Iodine chemistry in the eastern Pacific marine boundary layer

Juan C. Gómez Martín,1,2 Anoop S. Mahajan,1,6 Timothy D. Hay,1 Cristina Prados-Román,1 Carlos Ordóñez,1,7 Samantha M. MacDonald,2 John M.C. Plane,2 Mar Sorribas,3,8 Manuel Gil,3 J. Francisco Paredes Mora,4 Mario V. Agama Reyes,4 David E. Oram,5 Emma Leedham,5 and Alfonso Saiz-Lopez1

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[1] Observations of gas-phase iodine species were made during a field campaign in the eastern Pacific marine boundary layer (MBL). The Climate and Halogen Reactivity Tropical Experiment (CHARLEX) in the Galápagos Islands, running from September 2010 to present, is the first long-term ground-based study of trace gases in this region. Observations of gas-phase iodine species were made using long-path differential optical absorption spectroscopy (LP-DOAS), multi-axis DOAS (MAX-DOAS), and resonance and off-resonance fluorescence by lamp excitation (ROFLEX). These measurements were supported by ancillary measurements of ozone, nitrogen oxides, and meteorological variables. Selective halocarbon and ultrafine aerosol concentration measurements were also made. MAX-DOAS observations of iodine monoxide (IO) display a weak seasonal variation. The maximum differential slant column density was $3.8 \times 10^{13}$ molecule cm$^{-2}$ (detection limit $\sim 7 \times 10^{12}$ molecule cm$^{-2}$). The seasonal variation of reactive iodine IO$_x$ (= I + IO) is stronger, peaking at 1.6 pptv during the warm season (February–April). This suggests a dependence of the iodine sources on the annual cycle in sea surface temperature, although perturbations by changes in ocean surface iodide concentration and solar radiation are also possible. An observed negative correlation of IO$_x$ with chlorophyll-$a$ indicates a predominance of abiotic sources. The low IO mixing ratios measured (below the LP-DOAS detection limit of 0.9 pptv) are not consistent with satellite observations if IO is confined to the MBL. The IO$_x$ loading is consistent with the observed absence of strong ozone depletion and nucleation events, indicating a small impact of iodine chemistry on these climatically relevant factors in the eastern Pacific MBL.


1. Introduction

[2] The question of a potential climatic relevance of the photo-oxidation of iodine-containing gases released by the ocean into the marine boundary layer (MBL) has attracted considerable attention in the last few years, mainly as a result of accumulating evidence of widespread iodine oceanic sources [see Saiz-Lopez et al., 2012a and references therein]. This debate can be traced back to the seminal modeling work published in 1980 by Chameides and Davis [1980] and has recently gained momentum following the suggestion of a significant regional impact of halogens on O$_3$, NO$_x$, and HO$_x$ in the tropical Atlantic MBL [Read et al., 2008]. Additional impetus has been provided by the proposed participation of iodine in secondary aerosol formation, suggested by frequently observed iodine-driven coastal particle bursts [O’Dowd et al., 2002; Whitehead et al., 2009; Mahajan et al., 2010a].

[3] In Cape Verde (CV), a remote location assumed to be representative of the open ocean tropical MBL, 1–3 pptv (parts per trillion in volume, equivalent to pmol mol$^{-1}$) of iodine and bromine account for about half of the daily photochemical O$_3$ loss [Read et al., 2008]. Since active iodine has also been previously reported at similar or even larger volume mixing ratios (VMRs) in other locations representative of the open ocean environment such as the Canary Islands and Tasmania [Allan et al., 2000], it has...
been suggested that its impact on climatically active trace gases could be widespread and thus the integrated effect significant. On the other hand, Mahajan et al. [2010b] used a model updated with a state-of-the-art nucleation-coagulation code to show that IO VMRs of a few parts per trillion would not be sufficient to sustain nucleation events in the open ocean [Ehn et al., 2010; O’Dowd et al., 2010]; IO VMRs of at least 10 pptv would be required to generate particles which would grow large enough (>20 nm diameter) to have a reasonable chance of becoming cloud condensation nuclei.

In the eastern Pacific, new findings have recently relaunched the discussion on the role of iodine chemistry in the MBL. First are the low ozone levels measured at the Galápagos Islands extending from the MBL throughout the free troposphere [Thompson et al., 2003; Thompson et al., 2011], which cannot be satisfactorily explained by standard photochemistry [Saiz-Lopez et al., 2012b]. Second, the observation of significant column densities of IO over a large region of the eastern Pacific from the satellite-borne instrument SCIAMACHY [Schönhardt et al., 2008; Schönhardt, 2009], which would correspond to VMRs of up to ~20 pptv if the column is confined to the bottom-most 100 m, considering IO is predicted to show a steep gradient in the MBL [Mahajan et al., 2010b]. Such potentially high levels of reactive iodine over the ocean have stimulated new research on its possible sources and their response to changes in key physical oceanic parameters such as sea surface temperature (SST). A number of biological, chemical, and photochemical mechanisms have been proposed to explain the emission of iodine precursors from the ocean surface (for a comprehensive summary of these, see Saiz-Lopez et al. [2012a]). Laboratory and field data exist, linking very short-lived iodocarbons and phytoplankton activity [Snye-Wright et al., 2006; Hill and Manley, 2009; Arnold et al., 2010; Brownell et al., 2010; Lai et al., 2011]. However, there is increasing evidence that biological sources of iodine precursors are not the most significant [Garland and Curtis, 1981; Reeser et al., 2008; Martino et al., 2009; Sakamoto et al., 2009; Mahajan et al., 2012]. Furthermore, it has been shown that iodocarbons are not the major contributor to active iodine in the open ocean MBL but rather inorganic molecules such as I$_2$ [Jones et al., 2010; Mahajan et al., 2010b].

