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Observations of I₂ at a remote marine site

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Abstract. Inorganic iodine plays a significant role in the photochemistry of the marine boundary layer, but the sources and cycling of iodine are not well understood. We report the first I₂ observations in marine air that is not impacted by coastal macroalgal emissions or sea ice chemistry. The data clearly demonstrate that the very high I₂ levels previously reported for coastal air are not representative of open ocean conditions. In this study, gas phase I₂ was measured at the Cape Verde Atmospheric Observatory, a semi-remote site in the eastern tropical Atlantic, using atmospheric pressure chemical ionization tandem mass spectrometry. Atmospheric I₂ levels typically increased beginning at sunset, leveled off after midnight, and then rapidly decreased at sunrise. There was also a smaller midday maximum in I₂ that was probably caused by a measurement artifact. Ambient I₂ mixing ratios ranged from <0.02–0.6 pmol mol⁻¹ in May 2007 and <0.03–1.67 pmol mol⁻¹ in May 2009. The sea-air flux implied by the nighttime buildup of I₂ is too small to explain the observed daytime IO levels at this site. Iodocarbon measurements made in this region previously are also insufficient to explain the observed 1–2 pmol mol⁻¹ of daytime IO. The observations imply the existence of an unknown daytime source of gas phase inorganic iodine. Carpenter et al. (2013) recently proposed that sea surface emissions of HOI are several times larger than the flux of I₂. Such a flux could account for both the nighttime I₂ and the daytime IO observations.

1 Introduction

Iodine in the marine atmosphere is ultimately derived from the iodide, iodate, and organically bound iodine contained in seawater. Iodine emitted from the sea surface undergoes rapid photochemical transformations involving both gas phase and heterogeneous reactions (Vogt et al., 1999; von Glasow, 2003; Saiz-Lopez et al., 2008). Iodine chemistry can potentially influence climate through the catalytic destruction of tropospheric ozone and through the formation of aerosols, but the mechanisms and magnitudes of these processes are not fully understood. Marine iodine chemistry also impacts human health. The emissions, atmospheric transport, and deposition of marine iodine to the land surface influences the availability of this essential nutrient (Johnson, 2003, and references therein). Reactive forms of inorganic iodine may contribute to the conversion of elemental mercury to bioavailable oxidized states, posing a hazard to human and ecosystem health (Saiz-Lopez et al., 2008; Raofie et al., 2008).

Iodine can be emitted from the sea surface in several different forms. It has been known for some time that O₃ deposited to the sea surface can react with I⁻ in the surface seawater to release I₂. Rates of I₂ release from this process have been estimated at around 2 × 10⁶ molec cm⁻² s⁻¹, or 2.9 nmol m⁻² d⁻¹ (Garland and Curtis, 1981). More recent laboratory and modeling work has considered the release of HOI from this process as well, yielding estimates of daytime fluxes of 100 nmol m⁻² d⁻¹ and 10 nmol m⁻² d⁻¹ for HOI and I₂, respectively (Carpenter et al., 2013). That represents an increase of roughly 20 times the inorganic I

atom flux relative to what was previously thought. Because I⁻ is ubiquitous in the surface ocean, this process must occur globally and could therefore account for a flux of elemental I on the order of 2 Tg y⁻¹. Certain species of coastal macroalgae directly emit copious quantities of I₂, particularly while under oxidative stress (Saiz-Lopez and Plane, 2004; Dixneuf et al., 2009; McFiggans et al., 2004; Palmer et al., 2005). In the open ocean, planktonic algae may also release I₂, but the open ocean emission rate is not known (Amachi et al., 2000; Jones et al., 2010). Organoiodide compounds such as CH₂I₂ and CHClI₂ are also emitted from the sea surface. These gases are formed in seawater as a result of the interaction of HOI and/or I₂ with dissolved organic matter, likely as a result of ozonolysis (Martino et al., 2009). These compounds are rapidly photolyzed, in some cases releasing I atoms on timescales of minutes in the daytime marine boundary layer (Martino et al., 2005). The most abundant and longest-lived organoiodide compound, methyl iodide, has a photolysis lifetime of several days. The global I release attributed to organoiodides is on the order of 0.4–1 Tg I yr⁻¹, with CH₃I dominating (Jones et al., 2010, and references therein). A detailed review of marine iodine gas production mechanisms is found in Saiz-Lopez et al. (2012).

Once formed in air, iodine atoms can initiate catalytic ozone destruction cycles such as those below:

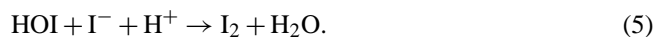


Net:



Catalytic destruction of tropospheric ozone by iodine is efficient in part because iodine radicals are relatively unreactive with organic trace gases.

Sea salt aerosols are thought to play a role in I_x cycling in marine air. I⁻ present in aerosols can be oxidized to the volatile forms ICl, IBr, and I₂ via reaction with the hypohalous acids HOCl, HOBr, or HOI. The hypohalous acids are generated by gas phase daytime photochemistry (e.g. Rxns 1-2) and can enter aerosols to react with I⁻:



Iodine radicals can also self-react to form iodine oxides such as I₂O₄ and other larger iodine oxide clusters (McFiggans et al., 2004; Saiz-Lopez et al., 2006). If iodine levels are sufficiently high, the formation of iodine oxides leads to rapid particle nucleation. IO_x-driven nucleation events have been observed downwind of I₂-emitting macroalgae beds. These events contribute to aerosol number and can potentially influence cloud properties in coastal regions (Saunders et al., 2010; Mahajan et al., 2010).

