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RESEARCH ARTICLE

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Characterization of iodine species in the marine aerosol: to understand their roles in particle formation processes

Abstract In this contribution, iodine chemistry in the Marine Boundary Layer (MBL) is introduced. A series of methodologies for the measurements of iodine species in the gas and particle phases of the coastal atmosphere has been developed. Iodine species in the gas phase in real air samples has been determined in two field campaigns at the west coast of Ireland, indicating that gaseous iodo-hydrocarbons and elemental iodine are the precursors of new particle formation. Particulate iodine speciation from the same measurement campaigns show that the non-water-soluble iodine compounds are the main iodine species during the marine particle formation. A seaweed-chamber experiment was performed, indicating that gaseous I_2 is one of the important precursors that lead to new particle formation in the presence of solar light in the ambient air at the coastal tidal area.

Keywords iodine species, iodine chemistry, marine boundary layer, particle formation.

1 Introduction

Atmospheric aerosol can affect the climate in direct and indirect ways. Marine clouds originate from the formation of marine aerosol and cloud condensation nuclei, which depend ultimately on the availability of new nanometer-scale particles in the marine boundary layer [1,2]. It has been proved that iodine-containing emissions from coastal and marine algae are not only suspected to be involved in tropospheric ozone degradation, but also in new particle formation processes. If this phenomenon occurs on a larger scale, it could have significant effects on global climate [3], due to marine aerosols and clouds scattering the incoming radiation and contributing a cooling effect to the Earth's radiation budget [4].

1.1 Iodine species in the MBL

Iodine species in sea water

Iodine species in seawater are mainly dissolved inorganic iodide (I^-) and iodate (IO_3^-), whose concentrations are in the order of 0.7×10^{-7} mol·L^{-1} or 3×10^{-7} mol·L^{-1} respectively [5, 6], as well as some nonvolatile dissolved organic iodine. It has been found that the iodate predominates in deep sea (>–250m), while iodate are reduced to iodide by phytoplankton assumedly in near-surface water [7], thus their concentrations become comparable or there could even be more iodide in the sea-air interface [8]. A complicated reaction-pack of iodide with oxygen [9] and ozone [10] at the sea surface might produce some other inorganic iodine species such as I_2, HOI [10, 11] and I_3^-.

Iodo-hydrocarbons (also namely volatile organic iodine, VOI) were observed in sea-surface water, such as CH_3I, CH_2I_2, CH_2ClI and C_3H_7I etc., with typical I concentrations in the order of 10^{-10} mol·L^{-1}. It was first suggested by Lovelock in 1975 that the marine algae were the source of those organohalogens [12], although the precise mechanism is still not clear up till now [13]. As a result, the seawater near the interface to the atmosphere becomes locally super-saturated with those iodo-hydrocarbons, thus causing a flux from the aqueous into the gas phase [14]. Figure 1 shows a picture of iodine species in the MBL approximately.

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Iodine species in the gas phase

It is believed that the ocean is the main source of gas-phase iodine species. Those volatile iodine species are emitted from algae and get saturated in the sea surface, causing the sea-air flux to the gas phase [15]. Measurements of iodine species in the atmosphere were made several decades ago, which indicated that volatilization of organic iodides from the ocean provides the main source of atmospheric iodine [16]. It was estimated previously that more than 5×10^{11} g of iodine is involved in the atmospheric cycle over the globe annually [9], including 6 to 12×10^{10} g of elemental iodine (I_2) [10]. However, recent studies obviously indicate that the iodine species in the gas phase are more complicated than ever before. Molecular iodine [17, 18], iodine oxide radicals such as IO [17, 19], OIO [17, 20], and acids like HI, HOI [18] were observed recently in the troposphere of several different coastal areas.

Iodine species in the aerosol particle

Particulate iodine species include nearly all of its oxidation states. In the MBL, there exist direct sea-salt aerosols, in which the dissolved inorganic (I^-, IO_3^-) and organic iodine are involved by the uptake of seawater. The higher iodine oxides in particles such as I_2O_4 or I_2O_5 are considered as the products from the photolysis of iodocarbons or molecular iodine in the presence of UV radiation and ozone, which cause the substantial bursts of the new particles in the marine atmosphere [21–23].

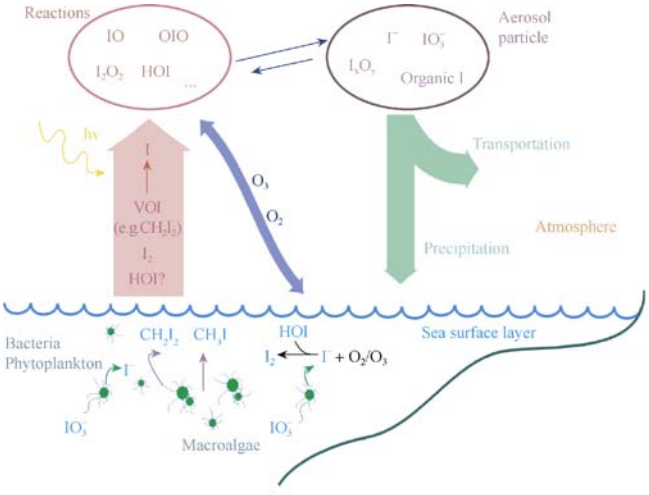


Fig. 1 Iodine species in the marine boundary layer (MBL)

1.2 Iodine chemistry in the MBL

Over the past few years, it has been demonstrated that iodine does have an important influence on atmospheric chemistry [24, 25], at least for several reason including the influence of iodine oxides on the oxidizing capacity of the troposphere, the formation of new particles, and the enrichment of iodine in marine aerosols and the transport of this essential dietary element to the continents [17]. Probably the hottest issue in the research about iodine chemistry in the atmosphere is the role of iodine species in the formation of new particles in the MBL.

