and Kritz (1980) both found significantly higher iodine (2–3 times) concentrations in the gas phase than in aerosol particles in marine air. Indeed, Moyers and Duce (1972) observed a direct correlation between total gaseous iodine and particulate iodine. This suggests that particle-gas interactions are important processes for iodine cycling in the boundary layer.

The lowest iodine concentrations in snow were observed at high altitudes, such as at the Summit Camp Greenland (3200 m.a.s.l.), the Swiss Alps and higher parts of the Black Forest; in agreement with the exponential decrease in iodine levels with increasing altitude found by Gilfedder et al. (2007b). As observed in Mace Head rainfall SOI in rain and snow from both Northern and Southern Hemispheres was the dominant iodine fraction in most samples, generally accounting for over 50% (but up to 80%) of the TSI (Tables 2 and 3). The SOI levels from Mt. Taranaki are thought to be low due to the age of the snow (e.g. partial melting and refreezing could have effected the iodine concentrations and speciation) and the very low levels of iodine found, which were only slightly above detection limits. In all continental rain and particularly in the snow samples, iodate was the least abundant species, often falling below the detection limit of the method ($\sim 0.2\,\mathrm{nmol\,l^{-1}}$). Also, iodate levels were always higher in coastal samples than those sampled further inland. The same unidentified species described above for Mace Head rain and aerosol samples (p4) were also found in most of the rain and snow samples from both the Northern and Southern Hemisphere locations (Fig. 9). In particular, the largest peak (p4) observed in aerosols from Mace Head could be traced directly from the aerosols into the rain (Fig. 8). As p4 was also found in rain and snow samples at the other sampling locations, it also seems at least plausible that this unidentified species is also present in the global aerosol population.

4 Discussion

The current understanding of iodine cycling in the atmosphere is that the majority of gaseous iodine is taken up, or nucleates, as iodine oxides such as HIO_3 or I_2O_5. Theoretically, iodate should be the only stable sink species for iodine and thus removed from further cycling reactions in the atmosphere. While such mechanisms have traditionally been implemented in models, it is obvious from the field results presented here and elsewhere that iodate is often the least abundant species in rain, snow and aerosols (Baker et al., 2000; Baker et al., 2001; Baker, 2004, 2005; Gilfedder et al., 2007a, b). Recent modelling studies have attempted to implement some simple organic matter – iodine reactions in an attempt to reconcile field data with theoretical calculations (Pechtl et al., 2007). However, even these simplified schemes are severely hampered by limited structural identification of the iodoorganic compounds, kinetic data and, indeed, even if organically bound iodine is a global phenomena. The data in Baker (2005) has, to a large extent, shown