We have recently reported the latitudinal distribution of IO in the eastern Pacific (53°S–48°N), obtained with a ship-based multi-axis differential optical absorption spectroscopy (MAX-DOAS) instrument during the HaloCAST-P cruise in April 2010 [Mahajan et al., 2012]. In this paper, we report on a long-term ground-based campaign in the Galápagos Islands (1°40′N–1°36′S, 89°16′–92°01′W, see Figure 1), located within the region where significant IO column densities have been retrieved using the SCIAMACHY instrument. Climate and Halogen Reactivity TropicaL Experiment (CHARLEX) is an ongoing field study, the first part of which took place at Isabela Island over 9 months from September 2010 to May 2011, with the support of the Galápagos National Park. The second part of the study has been running from June 2011 to the present in San Cristóbal Island, with a semi-automated suite of instruments located at the meteorological station of the Ecuadorian National Institute for Meteorology and Hydrology (INAMHI). The ground-based dataset presented here spans over nearly a
year and a half from September 2010 to February 2012 and includes data from both islands.

[6] The objectives of the present study are the following:

1. To study the temporal distribution of reactive iodine species in the eastern Pacific, complementing the spatial distribution reported elsewhere [Mahajan et al., 2012].
2. To validate satellite-based observations of IO [Schönhardt et al., 2008; Schönhardt, 2009].
3. To gain new insights on the emission of iodine precursors from the ocean by studying the correlation of both precursor and reactive iodine species with oceanic variables such as SST, chlorophyll-a (Chl-a), salinity, and chromophoric dissolved organic matter (CDOM).
4. To determine whether IO triggers new particle formation over the open ocean.
5. To quantify the role of halogens in generating the very low surface O$_3$ values observed in the equatorial eastern Pacific.

[7] In section 2 of this paper, we provide a brief description to the measurement sites and the experimental techniques that were employed; we then proceed in section 3 to present the results obtained with each instrument and to discuss their mutual consistency and correlations with in situ ancillary data and satellite imagery. Finally, in section 4, we discuss the atmospheric relevance of iodine in the eastern Pacific open ocean boundary layer.

2. Experimental

2.1. Measurement Sites and Ancillary Data Collection

[8] The volcanic Galápagos archipelago consists of a group of shield volcanoes perched on a shallow lava platform (300–900 m deep), which rises abruptly from the abyssal plains of the Nazca plate. The coastline of the islands does not show a pronounced slope, with lava tongues reaching the sea at low inclination and building reefs and tunnel systems where tidal pools form. However, beds of known iodine-emitting kelp are not present, and only sublittoral kelp populations have been reported [Graham et al., 2007]. The southern shores receive the prevailing southeasterly trade winds directly off the ocean for ~80% of the time (Figure 2), carrying clean air masses which have been over the open ocean for many days ([Chl-a] < 0.3 mg m$^{-3}$), with some of them passing over the highly productive Ecuadorian/Peruvian upwelling region ([Chl-a] > 1 mg m$^{-3}$). During the warm season, when the Intertropical Convergence Zone edge shifts southward close to the northernmost islands, there is a weakening of the southeasterlies, and some sporadic intrusions of northeasterlies in the south of the archipelago occur [Hayes et al., 1989; Wallace et al., 1989; Deser and Smith, 1998; Harriten and Datulayata, 2004; Ueyama and Deser, 2008]. Characteristic features of the Galápagos Islands are the large amplitude of the SST seasonal variability and the existence around them of spatially consistent, temporally variable areas with elevated primary productivity (salinity > 34 psu, [Chl-a] > 0.4 mg m$^{-3}$, SST < 24°C), associated with topographic upwelling from the Equatorial Undercurrent into surface waters [Schaeffer et al., 2008]. Thus, the southern coasts of the Galápagos Archipelago can be considered to be representative of the southeastern open ocean boundary layer, while being subjected to a wide range of SST and Chl-a conditions.

[9] During the first 9 months, the measurement site was at Puerto Villamil (0°57’27.3”S, 90°5’55.5”W), located in a shallow bay on the southern coast of Isabela Island (hereafter ISB) (see Figure 1). Mangrove bushes are scattered on the coast and on a group of islets (the Tintoreras) on the eastern side of the bay (see Figure 1, Puerto Villamil inset). Some shipping and fishing activities take place upwind between these islands and the coast, where there is a smaller passenger port with increased traffic during the warm season.

[10] The instruments were split into two groups: the absorption spectroscopy-based instruments were located inside a temperature-controlled field lab at the eastern side of the ~7 km wide Villamil Bay with a clear view of the opposite side, whereas the in situ instruments were installed on the second floor of a cabin situated at the head of a pier protruding from the coast to the south, thus allowing sampling of air masses directly off the ocean. Alongside the instruments designed for halogen radical measurements, a suite of commercial ancillary instruments was deployed, comprising two O$_3$ monitors (2BT 202 and 205), a NO$_x$ analyzer (Teledyne 200EU), two weather stations (Davis WeatherLink Vantage), and a global radiometer (Kipp & Zonen CPM11). Teflon tubing inlets for the NO$_x$ and O$_3$ instruments were guided using a pole pointing southward, sampling air 2 m away from the walls and about 5 m above sea level. The detection limits (DL) of these instruments were respectively 2 ppbv and 50 pptv.