Photolysis of iodine species

The current understanding of the main features of gas- and particle-phase iodine photochemistry is shown in Fig. 2. The cycle is initiated by photolysis of organic iodines with lifetimes ranging from several days (CH_3I, C_2H_5I, C_3H_7I)), several hours (CH_2ICl), an hour or less (CH_2IBr), to about 5 min at midday (CH_2I_2) [25]. More recently it was discovered that elemental iodine (I_2) has a lifetime of 5–10 seconds for overhead sun [26]. Although the lifetimes of the polyhalomethanes are controlled almost entirely by photodissociation, OH^- and Cl^- initiated attack could account for 10%–20% of the removal of CH_3I and compete with photolysis for removal of the propyl iodides [27]. An analysis of the secondary chemistry arising from OH or Cl abstraction of a hydrogen bonded to the same carbon as iodine shows that iodine atom release occurs with greater than 90% yield for CH_3I and slightly lower for the higher alkyl iodides [27].

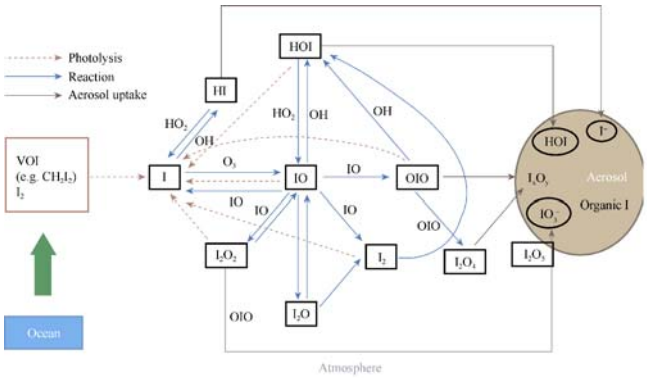


Fig. 2 Chemical pathways from gaseous iodine to aerosol production, based on the current knowledge of atmospheric chemistry and photochemistry

Iodocarbons with two chromophores, e.g., CH_2I_2, CH_2ICl, and CH_2IBr, were shown to be the most important iodine atom precursors in some environments [28]. The following reactions show the photolysis of CH_2IX (X=Cl, Br, I):

$$CH_2IX + h\nu \rightarrow CH_2I + X$$

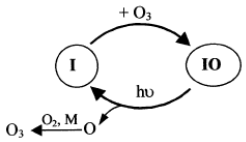
$$CH_2I + h\nu \rightarrow CH_2 + I$$

According to Cotter's experiments [27], it seems there is a fairly rapid release of both iodine atoms in the case of CH_2I_2.

Gas-phase processes

Unlike chlorine and bromine atoms, which react with a range of organic molecules, iodine atoms do not react with

either saturated or unsaturated organic compounds. Reacting with O_3, forming the iodine monoxide (IO) radical, is their major fate. Regeneration of iodine atoms through photolysis of IO is rapid; therefore, a daytime steady state exists between I and IO (collectively termed IO_x). This cycle has no net effect on IO_x or O_3 chemistry, as shown below.



Although this reaction cycle is the predominant pathway for I-to-IO inter-conversion, a number of temporary inorganic reservoir products are formed via IO_x radical termination reactions with HO_2, NO_x, and IO. Only cycles which regenerate I atoms without concomitant O atom formation can lead to catalytic O_3 loss. The reaction of IO with HO_2, forming hypoiodous acid, HOI, is an important example:

$$I + O_3 \rightarrow IO + O_2$$
$$IO + HO_2 \rightarrow HOI + O_2$$
$$HOI + h\nu \rightarrow OH + I$$

$$O_3 + HO_2 \rightarrow OH + 2O_2$$

HOI is believed to be the major component of inorganic iodine in the gaseous phase [29] and an important route to the aerosol phase. This cycle has also been suggested as the dominant O_3 loss cycle at NO_x levels below about 500 pptv [30]. For typical conditions at Mace Head, Ireland, Stutz et al. calculated 0.3 ppb h^{-1} O_3 loss at 100 pptv of NO_x from the HOI cycle, where the NO_x is not playing an important role in the iodine chemistry.

Finally, the relative rates of the branching channels of the self-reaction of IO radicals and the lifetimes of their products are important in determining both the gas and particulate chemistry of iodine. Early modeling studies assumed that the dimer of IO, I_2O_2, was the main product and also the major carrier of iodine to aerosol [16, 29, 31]. Cox et al. identified a reaction, forming iodine dioxide (OIO), as an additional channel, with a yield of ~40% [32–34].

$$IO + IO \rightarrow I + OIO$$

The photolysis pathway of OIO is critical in determining its ozone destruction potential; only this channel will result in net loss of O_3:

$$OIO + h\nu \rightarrow I + O_2$$
$$OIO + h\nu \rightarrow IO + O(^3P)$$

Quantum calculations indicate the upper reaction dominates in the visible region and that the photolysis lifetime of OIO is about 1 s, which would suggest that detectable OIO concentrations should be present only at night. This is in contrast to the work of Cox et al. and an independent computational study [35] that indicated a high photochemical stability for OIO. Apart from photolysis, the fate of OIO is uncertain, but it is assumed the uptake to aerosol and surfaces.