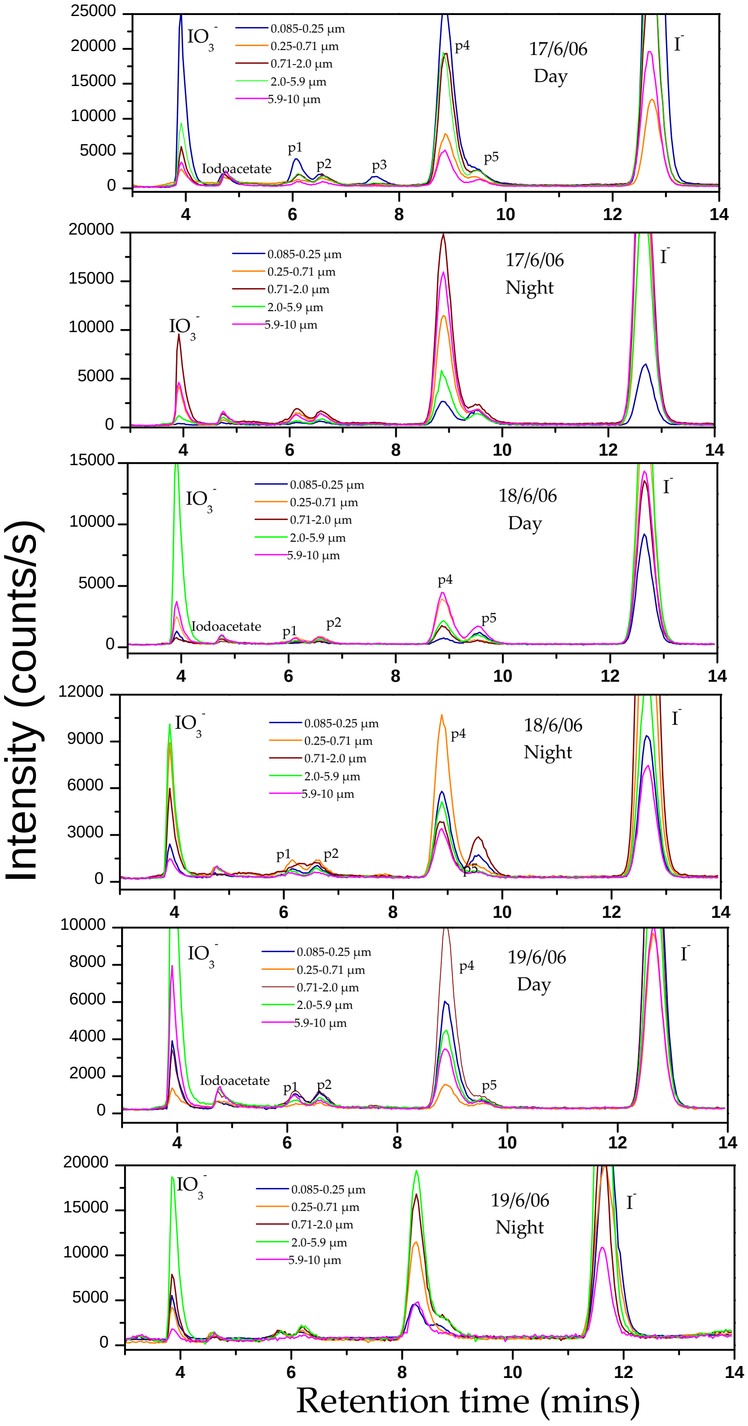

Fig. 5. IC-ICP-MS speciation chromatograms of aerosols from Mace Head 17–19 of June 2006. p1 to p5 are unidentified peaks 1 to peak 5.