Relatively little is known about the emissions and cycling of iodine over the open oceans, because there are few observations in marine air that are not influenced by macroalgal

emissions. Long path DOAS measurements of IO on Cape Verde found daytime IO levels of 1–2 ppt, which are sufficient to contribute significantly to ozone destruction (Read et al., 2008). The source of reactive iodine at CVAO remains an open question. Jones et al. (2010) measured air-sea dihalomethane fluxes in open ocean and upwelling Atlantic waters near Cape Verde. They observed iodocarbons in these waters at levels too low to account for the observed IO at CVAO and proposed that a large I₂ flux might account for the discrepancy. Using a 1D box model, they incorporated a constant I₂ flux large enough to achieve the IO levels observed at Cape Verde. This resulted in nighttime I₂ levels of up to 7 pmol mol⁻¹. Mahajan et al. (2010) used the same observations and a different vertically resolved model with an I₂ source which was allowed to vary. They concluded that an additional MBL source of I₂ may be required to explain the observed IO levels, but that the source may have a strong diel cycle (Mahajan et al., 2010). Mahajan et al. (2012) observed slant column IO densities corresponding to roughly 1 pmol mol⁻¹ during shipboard measurements in the eastern Pacific.

In this manuscript we report nighttime levels of gas phase I₂ at Cape Verde during measurement campaigns over three weeks in May–June 2007 and one week in May 2009. The only other reported observations of I₂ in marine air have been conducted in regions influenced by emissions from coastal macroalgae or by I₂ production on sea ice surfaces (Finley and Saltzman, 2008; Saiz-Lopez et al., 2012; Atkinson et al., 2012). These observations provide estimates of I₂ levels and production rates that are more representative of open ocean conditions than previous studies.

2 Study site and observational methods

2.1 Setting and ancillary observations

The field site was the Cape Verde Atmospheric Observatory (CVAO), located at 16.864° N, 24.867° W on the island of São Vicente. The site is situated about 50 m from a northeast facing coastline, about 10 m above sea level. The island is volcanic in origin and has a steep continental shelf. Meteorological conditions were very similar in the two study years, 2007 and 2009. Winds were consistently onshore during both years, and 15 min averaged windspeeds were 7.67 ± 1.47 m s⁻¹ (1 std dev) with a 3.6–10.4 range in 2009 and 6.17 ± 1.35 (2.2–8.7 range) in 2007. The planetary boundary layer at the site ranges from about 300 to 1500 m with no clear seasonal or diel pattern (Carpenter et al., 2011). NO_x (NO + NO₂) was measured by chemiluminescence at a height of 3 m above the ground. The instrument had a detection limit of <14 ppt for reported 15 min means. NO_x levels were typically below 25 ppt in 2007, without a discernible diel pattern. In 2009 the daytime NO_x levels were higher and had a distinct diel cycle, with a typical midday NO₂ maximum

of 40–50 pmol mol⁻¹ and a late afternoon NO maximum of about 15 pmol mol⁻¹. The 2009 NO_x measurements may have been influenced by the site diesel generator. The generator was located about 100 m away from the site in 2007, but it was moved directly adjacent to the downwind side of the site in 2009. O₃ was measured at 3 m by UV absorption. O₃ was 33.4 ± 5.3 nmol mol⁻¹ in 2007 and 36.2 ± 5.0 nmol mol⁻¹ in 2009 (mean ± 1 std. dev.). Lee et al. (2010) give an overview of NO_x and O₃ observations at the site. See Carpenter et al. (2011) for a thorough site overview.

2.2 I₂ detection by chemical ionization mass spectrometry

I₂ detection was carried out by chemical ionization triple quadrupole mass spectrometry using a modified Thermo TSQ Quantum instrument, with procedures similar to those in previously published studies of Cl₂, Br₂, and I₂ (Lawler et al., 2009; Finley and Saltzman, 2008). The mass spectrometer was fitted with a ⁶³Ni beta-emitting source, and ambient I₂ molecules were ionized to I₂⁻. The I₂⁻ ions were mass-selected in the first quadrupole (Q1), then dissociated by collision with Ar in Q2 (20 eV) to form I⁻, which was in turn mass selected (Q3) and detected by an electron multiplier after impaction on a dynode. Mass transitions for ICl⁻ → Cl⁻ and IBr⁻ → Br⁻ were also monitored.

The instrument background signal was assessed every hour by sampling ambient air which was scrubbed of I₂. The scrubber was a carbonate-coated plug of glass wool. Automated pneumatic gate valves controlled whether the instrument sampled scrubbed air or unmodified ambient air. This type of scrubber removes I₂ with high efficiency (~99%) when fresh but degrades after a few weeks of use. There was no evidence that the scrubber degraded over the campaign.