[11] Immediately after the end of the ISB campaign in May 2011, long-term measurements were resumed 150 km to the east, at the INAMHI meteorological station located at Puerto Baquerizo Moreno on San Cristóbal Island (hereafter SCR-PBM), WMO station code 84008 (0°54’14.53”S, 89°36’50.92”W). Simultaneous sonde and surface meteorological data indicate that weather conditions on the south coast of ISB and SCR-PBM are similar. The existing infrastructure of the permanently manned weather station at Puerto Baquerizo Moreno facilitates running a ground-based remote sensing instrument such as a MAX-DOAS, alongside an O$_3$ monitor, for a long time period with minimum effort and the addition of the station’s own weather data for contextualization: pressure (P), temperature (T), relative humidity (RH), precipitation, wind speed (WS) and direction, sunshine, and SST. Additional data from a meteorological station situated in Puerto Ayora (Santa Cruz Island) were also used.

[12] Further to the ground-based in situ data, Chl-a and CDOM index Level-3 daily global fields with a 9 km horizontal resolution obtained by the Aqua MODIS satellite instrument [NASA-GSFC, 2012] were analyzed. A time series of box-averaged Chl-a and CDOM data were produced for different predefined geographical boxes (Figure 2a) passed over by the 5 day back trajectories calculated with the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) dispersion model [Drauxler and Hess, 1997; Draxler and Hess, 1998; Draxler, 1999]. Time series of average and average-weighted exposure to Chl-a and CDOM of the air masses arriving at the study sites were also obtained by integrating the satellite data fields along the
back trajectories ($P > 850$ hPa), using a procedure similar to Arnold et al. [2010]. Regional averages of other satellite products such as tropospheric NO$_2$ columns from Ozone Monitoring Instrument (OMI) [NASA, 2012] were also compiled. Salinity data recorded by buoys of the Argo program [Roemmich and Gilson, 2009] in the region south of Galápagos ($0^\circ$–$10^\circ$S, $85^\circ$W–$93^\circ$W) were collected from the Argo website [GOOS, 2012].

2.2. Air Sample Halocarbon Analysis With GC-MS

[13] Air samples were collected during May and June 2011 at the coast of ISB in 3.2 L Silocans (Restek) filled to ~2.5 bar using a 1/4” perfluoroalkoxy sampling line and a diaphragm pump (KNF, Inc.). The samples were then shipped back to the University of East Anglia for halocarbon analysis by gas chromatography-mass spectrometry (GC-MS). The analytical technique was similar to that described by [Worton et al., 2008]. Air samples (500 mL) were dried with a nafion™ counterflow dryer prior to collection and preconcentration on a commercial thermal desorption system (Markes UNITY-II™/Air Server). The desorbed analytes were separated on a capillary column (Restek 100 m × 0.32 mm RTX 102) using a temperature program of 30°C (2 min), 8°C min$^{-1}$ to 150°C (16 min), and 20°C min$^{-1}$ to 220°C (5 min). The mass spectrometer (Agilent 5973 MSD) was operated in negative ion-chemical ionization mode using methane as the reagent gas. The quadrupole detector was run in single ion mode, monitoring $m/z$ 35/37 for chlorinated, $m/z$ 79/81 for brominated, and $m/z$ 127 for iodinated compounds. The samples were normally analyzed twice and referenced to a high-pressure working standard (34 L, electropolished stainless steel, Essex Cryogenics). This standard, which contains ambient air from a coastal site in California, was calibrated by repeated comparison to

Figure 2. (a) The 5 day back trajectories calculated with HYSPLIT. The color code indicates the number of days before arrival of the air mass at the site. All trajectories coming from the Northern Hemisphere occur in the warm season. The boxes indicate the different averaging regions used for obtaining time series of satellite-derived ocean variables. The thick edge box is the one to which the correlations reported in the text refer. (b) MODIS-A average Chl-a field for 2011. Several regions have been defined on the map in order to classify the trajectories by origin. The track of the HaloCAST-P cruise [Mahajan et al., 2012] is also shown (dashed white line).
calibrated gas standards supplied by NOAA-ESRL. The CH3I data are reported on the NOAA-2004 scale. Analytical precision was typically better than 5%.

2.3. Resonance and Off-resonance Fluorescence by Lamp Excitation (ROFLEX)

[14] Measurements of atomic iodine were performed in October 2010 and February 2011 using the resonance and off-resonance fluorescence by lamp excitation (ROFLEX) resonance fluorescence instrument [Gómez Martín et al., 2011]. Briefly, ambient air is pumped through a low-pressure chamber where the iodine atoms contained in the sample are excited by VUV radiation emitted by a radiofrequency discharge iodine lamp. Resonance fluorescence is then collected orthogonally by a photon-counting module. The ambient airflow can also be directed first through an iodine trap for a set time interval before being drawn into the fluorescence chamber, thus allowing a measurement of an iodine-free background signal. The iodine trap consists of a blackened glass tube in which I atoms are scavenged by ambient O3. Calibration experiments were conducted at the laboratory site before and after the measurement periods by concurrently measuring I2 off-resonance fluorescence by the ROFLEX instrument and absorption by incoherent broadband cavity-enhanced absorption spectroscopy, combined with broadband photolysis of known amounts of molecular iodine to generate atomic iodine. In October, the best iodine atom DL for 1h integration was 1.1 pptv, whereas in February it was 1.9 pptv (see Table 1).