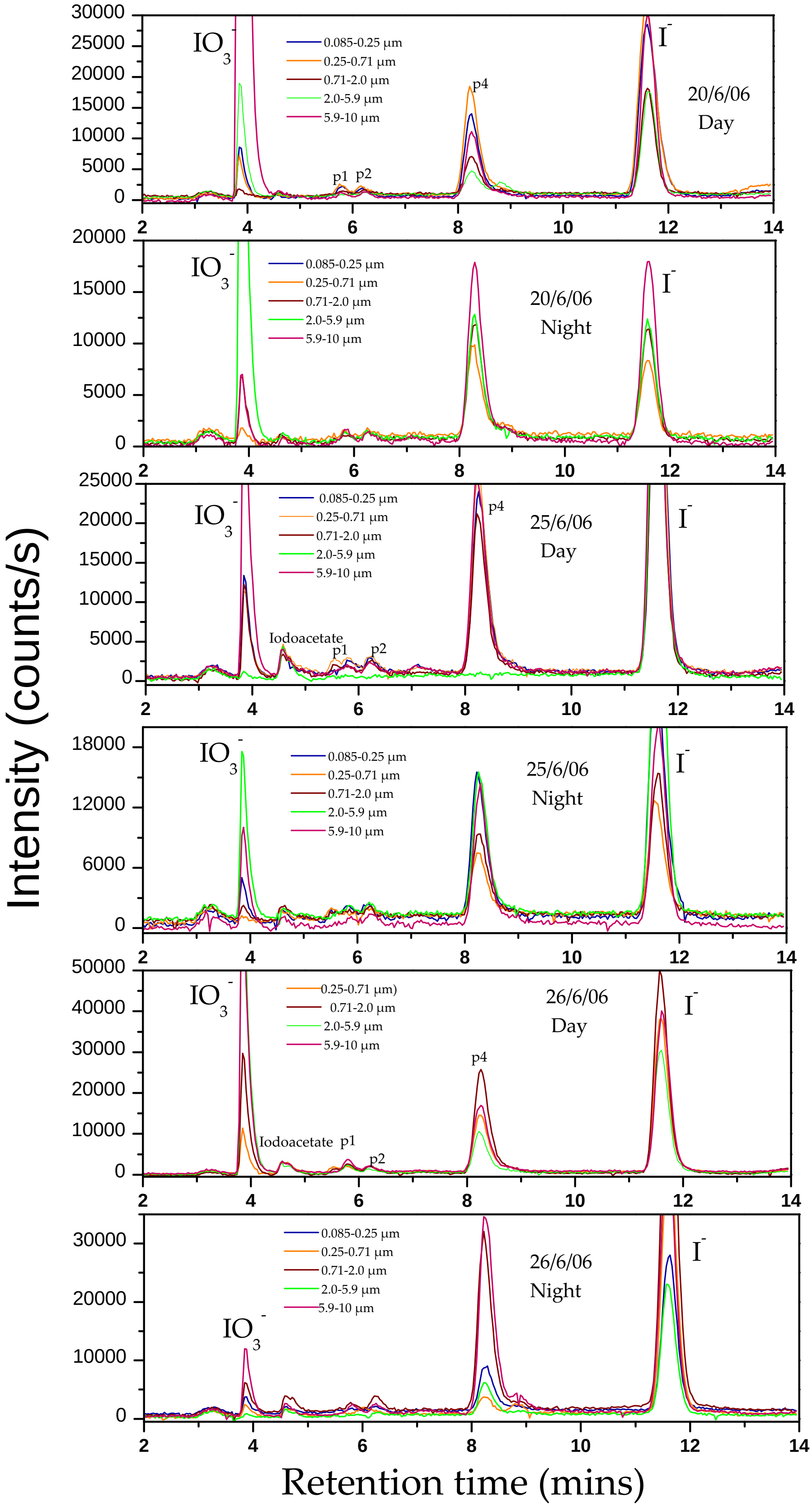

Fig. 6. IC-ICP-MS chromatograms of iodine species aerosols in from Mace Head.

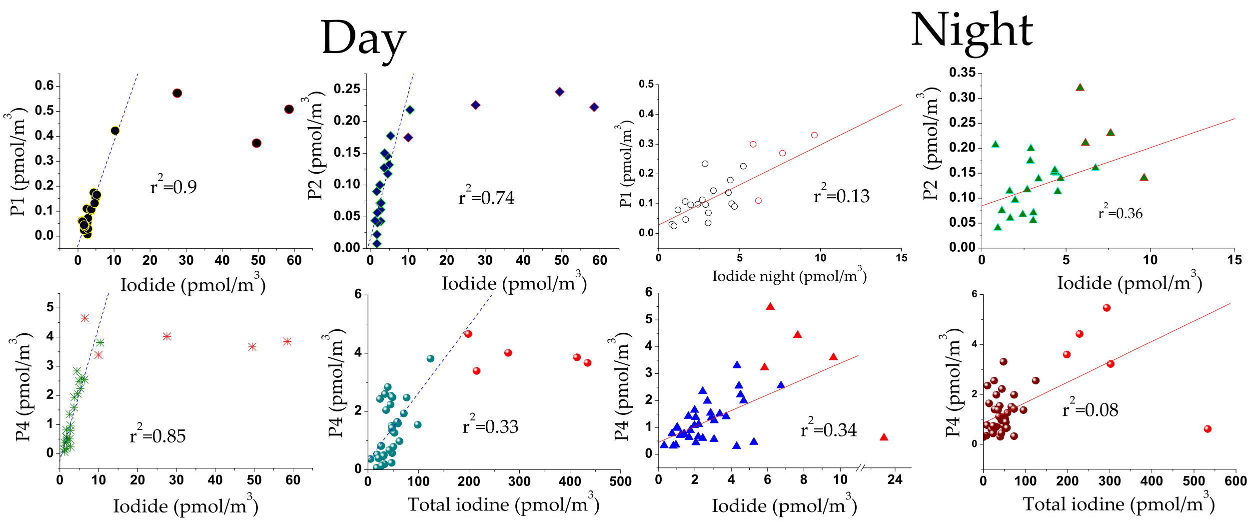

Fig. 7. Correlations between the unknown peaks and iodide and total soluble iodine. The points outlined in red are from the 15th of June are not included in the correlations due to suspected coastal influence.