Aerosol uptake and recycling

The net transfer of iodine from the gas to the condensed phase is reflected by the factor of 100- to 1000-fold enrichment of I in fine fraction marine aerosol by comparison to the I/Na ratio in seawater [36]. Some of the condensed iodine is, however, recycled back to the gas phase; the exact rates and mechanisms involved are key parameters for the prediction of the atmospheric impact of iodine. As shown in Fig. 2, HI, HOI, OIO and I_2O_2 are the major species taken up by aerosols from the gas phase: the uptake of HI forms iodide (I^-) in the particle, HOI are directly taken up from gas to particle [37], while the irreversible accumulation of OIO and I_2O_2 has been assumed as the main cause of iodate (IO_3^-) enrichment of marine aerosol [32]. Also a self-reaction of OIO was proposed to form low-volatility iodine oxides, such as I_2O_4 (or $[IO]^+[IO_3]^-$). This might finally lead to stable chainlike structures from further collisions with OIO [21, 38]. However, more recent work [39] suggests that self-reactions of OIO are unlikely to be an important mechanism for new particle formation, due to its short photolysis lifetime. And it was found that the reactive uptake of HOI in the MBL can liberate Cl atoms from sea-salt aerosol at a significant rate [40]. Therefore, the iodine chemistry from gaseous to particulate phase in the coastal atmosphere, the whole chain of events including the chemical nature of the condensing iodine species, are not completely understood so far.

Modeling of reactive iodine species

Several modeling approaches were performed recently by several research groups. An observationally constrained photochemical box model was developed to investigate the atmospheric chemistry of iodine in the MBL in 2000 [41] for instance. Using a model calculation, nucleation from the photolysis of CF_3I or CH_2I_2 in the presence of ozone and UV, demonstrates that IO and OIO concentrations reported in recent field measurements are not sufficient to account for significant aerosol production either in the coastal or open ocean marine boundary layer using the mechanism presented [42]. Instead, it was demonstrated that inhomogeneous sources of iodine oxides, i.e., “hot spots” with elevated iodine species emissions, could account for the aerosol production bursts observed in the coastal region near Mace Head, Ireland [43]. And more recently, using a newly measured molecular iodine photolysis rate, it was shown that, if atomic iodine is involved in the observed particle bursts, it is of the order of at least 1000 times more likely to result from molecular iodine photolysis than diiodomethane photolysis. A hypothesis for the molecular iodine release from intertidal macroalgae and the potential importance of macroalgal iodine particles in their contribution to cloud condensation nuclei (CCN) and global radiative forcing was presented by McFggans et al. [44]. Again, as discussed above, the total mechanism causing

gaseous iodine species to enrich in aerosol is not clear yet.

2 Method development and field measurements

The first iodine observation in the air can be dated back to the mid-nineteenth century, when Chatin (1850) measured total iodine from the air in Paris where he found 0.002 mg iodine in 4,000 L air sample [45, 46]. Due to the importance of the iodine chemistry cycle in the MBL, during the past 50 years various analytical techniques, including wet chemical analysis, neutron activation analysis (NAA), or gas chromatography and mass spectrometry (GC/MS) have been applied and much more has been discovered about inorganic, organic, particulate iodine species in the atmosphere. Many observations of iodine species in the gas phase of the MBL have been made during the past 10 years, as well as the iodine compounds in the marine particle phase. Besides the differential optical absorption spectroscopy (DOAS), NAA and inductively coupled plasma mass spectrometry (ICP/MS) are the techniques commonly used to detect iodine in the laboratory. In this work, methodologies for the in-situ determination of gaseous and particulate iodine species were developed and improved respectively, based on the different sampling methods and the ICP–MS detection system.

2.1 Gas-phase elemental iodine

In this work, a cylindrical diffusion denuder sampling technique was developed for the determination of elemental iodine (I_2) in the gas phase, followed by TMAH extraction and ICP-MS detection. Denudation techniques have been widely applied for the determination of trace components of an air sample. At the laminar air flow, the diffusion coefficient of a gas molecule is at least 100 times bigger than those of the particles greater than 10 nm diameter [47]. According to the Gormley-Kennedy Equation (1949), gas molecules can diffuse to the walls of an open channel much more rapidly than the particles. Consequently, gas molecules can be separated from the particles in the ambient air. Amylose (in starch) has a very specific reaction with molecular iodine, yielding a stable complex, with I_6 ($3I_2$) sliding into the amylase helix cavity, shown as reactions (1) [48, 49]. Based on this reaction and the diffusion of iodine molecule, a cylindrical denuder was designed to separate the molecular iodine from the particles in the air sample.

$$A + 3I_2 \Leftrightarrow AI - Complex \quad (1)$$

Denuder preparation and sampling

Brown glass tubes (ϕ_i 6 mm× ϕ_o 9 mm×50 mm) used as denuders, were soaked in 5% HNO_3 (Acros Organics) for 24 h, and washed with MilliQ water, then dried by pure nitrogen flushing through the denuders. Starch/amylose ethanol solution of 2 mg·mL^{-1} was prepared from starch (in fine powder, Fluka) mixing with ethanol (99.8%, p.a., Carl Roth), for coating the inner surfaces of the denuders. In order to coat the starch powder equably to the inner-denuder walls, four times of 0.5 mL coating-solution were instilled to the rotating denuder, simultaneously with N_2 flush at flow rate of 1.5 L·min^{-1} for drying. All prepared denuders were sealed with PP end-caps (polypropylene vessels (1.5 mL, Roth)) and readied for sampling. Denuder sampling was taken at the flow rate of 500 mL·min^{-1}, with sampling time varying between 15 and 60 minutes. The distances from the ocean/kelp surface to the denuder inlets were vertically 0.5 m~2.5 m. The open ends of sampling denuders were again sealed with PP-vessels after sampling.

Sample treatment and iodine measurement

The iodine-amylose complex at the denuder inner walls was washed and extracted with 4 mL of a TMAH-solution (TetraMethyl-Ammonium Hydroxide, 5 % by weight) at 90 °C for 3 hours. To avoid blocking any parts of the plasma sampling channel with matrix, all samples were diluted to 1 % TMAH before introduced into the nebulizer. Tellurium (200 ng·mL^{-1}, Merck) was added as internal standard for the ICP-MS (PQ2 Turbo Plus, VG elemental, UK) measurement.