An I₂ gas standard was generated by flowing N₂ over an I₂ permeation tube in a temperature-controlled PFA housing. This I₂/N₂ flow was subsampled and diluted with additional N₂ to a final sampled mixing ratio of 2–16 pmol mol⁻¹ in the method of Gallagher et al. (1997). I₂ in the dilution system was only exposed to PFA and PTFE surfaces. The standard gas flowed continuously through a length of PFA tubing up to a pneumatic PTFE valve near the top of the inlet. The valve was kept near the inlet to minimize equilibration time in the tubing. The outdoor tubing was shielded from radiation by opaque insulation to prevent photolysis of the standard I₂. During regular ambient sampling intervals, the I₂ standard was routed to a container of scrubber material. The output of the I₂ permeation tube was gravimetrically calibrated in the laboratory after the campaign. There were no standards for ICl or IBr.

Instrument sensitivity for I₂ was assessed by performing multipoint calibrations and one-point standard additions. Sensitivity was assumed to vary linearly between calibrations and standard additions. In both 2007 and 2009, the one-point I₂ standards were added on a 4 hour schedule on every

third day of measurements. Multipoint calibrations were run less frequently but consistently showed linear instrument response in the range of observed I₂. For these calibrations and single point standards, I₂ in N₂ was added near the front of the inlet.

2.3 Sample inlets

The air sampling inlet used in 2007 is the same as that described previously for Cl₂ observations made at this site (Lawler et al., 2009). The setup is illustrated in Fig. 1. Ambient air was drawn through a nominal 2 inch (5.1 cm ID) acrylonitrile-butadiene-styrene (ABS) pipe from a height of 3 m. The flow in this pipe was dynamically controlled at 63 LPM (STP: 273 K, 1 atm) using a butterfly valve (MKS) and mass flow meter (TSI), and PID controller (MKS).

A longer inlet was used for the 2009 study. Air was drawn from a height of 8 m above the ground into a nominal 6 inch (15.24 cm ID) ABS sample pipe at 130 LPM (STP). This flow was controlled using a differential pressure flow sensor, butterfly valve, and PID controller (Omega Engineering, MKS instruments). The flow measurement was calibrated against a mass flow meter (TSI) at the end of the measurements. A 63 LPM subsample was drawn from the center of the main flow through a coaxial nominal 2 inch (5.1 cm ID) ABS pipe, with the mass flow control system used in the 2007 deployment. The mass spectrometer sampled 1.3 LPM from the center of the 2 inch pipe. During 2009, scrubbed air was introduced directly into the 2 inch pipe at the base of the large 8 m inlet (Fig. 1).

There were minor differences in the standardization procedure between the two studies. I₂ gas standards were added in scrubbed air in 2007, and in ambient air in 2009. No significant difference in sensitivity has been found for scrubbed vs. unscrubbed air. The sensitivity was assumed to vary linearly between one-point standards, except for obvious step changes in sensitivity.

3 Results

3.1 May–June 2007

Measured I₂ ranged from <0.02–0.6 pmol mol⁻¹ with a regular diel pattern (Fig. 2). I₂ climbed over the course of the night and reached its highest values either shortly before dawn or a couple of hours before. I₂ levels always dropped dramatically at dawn, but usually remained at detectable levels. Surprisingly, I₂ levels increased during the daytime, reaching a peak around midday and then declining again before nighttime (see Sect. 4.3 regarding a daytime artifact). I₂ levels did not covary with O₃ levels. The daytime “blank” I₂ signals (scrubbed air) showed large I₂ signals that closely tracked the daytime I₂ increase, but blanks were consistently low and fairly constant over the night (Fig. 4).

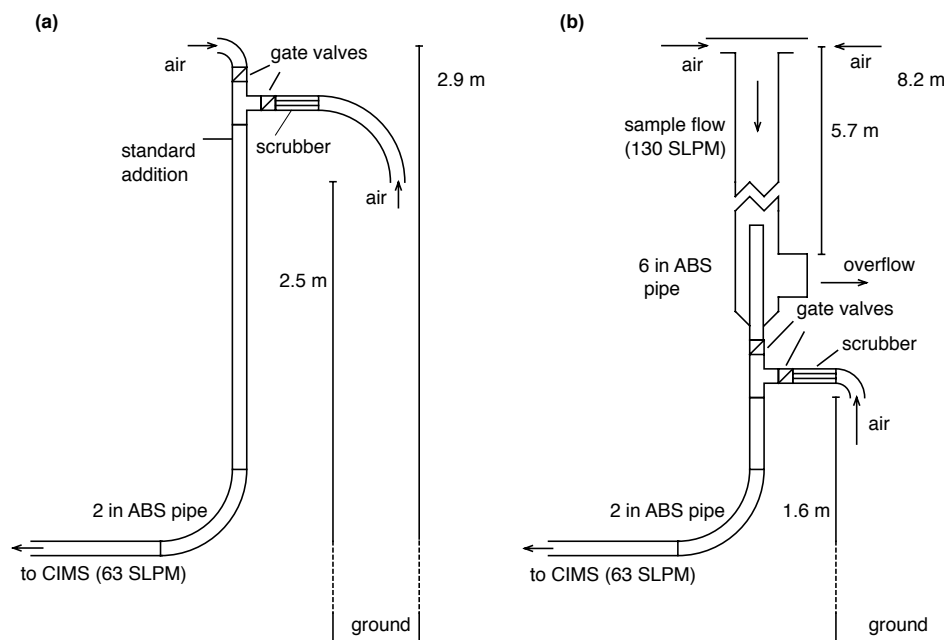


Fig. 1. (a) Sampling inlet used May–June 2007. (b) Sampling inlet used May 2009.