Table 2. Total soluble iodine concentrations and speciation in rain from Northern and Southern Hemispheres. All concentrations in nmol l^{-1} except where indicated.

Sample Location	Total iodine	Iodide	Iodate	SOI	% SOI
Lake Constance* S. Germany (n=26)	11±6.7	4.1±2.6	1.3±0.86	7.2±4.6	54
Lauchhammer E. Germany (n=1)		2	0.3		
Sedrun Swiss Alps (n=1)	10.1	4.1	0.17	5.8	56
Oakura New Zealand (n=1)	13.7	2.6	1.8	8.7	63
Barkers vale E. Australia (n=2)	5.2	1.8	0.47	3	58
Patagonia Chile (n=2)	4.02	2.7	<0.8	1.34	33

* Some of this data has been given in Gilfedder et al. (2007a).

that SOI is of global importance, but other studies using complementary methods are obviously required to add weight to Baker's findings.

The data presented here shows that SOI is the most abundant species in aerosols sampled at Mace Head. In addition to the calculated organic iodine fraction (i.e. total iodine – inorganic species) we also observed unidentified anionic iodine species in IC-ICP-MS chromatograms that can only be organic compounds. Although the most abundant of these species only made up, at maximum, 10–15% of the total soluble iodine (TSI), these species provide direct evidence that organically bound iodine exists in the aerosols. This is further shown by the tentative identification of low concentrations of iodoacetic acid. The unidentified peaks are most likely anionic organic iodine species of low molecular weight, as they are efficiently separated by the anion exchange resin. It is thought that these species are formed by oxidative and/or photolytic decomposition of SOI molecules of high molecular weight, such as iodinated marine gels or colloids and their decomposition products, observed globally in submicron aerosols by Leck and Bigg (2005), Leck and Bigg (2007) and Bigg (2007). These gels are transferred into the atmosphere by bubble bursting and have been observed by microscopy at less than 50 nm sizes. Marine gels decompose both photolytically and by acidification (Chin et al., 1998; Orellana and Verdugo, 2003). For example:

$$\text{Large org} - \text{I} + h\nu \quad \rightarrow \text{Small org} - \text{I} \qquad \text{(R1)}$$

$$\text{Small org} - \text{I} + h\nu \quad \rightarrow \text{I}^- + \text{CO}_2 \qquad \text{(R2)}$$

This very general reaction has been shown to occur in the marine environment, with iodide production rates on the order of 12–30 nM m^2 kW^{-1} h^{-1} (Wong and Cheng, 2001).