Denuder Sampling Efficiency

In order to test the efficiency of the I_2 denuder sampling, a breakthrough experiment using 2-stage denuder (coupling denuders) and a test gas source (containing I_2) was performed in the laboratory. Uncoated denuders, Starch-, TMAH-, Tetrabutyl-ammonium hydroxide (TBAH)-coated denuders were applied in the experiments. Results are shown in Fig. 3. As can be seen in Fig. 3a, more than 90% molecule iodine can be absorbed or adsorbed by starch-, TMAH- and TBAH-coated denuders at the first denuder, while no molecular iodine can be collected by the uncoated at either of the two stages. In those cases of starch-denuders, the breakthrough of the I_2 in the second denuder is not more than 15%, hence a single denuder is efficient enough for the trace iodine analysis in the atmosphere where the iodine contents are much less than those of the test gas in the laboratory.

TMAH can collect CH_2I_2 with 95% recovery at the first denuder (Fig. 3b). In this case, TMAH or TBAH is not specific for sampling the molecular iodine, but collecting other iodine-containing species too. The mechanism of the absorption or adsorption is not only the strong alkali property, but also the ability to form organic nitrogen compounds with iodine, in which the large cation R_4N^+ can be polymeric with polyiodide (I_x^{n-1}) [50]. Therefore, a TMAH-coated denuder might also be used for total iodine sampling in the gas phase in the future. But further experimental testing has to be done for the other iodine species.

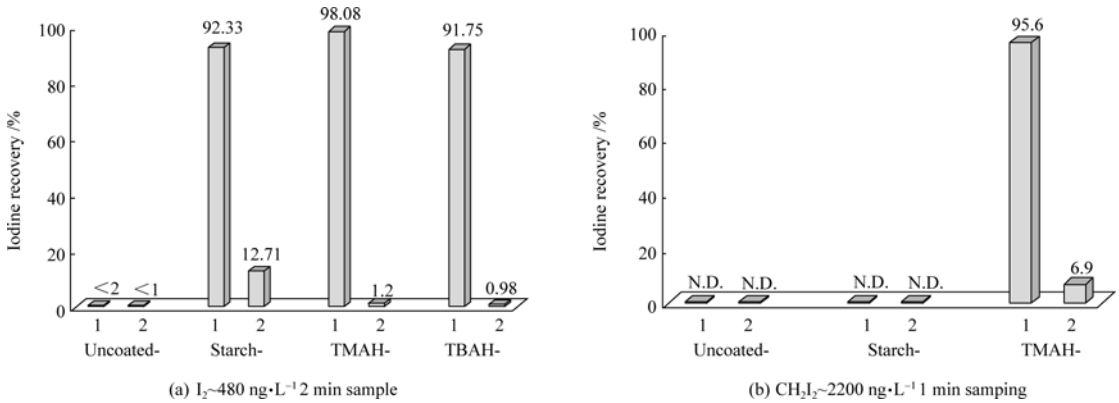


Fig. 3 Recovery of iodine sampling from I_2 (**a**) and CH_2I_2 (**b**) source using different coating denuders at sampling flow of 500 mL·min^{-1} (N.D.=Not Detected)

2.2 Particle-phase iodine species

Sampling

Particle samples (PM2.5) were collected on cellulose-nitrate filters (pore-size 0.45 μm) using a PM2.5 preseparator, a filter holder and a vacuum pump (flow rate 2.5~3.5 m^3·h^{-1}, 20~40 m^3 air/sample). Size-segregated particles, were sampled on Tedlar- or cellulose-nitrate-foils in a 5-stage burner-impactor (fractionated sizes: 0.085 μm –0.25 μm , 0.25 μm –0.71 μm , 0.71 μm –2.0 μm , 2.0 μm –5.9 μm , 5.9 μm –10 μm) using a vacuum pump (flow rate 4.2~4.5 m^3·h^{-1}, 50~100 m^3 air/sample).

Sample Treatment

The treatments of aerosol impacted filters and tedlar-foils are schematically shown in Fig. 4, including the total iodine and iodine species. For total iodine or non-water soluble iodine species, TMAH was applied for the extraction process [51]. Cellulose-nitrate filters were decomposed in the TMAH solution during the extraction process, which avoids any loss of iodine species due to a non-ideal extraction step. Since the tedlar foils are not decomposed, thus to avoid the loss of analytes, a shaking procedure was necessary. However, an additional filtration step is necessary to remove remaining particles in the sample after the TMAH extraction, especially for the cellulose-nitrate-filter samples, in order to avoid any blocking of the channels of the instruments, such as ICP torch, sampler and skimmer. Two types of membrane-filters (pore size 5 μm and 0.45 μm, ϕ=26 mm, filtration area 5.3 cm^2; Minisart, Sartorius AG, Goettingen, Germany) were used for two-step particle filtration before the ICP-MS measurements. Finally, all the sample solutions were diluted to 1% TMAH and tellurium (^{126}Te, 200 ng·mL^{-1}) added as internal standard for the ICP-MS measurements.