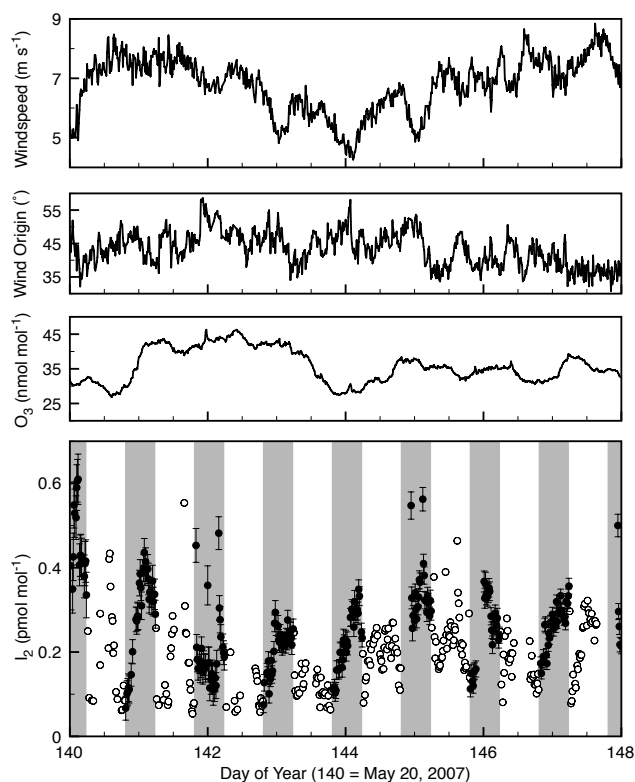


Fig. 2. Wind speed, wind direction, O₃ mixing ratios, and I₂ mixing ratios at CVAO during May 2007 time at CVAO. I₂ error bars are one standard error. Open circles are daytime points which likely include a measurement artifact and should be considered upper limits. The dark vertical bars represent nighttime hours.

The ICl sample and blank signals showed similar diel cycles and were statistically indistinguishable from one another. The two ICl mass transitions observed (162 → 35 and 164 → 37) had a sample signal ratio close to 1, rather than the 3 ratio expected for the two chlorine isotopes. These observations indicate that ICl was not the dominant species observed at these transitions. The sample and blank signals for IBr also matched one another, and IBr remained below detection. The actual detection limits for ICl and IBr were not assessed, but detection limits for Cl₂, BrCl, Br₂, and I₂ for this instrument are in the range of 0.1–2 pmol mol⁻¹, and ICl and IBr detection limits are also expected to be in this range.

3.2 May 2009

The 2009 I₂ levels were slightly higher than those in 2007, ranging from <0.03–1.67 pmol mol⁻¹ over one week of observations (Fig. 3). The diurnal pattern was very similar to that in 2007, with a nighttime maximum and a smaller daytime peak (see Sect. 4.3 regarding a daytime artifact). There was some day-to-day variability in the absolute levels, with the highest levels occurring late in the night on days 141 and 142. Late on day 141 there was a sudden reduction in windspeed and shift to more northerly flow. Unfortunately the meteorological instruments were not operating on day 142, when the very highest I₂ levels were measured. There was some difference in the instrument response to scrubbed air between the two deployments. In the 2009 deployment, I₂ blank signals remained low throughout the day, and did not exhibit the daytime peak observed in the ambient measurements (Fig. 4).

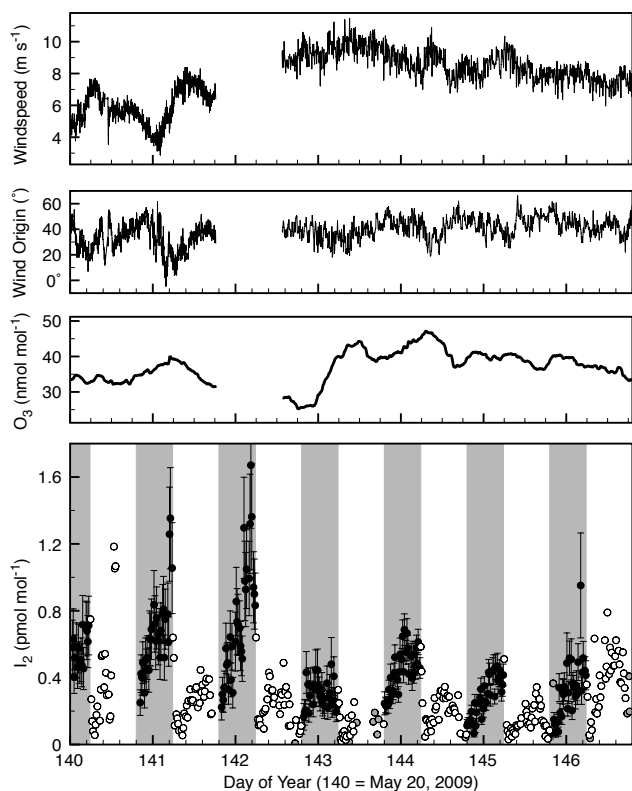


Fig. 3. Wind speed, wind direction, O₃ mixing ratios, and I₂ mixing ratios at CVAO during one week in May 2009. I₂ error bars are one standard error. Open circles are daytime points which likely include a measurement artifact and should be considered upper limits. Grey filled circles are points below the detection limit. The dark vertical bars represent nighttime hours. The gap in non-I₂ data about day 142 was due to power loss to some of the instruments.