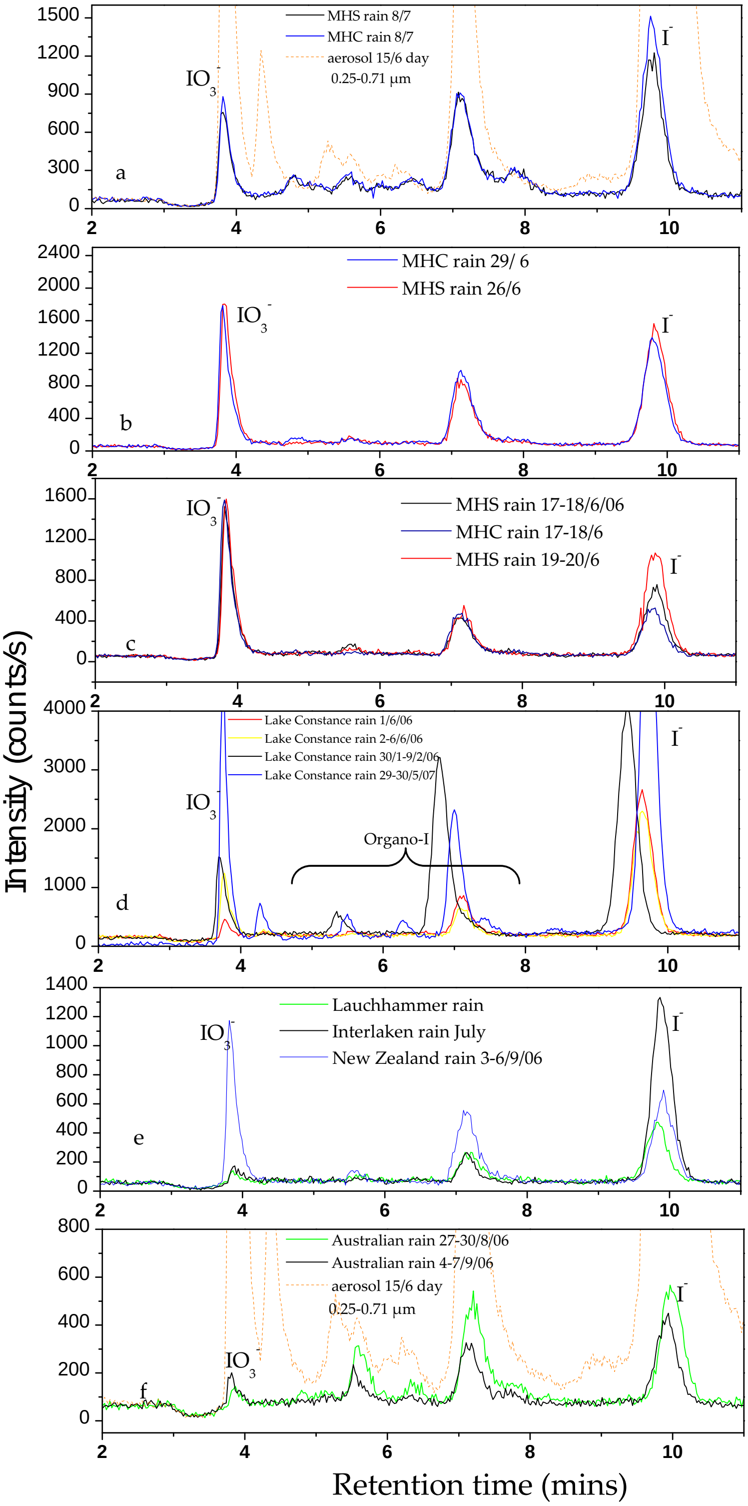

Fig. 8. IC-ICP-MS chromatograms of rain samples from the Southern and Northern Hemispheres. MHS is samples from Mace Head Station and MHC is samples from Mace Head Cottage. Note that in part **(a)** and **(f)** Mace Head aerosol sample 0.25–0.71 μm from the 15/6/06 is overlaid for a comparison between aerosol and rain speciation.