[15] In October, the instrument was located less than 30 m away from the high tide line and about 1 m above sea level. In February, the instrument was located, with the rest of the in situ instruments, closer to the sea but about 5 m above sea level. Although in principle the detection of I2 with ROFLEX is also possible, a DL of about 15 pptv was too high to allow observations in this environment.

2.4. Long-Path Differential Optical Absorption Spectroscopy (LP-DOAS)

[16] The long-path differential optical absorption spectroscopy (LP-DOAS) instrument [Plane and Saiz-Lopez, 2006] was operating at ISB from September 2010 to March 2011. It consists of a Newtonian telescope containing a 450 W Xe arc lamp and the transmitting and receiving optics. The light beam was folded back by a retroreflector array, which was placed on the opposite side of Villamil Bay about 4.54 km to the west, providing a total optical path of 9.08 km (Figure 1). The height of the light beam ranged from about 1 m above the sea at high tide near the telescope to about 5 m at the retroreflector side. The instrument employs a 0.5 m Czerny-Turner spectrometer with a 1200 grooves mm–1 grating, resulting in a spectral resolution of 0.25 nm full width at half maximum (FWHM) and covering a spectral region spanning ~40 nm. Recorded differential spectra averaged for 30 min to improve the signal-to-noise ratio were converted into optical densities, and the contributions of the individual absorbing species were then determined by multivariate fitting of a set of reference absorption cross-sections adapted to the spectrometer instrument function. During the campaign, measurements were alternated between four different spectral regions. The reference spectra fitted in the 425–440 nm window were IO [Gómez Martín et al., 2005], NO2 [Vandaele et al., 1998], H2O [Rothman et al., 2003], and glyoxal [Volkamer et al., 2005]. In the 530–570 nm window, the spectra fitted were OIO [Spiecz et al., 2005] and I2 [Saiz-Lopez et al., 2004]. The typical 2σ DL for IO was around 0.9 pptv depending on the visibility and spectral quality, corresponding to a root mean square (RMS) of the residual of 2 × 10–4. The 2σ DL for NO2 was ~100 pptv. DLs for I2, OIO, and BrO are shown in Table 1.

2.5. Multi-axis Differential Optical Absorption Spectroscopy (MAX-DOAS)

[17] At ISB, the MAX-DOAS scanning telescope was placed on the terrace of the laboratory, about 3 m above sea level and ~15 m away from the mean tide level, pointing toward the west almost parallel to the LP-DOAS light path (Figure 1). At SCR-PBM, the instrument is situated on the roof of a 5 m tall building ~160 m from the coastline, pointing toward the NNW, but not looking over the sea port. Similar to the LP-DOAS, the instrument alternates between two different spectral windows to allow the retrieval of BrO (318–358 nm) and IO (416–456 nm) spectral features.

[18] The instrument itself consists of a small telescope (2.5 cm diameter quartz lens set at the 7.5 cm focal distance from a fiber optic bundle, providing a 1° field of view) mounted on a stepper motor, which allows the collection of scattered sunlight from 19 discrete elevation angles between ~5° and 90° [Mahajan et al., 2010c]. The indoor unit, comprising a spectrometer (Princeton Instruments SP500i), a CCD camera (Princeton Instruments Pixis 400B), and a computer to log data, was placed in a temperature-stabilized room.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Location</th>
<th>Species</th>
<th>Max/pptv</th>
<th>DL/pptv a</th>
<th>Number of Days of Measurement</th>
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<tr>
<td>ROFLEX</td>
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<td>&lt;1.1 b</td>
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<tr>
<td>LP-DOAS</td>
<td>ISB</td>
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<td></td>
<td></td>
<td>OIO</td>
<td>0.9 ± 0.2</td>
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<td>115/68 d</td>
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<tr>
<td></td>
<td>SCR-PBM</td>
<td>OIO</td>
<td>0.7 ± 0.2</td>
<td>0.2</td>
<td>67/44 d</td>
</tr>
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</table>

SCR-PBM, Puerto Baquerizo Moreno on San Cristóbal Island

a1 h integration time.
bOctober 2010.
cFebruary 2011.
dNumber of days of measurements passing the quality filter/passing the cloud filter.
laboratory. In ISB, a 1200 grooves mm\(^{-1}\) grating was used, resulting in a 40 nm spectral window and a spectral resolution of 0.25 nm FWHM. Spectra were recorded with a 10 s exposure time per angle. In SCR-PBM, the spectral coverage was extended to 80 nm (0.5 nm FWHM), and the number of discrete angles per scan decreased to 6 (from 0° to 90°), with 30 s exposure per angle for better signal-to-noise and also to avoid redundancy in elevation angles. In order to further improve the signal-to-noise ratio, 1 h averaging for each elevation angle was adopted as a trade-off between the time per angle. In SCR-PBM, the spectral coverage was extended to 80 nm (0.5 nm FWHM), and the number of elevation angles was reduced. In order to further improve the signal-to-noise ratio, 1 h averaging for each elevation angle was adopted as a trade-off between the signal-to-noise ratio and the number of elevation angles. In order to further improve the signal-to-noise ratio, 1 h averaging for each elevation angle was adopted as a trade-off between the signal-to-noise ratio and the number of elevation angles.