3.3 Macroalgal emissions

This is the first study to examine the behavior of atmospheric I₂ in an environment not impacted by iodine-emitting macroalgae. To confirm this, macroalgae were collected from shallow near-site tidal pools and held before the instrument inlet in 2007. No enhancement in I₂ levels was observed for any of the few species found, but they were not positively identified. Large brown kelp (*Laminaria*) were not observed at the site. These are the dominant iodine emitters at well-studied North Atlantic coastal sites (McFiggans et al., 2004; Saiz-Lopez and Plane, 2004; Jones et al., 2009). A container of coastal surface seawater held before the inlet also resulted in no enhancement of I₂ signal. These observations suggest that the I₂ levels observed are representative of regional oceanic emissions and not influenced by strong local upwind coastal sources.

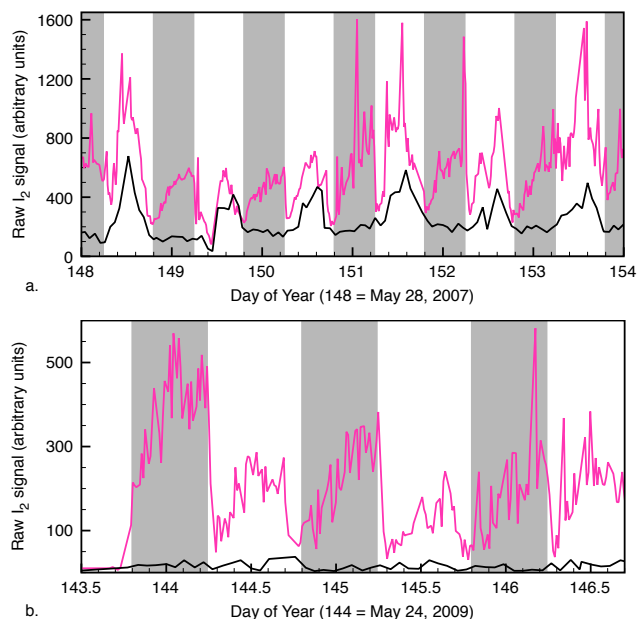


Fig. 4. Raw mass spectrometer I₂ signals from ambient air (magenta) and blank scrubbed air (black) during May 2007 (a) and May 2009 (b). The correlation of daytime I₂ signals in ambient air signal and blank air during May 2007 is evidence that some of the daytime I₂ is an artifact that is likely produced on the inlet walls. In 2009, this correlation was not apparent, most likely due to a change in inlet configuration. Gray shaded areas are nighttime hours.

4 Discussion

4.1 Nighttime I₂ emission rates

At night, I₂ mixing ratios increase steadily after dusk, then level off around midnight (Fig. 5). The Cape Verde observations indicate an average nighttime increase of about 0.17 pmol mol⁻¹. Chemical loss of I₂ is expected to be minimal. I₂ can be lost via NO₃ reaction, but DOAS observations have indicated that NO₃ mixing ratios are extremely low at this site (Mahajan et al., 2010). Assuming the sea surface is the source and that there are no atmospheric losses, this is a rate of roughly 0.5 pmol mol⁻¹ d⁻¹ over the period of constant increase. The rate of mixing ratio increase corresponds to a sea-to-air flux of 30 nmol m⁻² d⁻¹, assuming that emissions are diluted into a 1000 m boundary layer. This is about three times the rate estimated in the Carpenter et al. (2013) study.

4.2 I₂ as a source for daytime IO

Midday maximum IO levels ranging from 1–2 pmol mol⁻¹ were observed by long path DOAS at the CVAO site during May 2007 (Read et al., 2008). Mahajan et al. (2010) and Jones et al. (2010) proposed sea surface emissions of I₂ as the principal source of iodine at Cape Verde because air/sea fluxes of organoiodide compounds in the eastern

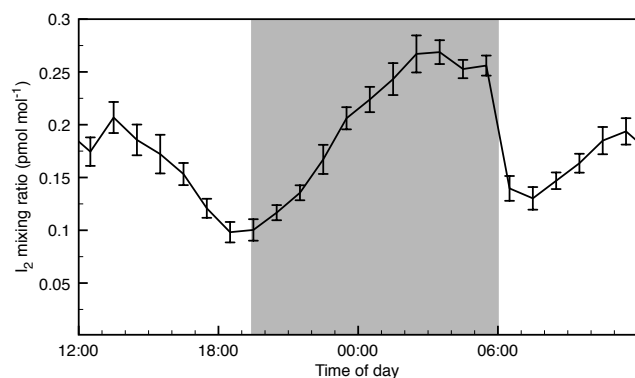


Fig. 5. Mean hourly binned I₂ mixing ratios measured over three weeks at CVAO in 2007. Error bars are one standard error. Shaded area represents nighttime hours. The mean observed solar cycle over the measurement period was used to assign sunrise and sunset.

tropical Atlantic were considerably lower than required to account for the observed IO. Model simulations showed that a constant I₂ flux of 170–320 nmol I₂ m⁻² d⁻¹ was needed to explain the observed IO (Jones et al., 2010). However, this scenario also led to a nighttime maximum of approximately 7 pmol mol⁻¹ of I₂ and a resultant spike in IO at sunrise, neither of which are evident in the Cape Verde data. Our I₂ observations do not support such a large nighttime source. Mahajan et al. (2010) implemented a diurnally varying I₂ source tuned to best replicate the observed IO levels. This source varied with solar flux, from zero at night to a midday maximum of 800 nmol I₂ m⁻² d⁻¹. That scenario yields nighttime I₂ and daytime IO levels that are more consistent with observations.