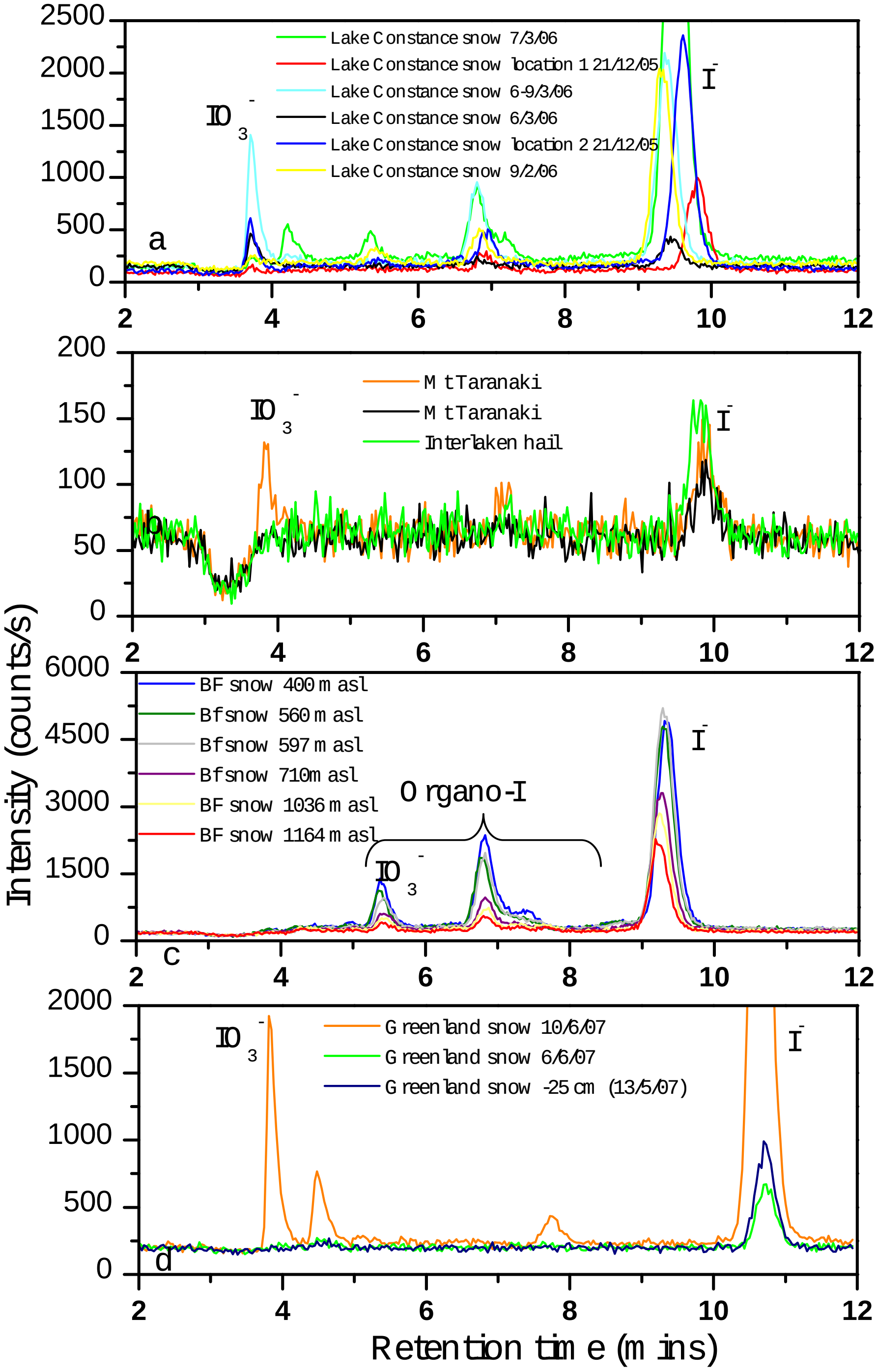

Fig. 9. IC-ICP-MS chromatograms of snow samples from different locations around the world. Lake Constance is in southern Germany, Mt. Taranaki is on the west coast of the north island of New Zealand, Interlaken is a sample taken from the mountains surrounding the city of Interlaken, Swiss Alps, Bf is snow from the Black Forest Germany.

Table 3. Total soluble iodine concentrations and speciation in snow from the Northern and Southern Hemispheres. All concentrations in nmol l^{-1} except where indicated.

Sample Location	Total iodine	Iodide	Iodate	SOI	% SOI
Summit Greenland (n=6)	4.02±0.2	0.42±0.24	< 0.2	3.53±0.42	88
Lake Constance* Germany (n=16)	5.3±2	2.7±1	0.4±0.2	2.6±1.2	48
Black Forest altitude profile# Germany (n=19)	18.7	5.7	0.4	12.6	72
Fiescherhorn glacier Switzerland (n=3)	4.04±1.7	1.4±0.1	< 0.2	2.6±0.8	68
Alps Hail Switzerland (n=1)	1.02	0.55	< 0.2	0.47	46
Mt. Taranaki+ New Zealand (n=1)	0.9	0.31	0.46	0.09	10

* Some of this data has been given in Gilfedder et al. (2007a). # No standard deviation given because concentrations decrease exponentially with increasing altitude as discussed in Gilfedder et al. (2007b). + Very old snow sampled about halfway up the cone of the dormant Mt. Taranaki volcano.