[19] For the retrieval of IO using the QDOAS routine [Fayt and van Roozendael, 2011], the cross-sections indicated above for LP-DOAS along with O\(_3\) (\(T=223\) K) [Bogumil et al., 2003] and the Ring [Grainger and Ring, 1962; Chance and Spurr, 1997; Vountas et al., 1998] were simultaneously fitted to the measured optical densities together with a third-order polynomial and a linear intensity offset to account for broadband extinction processes and for possible instrumental stray light, respectively. The spectral deconvolution for IO was performed in a wavelength window between 416 and 440 nm using the zenith spectrum of each individual scan as the reference. Typically, the RMS residual varied between 2.5 and 5.0 \(\times 10^{-4}\). The IO differential slant column density (DSCD) DL varied between 5 \(\times 10^{12}\) and 1 \(\times 10^{13}\) molecules cm\(^{-2}\). Similarly, the NO\(_2\) DSCD DL varied between 7 \(\times 10^{14}\) and 1.4 \(\times 10^{15}\) molecules cm\(^{-2}\).

[20] Quality filters are set to exclude data recorded at solar zenith angle (SZA) > 60° (a conservative limit to avoid influence of higher atmospheric layers), data yielding RMS 4 \(\times 10^{-4}\) in the retrieval process, and data recorded under cloudy conditions. The cloud cover in the Galápagos Islands is abundant, especially in the cold season [e.g., Trueman and d’Ozouville, 2010]. Clouds affect the MAX-DOAS measurements in different ways: they may reduce the incoming light and hence compromise the signal-to-noise ratio, and they also introduce heterogeneity in the light path. Therefore, a cloud filter was calculated for estimating sky conditions using the ratio of the radiation fluxes at the edges of the spectral window [Sniezech et al., 2010], in conjunction with radiometer data and visual inspection of the photographs from a colocated webcam. The use of this filter ensured that only data from clear sky conditions were used for further analysis.

[21] For selected days, with at least three viewing elevation angles that pass the quality and cloud filters, VMRs were retrieved from the MAX-DOAS DSCDs following the so-called O\(_4\) method [Wagner et al., 2004] to estimate the scattering properties of the atmosphere and using the NIMO fully spherical Monte Carlo radiative transfer model (RTM) [Hay et al., 2012]. This procedure is explained in detail in our previous paper on ship-based MAX-DOAS measurements in the eastern Pacific [Mahajan et al., 2012]. Briefly, an aerosol profile is estimated in order to reproduce the observed DSCDs of O\(_4\), whose vertical distribution is known by forward modeling using the RTM. Parameterized aerosol profiles with varying aerosol optical depths and shapes were prescribed, and the profile parameters are floated to obtain the best match between the forward model and the observed O\(_4\) DSCDs. The aerosols were modeled using the Heneyy-Greenstein parameterization with an asymmetry parameter of 0.75 based on observations of marine aerosols in tropical areas [Dubovik et al., 2002], and a single scattering albedo of 0.99 was chosen as an approximate representative value for unpolluted sea salt aerosols [Hu et al., 2007; Kudo et al., 2008]. The T and P profiles were taken from the meteorological sondes measurements, and the surface albedo was set to 0.07.

[22] Aerosol profiles are only available for days where UV spectra were measured (BrO window). The O\(_4\) spectral retrieval was unreliable in the visible, and only the 360 nm O\(_4\) band is useful for this purpose. Since the wavelength region alternated between visible and UV, it was not possible to retrieve aerosols on the same days as IO was measured. An aerosol profile from the previous or following day is then used in the RTM calculation of weighting functions for the retrieval of the vertical distribution of IO by optimal estimation [Rodgers, 2000]. The a priori IO profile used for the optimal estimation decreased linearly from 0.4 pptv at sea level to 0 pptv at 4 km, with a vertical resolution of 50 m and an error of 80% at each level.

[23] A second, more straightforward, method was also used to derive VMRs for the entire period of measurements, using the 3° viewing elevation angle DSCDs scaled with the simultaneously measured O\(_4\) DSCDs to account for light path changes caused by changes in the aerosol loading. This method is sensitive within a vertical mixing layer with the upper altitude defined by the mean last scattering altitude (LSA) of photons reaching the detector when looking at 3° elevation angle and can only provide an averaged VMR inside this layer, with no information about the vertical profile shape. In contrast to observations during a previous ship campaign across the eastern Pacific with the same instrument [Mahajan et al., 2012], the data recorded at 1° viewing elevation angle during the CHARLEX field study did not pass the quality filter and could not be used for deriving VMRs. This is mostly due to the shortened light path due to aerosols, as indicated by the O\(_4\) columns for the same angle. The consequences of this lack of information on the retrieved VMRs for the lowest layers are discussed below. Primary assumptions of this method are that the trace gas and O\(_4\) profiles have the same shape and that they are measured in the same wavelength region. Since the IO profile is predicted from chemical modeling to decrease more rapidly with altitude than the O\(_4\) profile, correction factors were calculated to remove the contribution to the O\(_4\) DSCD from above the mean LSA. The aerosol profiles, obtained by forward modeling of O\(_4\) DSCDs using the RTM, gave a mean LSA range of ~500 m to 2500 m with an overall mean of ~1200 m (Figure 3f). The contribution to the O\(_4\) DSCDs from O\(_4\) above 1200 m was removed using the single scattering geometrical approximation to calculate the relative path lengths above and below 1200 m for each measurement SZA. The O\(_4\)-derived path lengths were then calculated by dividing the O\(_4\) DSCDs by the average O\(_2\) squared concentration of 2.4 \(\times 10^{17}\) molecules cm\(^{-2}\) (based on the air density profile calculated from the PTU sonde measurements) up to 1200 m.