4.3 Observations of daytime I₂: positive artifact

Midday I₂ levels of 0.2 pmol mol⁻¹ are much larger than would be predicted by the nocturnal emission rate. The noon photolytic lifetime of I₂ under CVAO conditions is roughly 5 s. An I₂ flux large enough to support these levels would result in higher IO levels than observed (see Modeling section below).

The possibility exists that the daytime I₂ data were influenced by a positive analytical interference. Previous studies have observed the production of Br₂ from HOBr and HOCl even on relatively clean inlets, apparently without formation of BrCl (Neuman et al., 2010; Lawler et al., 2011). By analogy, inlet I₂ production without concomitant ICl or IBr production may be possible. In this study, the daytime blank behavior was different between the 2007 and 2009 deployments, likely as a result of changes in inlet configuration. In 2007, the blank was assessed by exposing scrubbed ambient air to the same 3 m long, 2 inch ID flow path as the ambient air sample. In this configuration, daytime blank I₂ signals tracked the ambient signals (see Sect. 3.1). In 2009, scrubbed air was exposed only to the last stage of the inlet, potentially

a cleaner surface than the inlet entrance. The blank was much lower and did not track the ambient levels in the 2009 deployment.

We hypothesize that the daytime I₂ is generated via heterogeneous reactions of a photochemically produced oxidant with I⁻ on the walls of the instrument inlet. This would require the oxidant to have the following characteristics; (1) to occur at levels of several pmol mol⁻¹ (or greater), comparable to the measured I₂, (2) to be present at significant levels only during daytime, and (3) to be transmitted at least partially through the carbonate scrubber. The first consideration eliminates OH and the second eliminates O₃ as likely candidates. The hypohalous acids HOI, HOBr, and HOCl are photochemically generated daytime oxidants that are present in air at pmol mol⁻¹ levels, and are capable of oxidizing I⁻. HOI can produce I₂ directly upon reaction with I⁻ in solution, e.g. (Allen and Keefer, 1955; Vogt et al., 1999). HOBr and HOCl might be expected to initially form IBr and ICl from reaction with I⁻, and further reaction would be required to form I₂. However, the mixed halogens were not observed in this study.

Given that two different inlet configurations were used, it is not surprising that different blank behavior was observed in the two deployments. However, it is surprising that both configurations yielded similar blank-corrected daytime I₂ mixing ratios and a similar pattern of variability with a pronounced midday maximum. Further work is needed to fully understand the origin of the daytime I₂ signals.

5 Modeling

Four model simulations (BASE, FLAT, PHOTO, and HOI, as defined below) were conducted to investigate the possible sources of reactive iodine at Cape Verde, given the constraints of observed daytime IO and nighttime I₂ (Fig. 7). The one-dimensional chemical transport model THAMO (Tropospheric HALogen chemistry MOdel) was used for these simulations (Saiz-Lopez et al., 2008). The model includes gas phase reactive halogen, HO_x, NO_x, and hydrocarbon chemistry, including a module treating ultrafine particle formation by coagulation of iodine oxides. It also accounts for recycling of reactive halogens through marine aerosols. In the past, this model has been used to study IO, HO_x, and HCHO observations at Cape Verde (Mahajan et al., 2010, 2011). The model reaction scheme and structure have been described in detail previously (Mahajan et al., 2010; Saiz-Lopez et al., 2008). For all the simulations, the model was constrained with observations of O₃ (Carpenter et al., 2011; Lee et al., 2010), HO_x (Whalley et al., 2010), NO_x (Lee et al., 2009), CH₄ and HCHO (Mahajan et al., 2011), and NMHCs (Read et al., 2009) from CVAO. The vertical mixing was calculated using the measured wind speed (Carpenter et al., 2010), using a description detailed by Saiz-Lopez et al. (2008). The model was allowed to run for ten days, usually reaching steady state

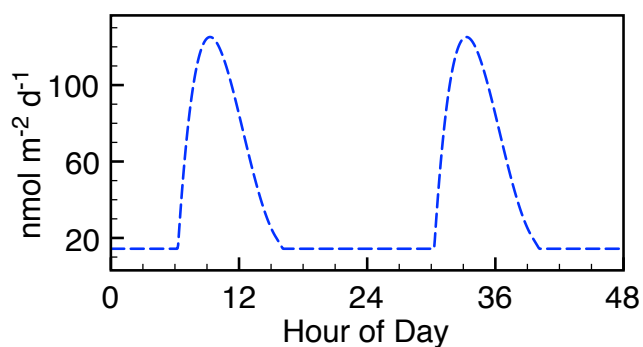


Fig. 6. Flux of I₂ added in PHOTO model run.

in 3–4 days. Day 9 of each simulation was used for comparisons between individual scenarios.