For the analysis of water-soluble iodine species, an ion-exchange technique [52] was used to separate iodate (IO_3^-) and iodide (I^-), followed by the ICP-MS, as shown in Fig. 2 as well. A certain amount of AG2-X8 (Bio-Rad Laboratories, CA, USA) resin was soaked in de-ionized water for 24 h and the resin slurry was packed in a glass column of i.d. 5.3 mm and 30 mm length and fixed by glass wool plugs. To purify the resin in the self-made column, 15 mL de-ionized water was used to wash the packed column, followed by 10 mL HNO_3 (1 M) and 15 mL de-ionized water. 10 mL HNO_3 of low concentration (e.g., 0.008 M) was used to elute the iodate bonded to the resin in the column, and 15 mL HNO_3 of higher concentration (e.g., 0.3 M) was used for iodide. TMAH was added to all samples after the separation procedure, in order to reduce the memory effect iodine in the ICP–MS system. In order to reduce the matrix effects for the ICP-MS measurement, pH values were adjusted to 10~12 in all samples, that is about 1% TMAH in the final solutions. 200 ng·mL^{-1} tellurium (^{126}Te) was added as the internal standard for the ICP-MS measurements.

2.3 Field measurements

Part of this work was a contribution to the international European Union (EU) project named “Quantification of Aerosol Nucleation in the European Boundary Layer” (QUEST). The first measurement campaign at the western coast of Ireland was the second campaign of the project. It was performed from the end of May to early June in 2002. All measurements were taken at the Mace Head Atmospheric Research Station (MHARS, 53°20’N, 9°54’W), located about 100 m from the tidal zone and surrounded by rocky area.

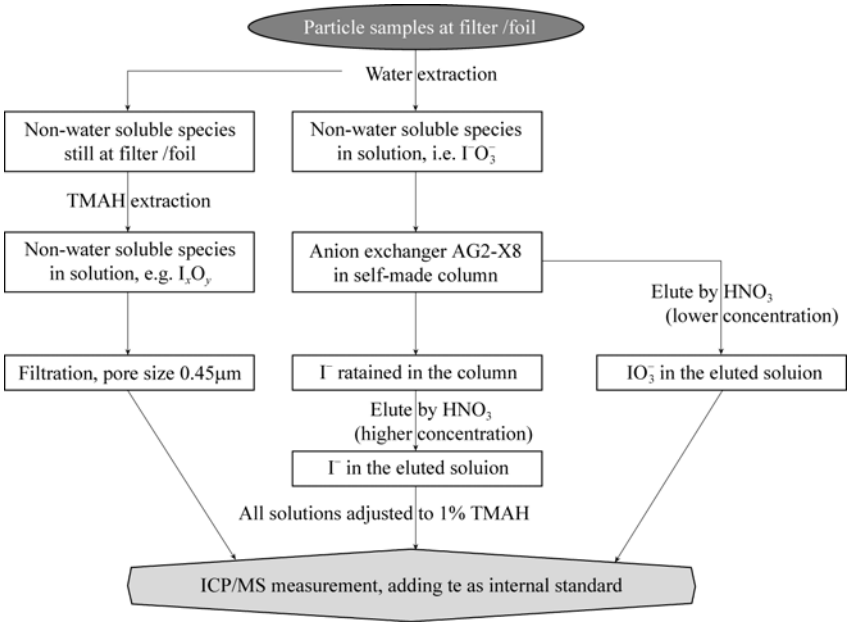


Fig. 4 Sample treatment procedure for iodine and its species in the aerosol sample

However in certain areas around this station, the seaweed density is much higher than at the rocky area around the station itself. As a result, it is believed that "hot-spots" nearby, such as Mwneesh area, should have greater potential in terms of particle formation. This hypothesis was proved to be true during QUEST airborne measurements. These hot-spots are likely to have a significant regional impact on the aerosol population. After the use of a research aircraft to identify the so-called hot-spots, it was proposed to conduct a BIOFLUX study at a particularly strong hot-spot site to examine the relationship between the flux of biogenic iodine gases into the boundary layer and the resulting flux of particles [53]. A BIOFLUX field campaign was conducted in Carna, Galway, Ireland, in September 2003 to identify the particle formation and biogenic gas fluxes from marine algae. Additionally, a seaweed-chamber experiment was performed to test the hypothesis that biogenic gas emissions during low tide explain new particle bursts at the coastal environment during the campaign. Three combinations of seaweeds were tested: Laminaria, Fucus, and a mixture of these two species.

3 Results and discussion

3.1 Gaseous elemental iodine

Field measurements performed at the seaweed "hot-spots" at the western coast of Ireland, showed that the concentration of I_2 in the atmosphere was up to 1.6 ng·L^{-1} (~140 pptV), with a determination limit of 0.10 ng·L^{-1} at a sampling volume of 15 L (500 mL·min^{-1}×30 min). These concentrations are higher than those from DOAS measurements (maximum level 93 ppt) [17], because of the much shorter distance between the sampling position and the kelp surface for the in-situ measurements. The gaseous I_2 content varied widely with the sampling site and water tidal level, the time of day and weather conditions etc.

Figure 5 shows the gaseous I_2 contents from different sampling sites and seaweed-chamber experiments. As can be seen, elemental iodine concentrations at "Mwneesh Bridge" were about 3 times higher than those at "MRI-Carna", obviously due to the larger amount of seaweeds at this sampling site as well as the shorter distance between the seaweeds and denuder sampler inlets. The iodine concentration measured within the seaweed chamber was about one order of magnitude higher than the ambient concentrations.

It was found that the gaseous I_2 contents were not significantly related to the tide level, although it was suggested that the enhanced molecular iodine emissions were linked to the significant concentration of inorganic iodine species in tidal water as the water level subsides [44], in which the process was first linked to macroalgae as a source of precursor and second, and more particularly, to the concentrating effects of inorganic iodine species driven by tides that would not apply over the open ocean. At least, I_2 contents were not found to be zero when there were no kelps exposed to the atmosphere at high tidal level.