### 2.6. Particle Counter

[24] The particle analyzers were not deployed during the 9 month period in Isabela Island (for logistical reasons), and measurements were conducted only in July and August...
2011 at San Cristóbal. Particles were sampled at two different sites: the meteorological station at SCR-PBM, which can be considered as a background rural area (see below), and La Lobería (hereafter SCR-LBR), a coastal site 2.3 km south of SCR-PBM (see Figure 1), which is a remote marine environment.

[25] A submicron particle size spectrometer (SMPS), comprising a neutralizer (TSI-Model 3077) and a Differential Mobility Analyzer (TSI-Model 3081), was used to measure the size distribution of ambient aerosol particles. Particles were counted using an ultrafine concentration particle counter (UCPC) (TSI-Model 3776) (see Mahajan et al. [2010a] for a detailed description of this setup). A scan-up time of 270 s and a time resolution of 300 s allowed measurements of a size range between 9 and 438 nm (diameter). The total number concentration of particles larger than 9 nm was evaluated integrating the size distribution measured by the SMPS. Additionally, the total number concentration of particles larger than 3 nm was measured by a second UCPC (TSI-Model 3776). The UCPC total number concentrations were saved every minute and averaged to 5 min resolution to match the SMPS data. The accuracy of both systems is ±10%. The total particle concentration in the 3–9 nm range was calculated by taking the difference of data collected simultaneously by the SMPS and the UCPC instruments.

[26] At the SCR-PBM site, the SMPS and UCPC units were housed in the MAX-DOAS laboratory. UCPC sampling was carried out from 21 July 2011 until 10 August 2011, and the SMPS was run from 30 July 2011 through 5 August 2011. The aerosol inlet was mounted ~1 m above the roof of the 5 m tall building and connected to the sampling units by a 3 m long stainless steel tube with 10 mm inner diameter. Ambient airflows were dried to RH < 30% (Perma Pure Inc.) before sampling. Losses resulting from diffusion and gravitational settling inside the aerosol sampling system were estimated to be less than 10% for particles smaller than 1 μm.

[27] At SCR-LBR, the UCPC measured from 6 August 2011 to 10 August 2011. The sampling site was 100 m from the shoreline and about 3 m above the average sea level. The inlet was located ~1 m above the instrument housing, and the air was drawn into the UCPC inlet through a 1.5 m long stainless steel tube with 4 mm inner diameter.
3. Results and Discussion

3.1. Meteorology and Background Chemical Composition

[32] Daily averaged meteorological variables are shown in Figure 3. La Niña or El Niño–Southern Oscillation (ENSO)-neutral conditions were experienced throughout the campaign [NOAA, 2012]. Strong La Niña conditions were observed during the 2010 cold season, with SST anomalies in the El Niño 1+2 region of up to −2°C, followed by a transition to neutral ENSO during the 2011 warm season. During the cold season of 2011, moderate La Niña conditions were experienced (SST anomalies > −1.2°C) in transition to neutral ENSO in the warm season of 2012. The air temperature registered at the meteorological stations of San Cristóbal and Santa Cruz during 2010 and 2011 were within ±1°C around the average (the records started in 1951 and 1964, respectively), except during the 2010 cold season, when the temperature anomalies dropped below −1.5°C. Precipitation was normal throughout the campaign, except for February and April 2011, when rain was more frequent than usual (all ancillary and in situ data recorded during rain periods has been filtered out). The cloud cover was equally persistent during the cold seasons of 2010 and 2011 and reached its minimum in March 2011.

[33] The wind vectors in Figure 3c show the expected pattern for the Eastern Equatorial Pacific [Hayes et al., 1989; Wallace et al., 1989], with weaker meridional components during the warm season, even changing sign in March 1989; but simultaneously the wind strength increases from the 1989

[34] After applying quality and cloud

[35] The O₃ VMRs are generally low (<32 ppbv) as expected for a remote clean environment and show a pronounced seasonal cycle driven by SST-controlled H₂O evaporation from the ocean, via the H₂O + O₃ reaction. The minimum O₃ VMRs are reached in the warm season when the ambient water vapor peaks and can be as low as a few parts per billion in volume (even below the ozone monitor DL at times). The O₃ daily average high-pass filtered data (seasonal trend removed) are also correlated to SST and water vapor. On the other hand, the O₃ daily cycle does not show a photolytic profile compared, for example, to the observations at CV [Read et al., 2008], with the exception of limited photolytic depletion in October 2010 (2.5 ppbv on average) and nighttime depletion due to local NO emissions during January to April 2011 and 2012 (sometimes up to 15 ppbv of O₃ are destroyed in a single night). Such NO₃ nighttime chemistry is a local phenomenon in populated areas of the islands, related to emissions from fishing, shipping, and tourism activities and local fossil-fuel energy plants. During the warm season nights, NO₃ is emitted to slow moving air masses with negative meridional component, thus reaching the detector depleted in O₃. Early in the morning, NO₃ photolysis initiates ozone production, but simultaneously the wind strength increases from the south, bringing fresh open ocean air. For the current analysis, the O₃ data recorded during the warm season have been filtered by setting NO₃ and WS thresholds (data are rejected if [NO₃] > 200 pptv and WS < 1 m s⁻¹) in order to remove local interferences on the otherwise clean air masses arriving at the archipelago. A dedicated study of the O₃ dataset will be published elsewhere.