In the BASE simulation, standard model chemistry was employed and average sea-air fluxes of halocarbons measured by Jones et al. (2010) near the Cape Verde site were included: CH₂I₂ (13.0 nmol m² d⁻¹), CH₂IBr (10.9 nmol m² d⁻¹), CH₂ICl (16.2 nmol m² d⁻¹), CH₃I (48.5 nmol m² d⁻¹), C₂H₅I (4.1 nmol m² d⁻¹), and 1-C₃H₇I (0.9 nmol m² d⁻¹). This simulation significantly underpredicts both IO and I₂ observations made at the site (Fig. 7). This result implies that there are additional important sources of reactive iodine in this environment, or that models currently underestimate the rate of aerosol recycling of reactive iodine.

In the FLAT simulation, a constant I₂ flux of 14.3 nmol m² d⁻¹ from the ocean surface was added to the MBL, in addition to the halocarbon flux already present. This was intended to represent an I₂ source from O₃ deposition to the ocean surface, or a hypothetical biological background source. The flux was tuned to achieve nighttime I₂ levels comparable to observations (~0.2–0.3 pmol mol⁻¹). The I₂ profile matched the nighttime I₂ observations well, but the flat daytime I₂ source was not sufficient to achieve the mean IO levels observed during the day (Fig. 7). Jones et al. (2010) found that a constant I₂ flux of at least 170 nmol m² d⁻¹ would be required to achieve observed IO levels. The leveling off of I₂ overnight in the model is due to mixing. Modeled IO was ~0.8 pmol mol⁻¹ during the daytime, compared to observed levels of ~1.5 pmol mol⁻¹. The modeled IO diel profile in this and the other cases shows prominent peaks around sunrise and sunset. These are an artifact resulting from the problem of treating highly photolyzable species in a model with discrete time steps. Daytime I₂ levels remained very low, peaking at 0.02 pmol mol⁻¹.

In the PHOTO simulation, the prescribed flux of I₂ was retained for the nighttime, and an additional I₂ flux was included in the daytime. This was intended to simulate a light-dependent I₂ source, which could be due to photochemical reactions in aerosols or at the sea surface, or due to day-

time biological production in the sea surface. The daytime source was tuned to achieve average observed daytime IO levels. The total prescribed I₂ flux reached a maximum of 125 nmol m⁻² d⁻¹, almost a tenfold increase compared to the nighttime flux necessary to reproduce the observed I₂. This maximum flux was reached at about 09:20 LT and was set back to the constant (nighttime) flux by shortly after 16:00 LT (Fig. 6). For comparison, Mahajan et al. (2010) used a time-varying flux which peaked at 818 nmol m⁻² d⁻¹ and was zero at night to fit the same IO observations. The strong midday flux results in much higher midday IO levels. This simulation matches the daytime IO and nighttime I₂ observations reasonably well and predicts a midmorning I₂ peak (Fig. 7). The model still does not reproduce daytime I₂ levels as high as observed, particularly in the afternoon. The model predicts midmorning I₂ levels over half as large as observed. Reproduction of the observed afternoon I₂ levels using an extra source of I₂ from the surface would result in a late evening peak in IO. Such a peak was not observed. To summarize, the daytime IO and nighttime I₂ may be explained by the addition of a time-varying surface I₂ source, but the observed daytime IO and I₂ cannot simultaneously be explained simply by an additional source. We think this lack of agreement is most likely explained by the positive measurement artifact in the daytime I₂.

In the HOI simulation, sea-air fluxes of both HOI and I₂ were prescribed without modification or optimization after Carpenter et al. (2013), where daytime fluxes were roughly 10 nmol I₂ m⁻² d⁻¹ and 100 nmol HOI m⁻² d⁻¹. Carpenter et al. (2013) showed that THAMO simulations using these fluxes yielded good agreement with IO observations at CVAO, but I₂ observations were not available in that study. Their sea-air fluxes of HOI are highest at night and the I₂ fluxes are highest during the day due to the different air-sea gradients of the two species between night and day. In the daytime, I₂ levels are extremely low due to rapid photolysis and no known gas phase source. HOI, on the other hand, photolyzes more slowly and can be formed in the gas phase. HOI is also thought to have a significant aerosol sink during the nighttime, as opposed to I₂. The HOI simulation does a good job representing both the daytime IO and the nighttime I₂ mixing ratios (Fig. 7). This run resulted in slightly higher daytime IO and slightly lower nighttime I₂ than the PHOTO simulation. This simulation does not predict a morning I₂ increase. The HOI case predicts the highest levels of ICl of all the runs, up to 6 pmol mol⁻¹.