Moreover, (R1) is further suggested by the number of observations of iodide enrichment being significantly higher during the day compared to the night. Some caution must be used in extrapolating rate constants from the marine environment however, as both chemical and physical conditions are vastly different to aerosols. Iodine bound to the organic molecules in the aerosols and precipitation must originate from the gas phase rather than via bubble bursting, as enrichment factors relative to ocean water are consistently higher than 1000 and up to 10 000 (Duce et al., 1965; Moyers and Duce, 1972; Rancher and Kritz, 1980; Sturges and Barrie, 1988). In contrast, bubble bursting can only produce, at maximum, enrichment factors of ~50 (Seto and Duce, 1972). If iodine is taken up by aerosols as iodine oxides, as currently thought, it must be rapidly reduced to species such as I^- and HOI. Until recently there has been no mechanism for the reduction of iodate in the atmosphere. However, Pechtl et al. (2007) have proposed a reaction which may be able to fulfill this function:

$$IO_3^- + I^- + 2H^+ \quad \rightarrow HIO_2 + HOI \tag{R3}$$

Alternatively to (R3) the organic matter from the surface layer of the ocean may possess sufficient reductive potential to reduce the iodate to more reactive intermediate species, although this remains to be seen. According to the modelling work of Pechtl et al. (2007) HOI will also be formed by oxidation of iodide at diffusion controlled rates (i.e. very fast). For example:

$$I^- + ICl \rightarrow I_2 + Cl^- \tag{R4}$$

$$I_2 + H_2O \rightarrow HOI + I^- + H^+ \tag{R5}$$

In either case, it is most likely that it is HOI which is responsible for iodination of organic matter (as first suggested by Baker, 2005), as it is highly electrophilic. Hypoiodious acid, as well as other reactive iodine species such as I_2, have a strong affinity for carbon bonds, and double bonds in particular. It could be expected that the marine gels (derived from spontaneous polymerization of marine DOM in the ocean microlayer and tends to be concentrated in submicron particles by the bubble bursting process (Chin et al., 1998; O'Dowd et al., 2004), are an ideal substrate for iodination. For example,

$$HOI + org - H \rightarrow org - I + H_2O \tag{R6}$$

In this reaction iodine substitutes a hydrogen atom from the carbon substrate. As an alternative to (R1), the HOI may also react with small organic compounds to form the iodoacetic acid and the other unknown compounds observed in the chromatograms. It is anticipated that the reaction rate between HOI and organic material varies as the composition of the organics change e.g. by oxidative processes during aging. This is due firstly to HOI's preference for unsaturated bonds and secondly to the progressive oxidation of the complex molecular structure of aerosol organic matter (e.g. HULIS). Unsaturated bonds are particularly prone to oxidation (by e.g. O_3, OH or even XO), and thus the most optimal halogenation sites are expected to decrease with time. It is also feasible that once there is no, or few, available halogenation sites, reduction of HOI by organic matter may play a role in maintaining iodide concentrations as implied in the reaction cheme of Pechtl et al. (2007). For example,

$$R^\bullet + HOI \rightarrow R - O + I^- + H^+ \tag{R7}$$

One interesting implication of the combination of (R1), (R2), (R4), (R5), (R6) and (R7) is that iodine may cycle between iodide and organic iodine and escape both degassing from the aerosols and oxidation to higher valance states. Interestingly, this may also increase the rate of (R3), which is limited by the iodide concentrations in the aerosols (Pechtl et al., 2007). Obviously, such a hypothesis depends on the as yet unknown rates of most of these equations and remains purely speculative. Indeed, as just mentioned, the rate of

(R6) may change with time depending on the organic substrate characteristics and reduction potential. Also, (R1) is dependent on solar radiation and therefore should not be active during the night, suggesting that a diurnal cycle should be observed in the day-night data.