Compared to the DOAS results [17], it was found that the daytime I_2 contents were higher than those measured during the night-time or evening. It was suggested that the rapid photolysis of I_2 in the lower atmosphere (lifetime=5～10 s for an overhead sun) results from the strong absorption of visible wavelengths (400 nm< λ <700 nm) which penetrate down to the troposphere [26]. However, if

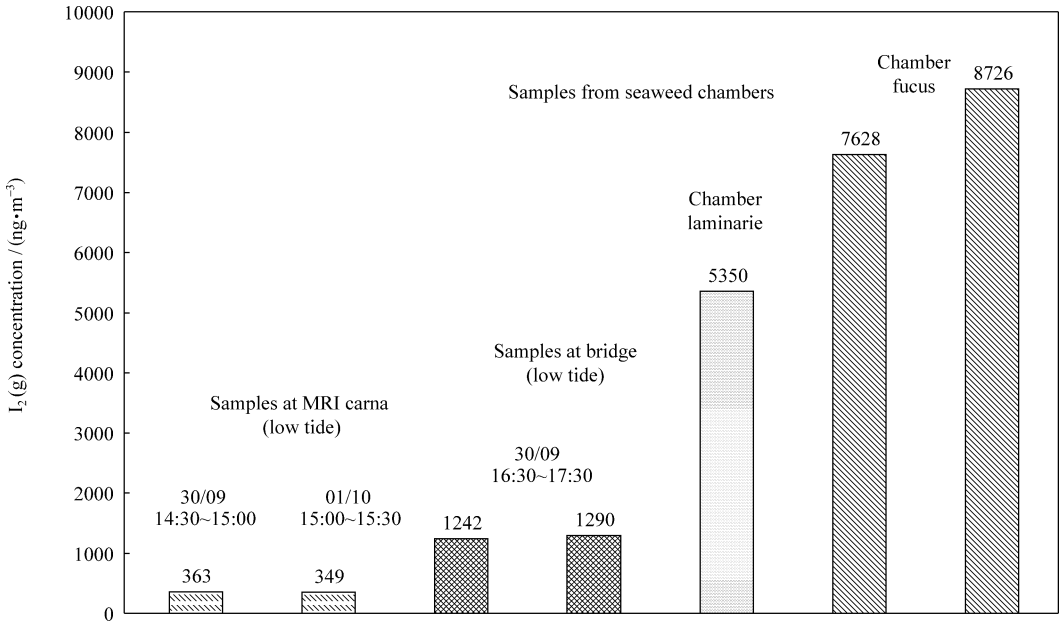


Fig.5 Molecular iodine concentrations measured with the denuder system; Comparison of different sampling sites and seaweed-chamber experiments

molecular iodine is directly emitted from kelps at low-tide level and fades due to the photolysis process at daytime, the contents might depends strongly on the tidal level and solar radiation; or if I_2 is one of the by-products of the photolysis process from other organic iodine in the presence of ozone and solar radiation [1], it would be found that daytime contents become higher. Since the emission source of elemental iodine is not clear, and the iodine photochemical pathways are complicated, it is difficult to explain the observed I_2 contents so far. It seems that there might be a thermodynamic and chemical equilibrium which governs the I_2 concentration in the gas phase of the coastal atmosphere.

3.2 Particulate iodine

From the results of total iodine measurements in PM2.5 during the BIOFLUX campaign, the following can be clearly observed. Firstly, at a hot-spot of seaweeds, due to the higher total amount of iodine source, the results from BIOFLUX are usually 2 to 5 times higher than those taken from Mace Head Station (1~4 $ng \cdot m^{-3}$). Secondly, the daytime iodine concentrations are higher than the night-time measurement. Thirdly, the morning concentrations are lower than those measured in the afternoon. This is obviously because the new particle formation (Nucleation Event) always happened at daytime during the solar radiation between 9:00 to 16:00, and the stronger event was observed to occur usually around and after mid-day, according to the nanometer particle data (Scanning Mobility Particle Sizer (SMPS) was measuring at the same time), which would show a sudden unusual high number concentration of nanometer-particle (D_a<10 nm, N>10^5 cm^{-3}) when the event occurs.

The maximum iodine concentration 21.13 $ng \cdot m^{-3}$ was obtained during a strong nucleation event, while the minimum was found in the night measurements. Assuming nanometer-particle as a sphere model and with the primary chemical composition of iodine oxide species (e.g., I_2O_4, with a density of about 4.0 $g \cdot cm^{-3}$ in this case) and calculating the mass of a nanometer-particle during the aerosol nucleation events, then a typical total iodine concentration of about 10 $ng \cdot m^{-3}$ is estimated to equal to the number concentrations of ~5×10^6 cm^{-3} 1 nm-particle or ~6×10^5 cm^{-3} 2 nm-particle or ~4×10^4 cm^{-3} 5 nm-particles. These calculated data are very close to the number concentration of nanoparticles which were measured by the nano-SMPS when the new particle formation occurred during the field campaign.

Figure 6 shows some typical iodine species concentrations in PM2.5 particle samples. The absolute contents of each iodine species may not be able to significantly indicate or explain the iodine emission leading to the new particle formation, while the ratio of iodate/iodide and water-soluble/-unsoluble species could be relatively important to conclude and clarify the iodine chemistry in the coastal atmosphere. As can be seen in Fig. 6, iodide concentrations are usually higher than those of iodate in all samples with a ratio of about 2~5:1, while iodide/iodate ratio in a seawater sample (at the interface to the air) is at a wide range of 1~4:1 [8]. It looks very possible that those water-solved iodine species were transferred through the sea-air interface, and directly taken up into the particle phase. On the other hand, mechanic studies have suggested that particulate iodate can be accumulated from the iodine oxides (e.g., I_2O_2, I_2O_4 etc.) in higher oxidation

state as the aerosol ages [16, 41] and iodide may be taken up into particle phase from the HI, as shown in Fig. 2.