6 Discussion: I_x sources and halogen cycling

The modeling scenarios which best represent the observed inorganic iodine at CVAO are the PHOTO and HOI cases. The laboratory observations of HOI production from seawater ozonolysis provide a strong case that this process should be considered in MBL halogen chemistry. The good

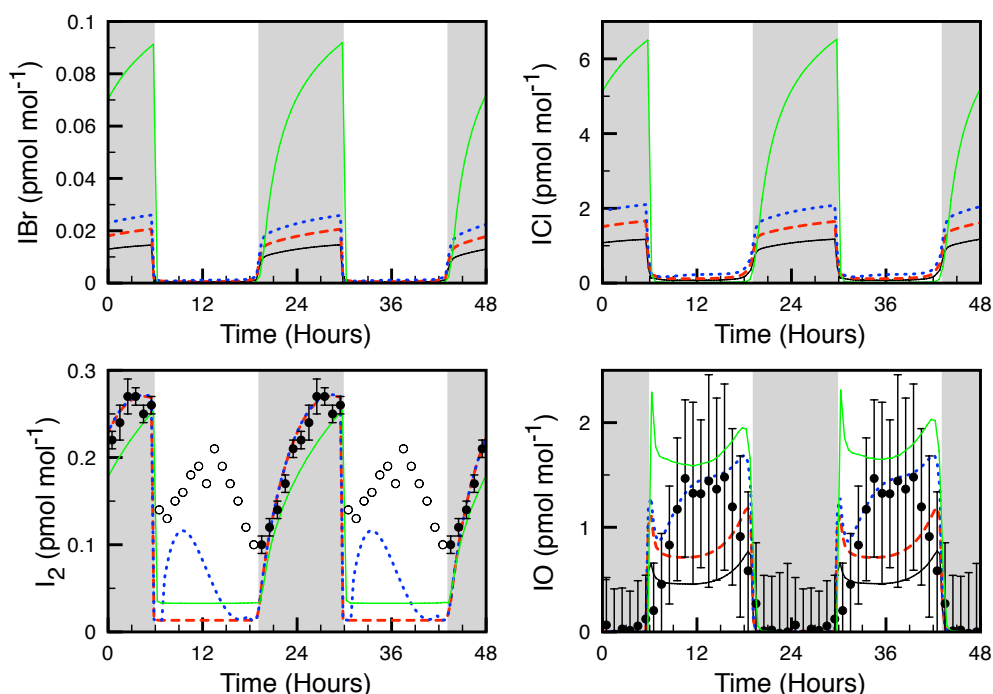


Fig. 7. THAMO box model results for four simulations. BASE (halocarbons only): black solid line. FLAT (constant I₂ flux): red dashed line. PHOTO (enhanced daytime I₂ source): dotted blue line. HOI (added flux of HOI): green solid line. Average I₂ and IO observations plotted as circles with one standard error bars. The upper limit daytime I₂ observations are plotted as open circles. Dark shading represents nighttime hours.

agreement between the lab-estimated fluxes and the observational data supports the idea that sea surface-derived HOI is the major source of gas phase inorganic iodine at CVAO. This is likely true for all ocean regions not impacted by strong local emissions such as macroalgae beds. The photolytic I₂ source considered in the PHOTO case would require novel chemistry and complex kinetics to generate the peculiar diurnal cycle required (Fig. 6). While this remains a possibility, the HOI flux is clearly a more straightforward explanation. Similarly, a direct biological source of I₂ is not precluded by the observations, but it would also require very strong diurnal variability. The seawater ozonolysis source of HOI appears to be sufficient to explain most of the flux of inorganic I to the atmosphere at this site and is clearly the more straightforward explanation.

Both the PHOTO and HOI cases generate at least 3 pmol mol⁻¹ of ICl at night. This is a consequence of HOI uptake in particles followed by reaction with Cl⁻. ICl was not detected either in 2007 or in 2009, despite monitoring the relevant mass transitions for several days in each case. There is no reason to suspect that the instrument was not similarly sensitive to ICl as to I₂, despite the lack of a specific calibration standard for ICl. Similarly, BrCl has not been observed at CVAO despite evidence for active bromine cycling (Lawler et al., 2009; Read et al., 2008). These observations strongly suggest that current models overpredict the conversion of HOBr and HOI to the interhalogens BrCl and ICl in

aerosols. It remains unclear whether all hypohalous acids (including HOCl) undergo significant losses to organic species in particles, or whether the equilibrium reactions among the various dissolved halogen species need to be reexamined.

7 Conclusions

We report the first MBL I₂ observations in marine air that is not impacted by coastal macroalgal emissions or sea ice chemistry. The data clearly demonstrate that the very high I₂ levels previously reported for coastal air are not representative of open ocean conditions. The very low observed nighttime levels provide an upper bound for I₂ production by reaction of O₃ on the surface ocean in this region. The “dark” processes producing I₂ at night are too slow to explain the levels of IO observed in the daytime, given known iodine recycling mechanisms. The sea-air flux of HOI generated by ozonolysis of seawater and recently proposed by Carpenter et al. (2013) could explain the observations. If this is the case, then IO levels similar to those at CVAO should occur over most of the world oceans. O₃-stimulated release of iodine from the sea surface induces catalytic ozone destruction, limiting the lifetime of O₃ over the oceans. The impacts of this chemistry on the evolution of continental outflow in the marine boundary layer should be investigated further. The apparent lack of significant levels of ICl at CVAO

is a challenge to our understanding of aerosol halogen recycling. This discrepancy should be addressed with laboratory studies of synthetic and natural halide solutions and with well-calibrated field observations.

Supplementary material related to this article is available online at <http://www.atmos-chem-phys.net/14/2669/2014/acp-14-2669-2014-supplement.pdf>.

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