3.2. Reactive Iodine Loading

[36] For the present study, 5 day back trajectories arriving at the measurement sites, calculated with HYSPLIT (Figure 2a), have been classified according to the contribution from different oceanic regions, roughly defined according to their primary productivity in the Southern Hemisphere and to their proximity to land masses in the Northern Hemisphere (Figure 2b). Each air mass spends between 60% and 89% of the trajectory time over low-chlorophyll regions (<0.3 mg m⁻³) in the open ocean. The weakening of the meridional component of the wind in the warm season implies that air masses pass closer to the coastal upwelling region and spend more time around it and the archipelago itself, reaching the Galápagos from the east rather than the southeast.

[37] Chl-a (Figure 3a), salinity (Figure 3d), and CDOM (not shown) are anticorrelated to SST and show a seasonal maximum during the cold season. South of Galápagos (averaging box defined by the coordinates 5.97°–9.7°S × 93.48°–88.48°W), the highest values for these three parameters are observed in the 2010 cold season. After removing the seasonal trend from the time series of 3 day composites using a low-pass filter (cutoff frequency=0.01 day⁻¹), a 99% significant anticorrelation remains between SST and Chl-a (R=0.35), CDOM (R=0.29), and salinity (R=0.20). For higher cutoff frequencies (0.05 day⁻¹), only the Chl-a versus SST correlation persists at 99% significance (R=0.31).

[38] An example of an aerosol profile is shown in Figure 5a. Aerosol profiles with a sharp peak in extinction in the first few meters above the surface (~1 km⁻¹) and monotonically decreasing toward the top of the MBL (~0.1 km⁻¹ at 200 m, ~0.05 km⁻¹ at 1000 m) resulted in the best fit of forward modeled O₃ to the measured O₃ DSCDs.
The closeness of most IO DSCDs to the detection limit and the poor sampling of elevation angles—imposed by the need of longer averaging—preclude the retrieval of IO vertical profiles in the MBL using optimal estimation. Moreover, the lack of viewing elevation angle data leads to a poor sensitivity of the optimal estimation in the lowermost 200 m. With the available viewing angles, the averaging kernels indicate a high degree of vertical smoothing in the retrieved profile and thus a more accurate estimation of average VMRs for a layer of 1000 m than for 200 m. For ISB, where more elevation angles are available, the average degrees of freedom of information for the 1000 m layer, derived from the measurements over and above the a priori profile information, is ~0.63, while for SCR it is ~0.45. In Figure 5, a retrieved IO profile is compared to modeled IO vertical profiles (see below) obtained using a sea-to-air flux of inorganic iodine precursors based on measurements at CV [Mahajan et al., 2010b]. The uncertainty of the retrieved profile (SCR 22 February 2012, 14:00 h) encompasses to a large extent the expected range of variation of the IO profile between midday and late afternoon. This illustrates the insufficient quality of the data for obtaining reliable information about vertical distribution of IO.

For the days for which RTM calculations were performed (22 days, 65 sets of viewing elevation angles), the VMRs obtained using the O4 scaling of DSCDs

Figure 4. (a) The 1 h average IO DSCDs for different viewing elevation angles (3°–30°) for the complete measurement period. The data point with error bar corresponds to the spectral fit shown. The insert shows an example of a day of data (30 December 2011). (b) Spectral fit of data recorded at San Cristóbal Island, 30 December 2011, 15:30 LT, SZA = 55.4°, 3° elevation angle. (c) The residual optical density of the fit.

Figure 5. (a) Typical aerosol profile resulting from fitting forward modeled O4 to the measured O4 DSCDs. (b) A priori (thin red line) and retrieved (thin black line and error bars) IO profiles using optimal estimation, from data obtained at SCR (22 February 2012, 14:00 h; degrees of freedom of information = 0.84). Also shown are modeled MBL IO vertical profiles at noon (thick red line) and late afternoon (thick blue line) obtained using a sea-to-air flux of inorganic iodine precursors based on measurements at CV [Mahajan et al., 2010b].

Figure 6. Comparison between the optimal estimation method and the O4-scaling method to retrieve IO mixing ratios. The methods agree within 25% (1σ) for last scattering heights (LSA) lower than 1000 m. The color code refers to single scattering altitude as determined by O4 profile estimation. The thin black line corresponds to the 1:1 ratio. Linear fits indicate the ratio of one method to the other for all values shown in the scatter plot (red line) or just the values with LSA < 1000 m (black line).
agree within 25% with the retrieved VMRs for O$_4$-derived
path lengths shorter than 19 km (see Figure 6), corresponding
to a LSA of 1000 m based on single scattering (O$_4$-derived
path lengths range from 11 km to 29 km, corresponding
to LSA of 600 m and 1600 m, respectively). For LSA
larger than 1000 m, the O$_4$ scaled 3$^\circ$ VMRs are systemati-
cally lower (green, blue, and cyan symbols in Figure 6) than
the retrieved 1000 m VMRs due to light path overestima-
tion caused by the different profile shapes of O$_4$ and IO.