The ratio of water-soluble (iodate+iodide) and non-water-soluble species (probably iodine oxide I_xO_y and organic iodine compounds) was found in the range of 1:1 to 1:2 or even up to 1:3 during the measurement campaign. It seems that higher concentrated non-water-soluble species, as products which undergo gas-to-particle conversion, can be obtained in those samples with higher number concentration of nanometer-particles, i.e. the water-insoluble species dominate the total iodine in the particle phase while the nucleation event occurs. In Fig. 6, it was observed that the concentration of water-insoluble species depended on the strength of the aerosol nucleation, e.g., 16/09 afternoon data are higher than other nucleation event data, such as 20th and 21st/09 measurements, and the data measured during the non-event period. This conclusion supports the current understanding of the iodine chemistry in the Marine Boundary Layer (MBL), in which particulate iodine species as the particle end-products is suggested to be dominated by iodine oxides.

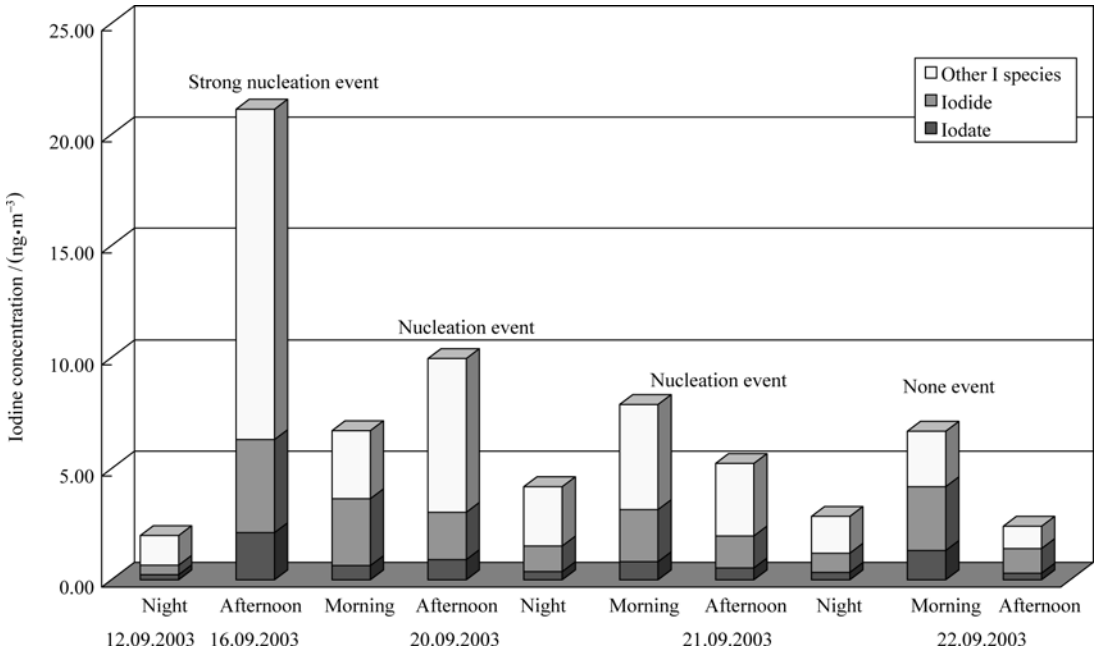


Fig. 6 Typical concentrations of iodine species in PM2.5 during the BIOFLUX campaign

Iodate is not the only iodine species that is permanently removed to the aerosol phase. If the rate of iodate formation is fast with respect to iodine deposition fluxes, iodate would be expected to dominate iodine speciation in deposition. Recent work on the iodine speciation in both rain and aerosol implied that rates of iodate formation and iodide volatilization through reaction with hypohalous acids are relatively slow [54]. The results presented here may support this implication as well, although the aerosol sampled here was relatively newly formed compared to those of which is deposited. More recent work, which was performed in the open ocean of the Atlantic has obtained similar results and the iodate concentration was even found to be below the detection limit in several samples from the northern hemisphere and could not be detected at all in the southern hemisphere samples. Conversely, iodide, which has been suggested not to reach significant concentrations in seasalt or sulphate aerosol, was present at detectable levels in all samples and even at higher concentrations than iodate [55]. These results might raise serious questions about current understanding of aerosol iodine chemistry in the marine atmosphere.

3.3 Seaweed-chamber experiments

Two representative types of macro-algae were used for the experiments, i.e., *Fucus Vesiculosus* and *Laminaria Digitata*, which are the most important macroalgae and widely spread in the western coast of Ireland. These macroalgae were then put into the PMMA-made chamber (dimension of 2 m × 1 m × 1 m) together with several liters of seawater to keep them alive. To measure the gaseous iodine species, chamber air was sampled and measured using the developed methods for iodine species analysis. However, only gaseous elemental iodine in the seaweed-chamber experiments was quantified using the denuder sampling technique followed by the ICP-MS detection.

Regardless of the species of seaweeds found in the chamber, nanoparticles were formed in the chamber as soon as the chamber was covered. Size distribution measurements with nano-SMPS and ELPI from the chamber experiments showed that the concentration of these newly formed particles reached up to 4×10^6 cm^{-3}. These nanometer-particles grew very rapidly to 0.5 μm size in

diameter in less than 10 minutes. As particles grew towards the larger size, nanoparticles were formed again, and then followed the previous growth patterns, showing an evolution of size modes in wave types. These wave-like particle formation and growth pattern lasted until sunset, even some minutes after the sun set. No new particles were formed during night-time without solar radiation. Though it was not as strong as the first day, nanoparticles were formed again early in the morning of the experiment day as soon as the sun rose. Therefore, these seaweed experiments clearly showed that particles can be formed quite efficiently from the nucleation of biogenically emitted gases even when there is a small amount of solar radiation available [53].