This ties into the diurnal sampling at Mace Head, where we attempted to identify differences in speciation during day and night, but no strong difference was observed except for iodide. There may be two reasons for this, and the lack of an obvious cycle does not automatically render the first step of (R1) invalid. Firstly, the samples were all taken on rainy days, as the primary aim at the outset of the experiment was to trace iodine species from the aerosol phase into the droplet phase. Such conditions would not be conducive to a robust testing of (R1). Secondly, we have only measured the soluble organic iodine, whereas the majority of organic matter in submicron aerosols from Mace Head is insoluble (O'Dowd et al., 2004). As such, any temporal and/or diurnal trends in the data may be obscured by the extraction method which may only sample a small portion of the total organic iodine. For example, we may only be sampling the second step in (R1), where the largest of the insoluble organic matter has been partially oxidized to give more soluble, although still relatively large, compounds. Future studies focused on the diurnal cycling of iodine should select days with high solar intensities and analyze the total iodine in the samples in addition to the water-soluble iodine to maximize the possibility of observing the iodination-deiodination mechanism.

So far we have only considered iodine-organic interactions in the aqueous/particle phase. While there have been a limited number of studies on the interactions between halogens and organics in the gas phase it is a worthy area of future research. For example, Toyota et al. (2004) have found that up to 20% of atmospheric Br may end up as organically bound Br formed through gas phase reactions between gaseous Br radicals and simple organics (up to C_3 hydrocarbons). Also, as mentioned in the introduction, Rosinski and Parungo (1966) showed that iodine and biogenic gases react (forming iodoorganics as observed by mass spectrometry) to decrease the freezing temperature of ice nuclei. Moreover, chamber studies with brown macroalgae *Drvillaea potatorum* at Cape Grim Australia found that particles produced on exposure to ozone and light were only stable in xylene, suggestive of an organic aromatic species (Cainey et al., 2007); a finding quite different to that observed in chamber experiments in the UK by McFiggans et al. (2004). Nucleation of an organic iodine species would still be consistent with the low solubility of 8 nm size aerosols found with a UF-TDMA by Väkevä et al. (2002). Therefore, while iodine oxide nucleation is still the most plausible mechanism for the large nucleation bursts observed at Mace Head (given the rather robust laboratory data of McFiggans et al. (2004) and fast kinetics of the IO-IO reaction) it would still be useful to run some chamber studies on iodine-organic interactions in the gas phase.

5 Conclusions

Atmospheric iodine chemistry is of increasing interest due to the nucleation of iodine gases to form new nucleation sized aerosols and its potential role in tropospheric ozone depletion. The nucleating aerosol species, as well as iodine taken up from the gas phase, should, thermodynamically, be iodine oxides such as I_2O_5 and HIO_3. However, as shown here, iodine oxides are the least abundant iodine species in accumulation and course mode aerosols, rain and snow with soluble organic iodine (SOI) species being the dominant fraction. Up to five organic anionic species were observed in the IC-ICP-MS chromatograms, although, other than iodoacetic acid, remain unidentified. The most important consequence of the SOI in the aerosols is probably to increase the residence time of iodine within the particles (in particular by retarding iodine release to the gas phase) thus possibly decreasing ozone destruction. Increased residence time may also facilitate iodine transport out of the marine boundary layer into the free troposphere, and possibly even to the tropopause, by convective systems. This could explain the large iodine peak in aerosol spectra obtained by PALMS while sampling in the lower stratosphere (see Fig. 3 in Murphy et al., 2007). While it is most likely that organically bound iodine forms by aqueous phase chemistry in the aerosol, it would be useful for future laboratory studies to investigate the possibility of iodine-organic reactions in the gas phase and subsequent condensation as an alternative to the IO_2-IO_2 nucleation hypothesis.

Acknowledgements. We would like to thank Joele Buxmann and Katja Seitz for taking the Mace Head rain samples, Roland von Glasow and Matthias Piot for the snow samples from Greenland and Fred McGregor for the rain sample from New Zealand. BSG would like to thank Roland von Glasow and Alex Baker for very stimulating discussions about atmospheric iodine chemistry during an invited visit to UEA and the two reviewers for improving the quality of the manuscript. This project was supported by a DFG grant to H. Biester under contract No. BI-734/4-5.

Edited by: A. Pszenny

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