Figure 7a shows the relation between the amount of seaweeds and the I_2 (g) concentration. Molecular iodine concentrations were found to have positive correlation with the seaweeds mass in the chamber, indicating kelps are one of the emission sources of elemental iodine. If combining the amount and exposed surface of the macroalgae and total air flow in the chamber, it was estimated that the emission rates of iodine from those kelps are: for *L. digitata*, 0.019~0.022 ng/min/kg; for *F. vesiculosus*, 0.025~0.029 ng/min/kg.

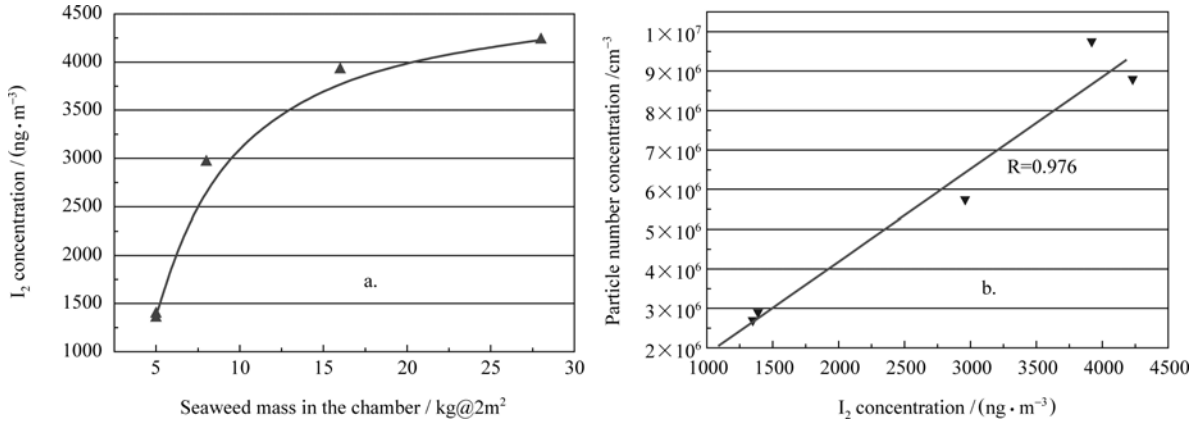


Fig. 7 Relations between, (**a**) sea weeds amount and I_2(g) concentration(**b**) I_2(g) and steady state nano-particle concentration

The relation between gaseous I_2 concentration and the steady-state nanometer-particle concentration in the chamber is shown in Fig. 7b. As can be seen, during the pseudo-steady state particle formation, nanometer-particle concentrations (data acquired from a Scanning Mobility Particle Sizer for nano-particles at the same time) were also found to have a linear correlation ($R = 0.976$) with elemental iodine in the gas phase of the seaweed chamber, clearly indicating that gaseous I_2 is one of the important precursors of the new particle formation in the coastal atmosphere, although the data set are relatively limited. Still, due to the failure of VOIs quantification in the seaweed-chamber experiment, the effects of new particle formation by the VOIs could not be identified in the experiments. The question of whether I_2 or VOIs are more important as precursors that have more significant effects on the nanometer-particle formation, cannot be answered in these experiments so far. More experiments and deeper knowledge are required to fully interpret the whole chain from gas-to-particle conversion.

First results of the seaweed-chamber experiment have proved that gaseous elemental iodine can be emitted by the two types of macroalgae investigated and gaseous I_2 is one of the important precursors that lead to new particle formation in the presence of solar light in the ambient air at the coastal tidal area. However, so far the phenomenon of particle formation linked to gaseous I_2 emission have not been observed and proved experimentally at the open ocean surface where there would not be plenty of algae exposed to the atmosphere directly. Nevertheless, even if these aerosol nucleations occur merely at the coastal area at low tide and under solar radiation, those natural new particles formed in the global scale would still be an appreciable amount, which might grow sequentially and lead to Cloud Condensation Nuclei (CCN) [3].

4 Conclusions

For the first time, in-situ elemental iodine was determined in the gas phase of the coastal atmosphere in west Ireland at certain hot-spots of seaweed population, showing that the concentrations of I_2 were in the range of 0~1.6 ng·L^{-1} . The seaweed-chamber experiments performed at the field research station showed that the I_2 emission rate from algae was in the range of 0.019~0.022 ng/min/kg at 2 m^2 exposed surface area. And during the pseudo-steady state particle formation, nanometer-particle concentrations were found to have a linear correlation with elemental iodine in the gas phase of the seaweed chamber, indicating that gaseous I_2 is one of the important precursors of the new ultrafine particle formation in the coastal atmosphere.

Iodine contents in particle phase were measured in both field campaigns at and around the Mace Head Atmospheric Research Station located in the western coast of Ireland. Total iodine concentrations were found to be in the range of 1.0~21.0 ng·m^{-3} in the PM2.5 samples, which had a significant correlation to the nanometer-particle number

concentrations and to the strength of the aerosol nucleation events observed in the atmosphere. The particulate iodine species analysis indicates that iodide contents are usually higher than those of iodate in all samples, with a ratio of about 2~5:1. The ratio of water-soluble (iodate+iodide) and non-water soluble species (probably iodine oxides and organic iodine compounds) was observed to be in the range of 1:1 to 1:2. It appears that higher concentrated water-insoluble species, as the products of the photolysis from the gas phase into the particle phase, could be obtained in those samples taken during the nucleation events. Iodine oxides are suggested to be primary in the non-water soluble species. However, further laboratory experiments and field measurements have to be done in the future to discover more knowledge, in order to completely understand the role of iodine compounds in the aerosol nucleation and particle growth process in the coastal atmosphere.

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