[37] The high errors in the VMRs for the optimal estimation
arise from the high a priori errors required to optimize the
residual RMS of the forward model fit to the measurements,
while the high DSCD errors and the lack of vertical profile
information from low elevation angles means that the retrieval
errors are only slightly reduced below the original a priori
errors. The errors in the O$_4$ method are harder to estimate,
given that there is only information from one elevation angle
and differences between the IO and O$_4$ profile shapes are
unknown. The estimated errors are based on the range of
LSA caused by the different aerosol profiles from the O$_4$
forward modeling fits to the measurements, which result
in uncertainty in the mean O$_4$ extinction coefficient along
the path. The O$_4$ and IO DSCD errors are also propagated
into the O$_4$-derived VMR errors. These errors probably un-
derestimate the true errors, while the optimal estimation
errors most likely overestimate the true errors.

[38] The filtered IO time series scaled by O$_4$ (hereafter
referred to as “MBL-averaged IO”) is shown in Figure 7b.
Regarding the differences between ISB and SCR-PBM, the
3$^\circ$ elevation angle light path for O$_4$ is generally longer at
SCR-PBM (average 23 km) than at ISB (average 19 km)
due to a higher single scattering mixing layer height (LSA =
1300 ± 300 versus LSA = 1000 ± 300 m). This difference is
consistent with simultaneous radiosonde measurements at
ISB and SCR-PBM showing a generally lower inversion
layer at ISB. This is reflected by the reduction of the IO
DSCDs at SCR-PBM relative to ISB when converted to
VMRs (compare Figures 3f and 5b). The ratio of the average
filtered IO DSCD for ISB ((1.5 ± 0.7) × 10$^{13}$ molecule cm$^{-2}$
) to that for SCR-PBM ((2.3 ± 0.6) × 10$^{13}$ molecule cm$^{-2}$
) is 0.68, while the ratio between the corresponding averaged
VMRs is 0.85 ((0.36 ± 0.19) pptv/(0.41 ± 0.11) pptv). The
quoted 1σ standard deviation indicates that there is more
variability at ISB than at SCR-PBM.

[39] IO was under the LP-DOAS 1σ DL of ~0.9 pptv
for 1 h averages throughout the measurement period of

Figure 7. Hourly averages of (a) ozone, (b) IO mixing ratios and DL (data points passing the quality and
cloud filters), (c) modeled I atom mixing ratios using Figures 7a and 7b (see text), and (d) CH$_3$I and total
reactive iodine IO$_x$ = I + IO from IO MAX-DOAS measurements. MAX-DOAS and LP-DOAS detection
limits (DLs) are shown in red in Figure 7b. ROFLEX DLs are shown in blue in Figure 7c.
this instrument. Ninety-nine percent of the cloud-filtered MBL-averaged IO for the same period are also below 0.9 pptv. Comparison of the LP-DOAS and MAX-DOAS must be treated with caution, since as explained above the MAX-DOAS calibrated values are averaged over a ~1000 m height layer, while the LP-DOAS instrument was measuring between 1 and 5 m over the ocean surface. The highest O$_3$-scaled VMRs, i.e., those containing the LP-DOAS detection limit within their error bar (this occurs on 10 days during the ISB period), are found for the lowest single scattering heights (average 600 m) and O$_3$ path lengths (average 11 km). Figure 8 shows the dependence of 3° IO DSCDs on O$_3$ path length and LSA (Figure 8a) and VMRs resulting from dividing the former by the O$_3$ path length (Figure 8b). Note that for the fixed elevation angle of 3°, the IO VMRs are generally larger for the shortest path lengths and LSAs, which suggests that most of the IO is located in the lowermost part of the MBL. Cumulative averages of the modeled IO profiles in Figure 5 (i.e., averages of the IO profile from the surface up to each particular height) are also shown for comparison.

Figure 8. (a) IO DSCDs and (b) IO VMRs from the O$_3$-scaling method versus O$_3$ path length/last scattering height (LSA). Red and blue squares correspond to data obtained in ISB and SCR, respectively. Black lines are linear fits to the full dataset (correlation coefficients shown). The framed red squares correspond to MAX-DOAS data obtained during the LP-DOAS period, containing the average LP-DOAS DL within the error bar. Cumulative averages of the modeled IO vertical profiles in Figure 5 (white circles, noon; white squares, late afternoon) are also shown (each point is the average of the IO profile from the surface up to that particular height).

[40] Atomic iodine was under the ROFLEX DL (1.1 pptv) for 1 h averages during October and generally below the 1.9 pptv DL during February 2011. Besides the direct measurement of upper limits, the iodine atom VMRs can be estimated by using a box model with standard HO$_3$ and halogen chemistry, constrained by NO$_2$-filtered, O$_3$, and IO measurements (Figures 7a and 7b, respectively) [Mahajan et al., 2012]. The calculated ratio of [IO] to [I] at noon for low NO$_3$ (20 pptv, open ocean background conditions [Lee et al., 2010] and equal to the MAX-DOAS 1 σ DL for NO$_2$)

\[ \frac{[\text{IO}]}{[\text{I}]} = 0.13 \times [\text{O}_3] \]

Calculated I atom VMRs from MBL-averaged IO are consistent with the ROFLEX DL (Figure 7c), although they are not directly comparable as mentioned above for IO. On the other hand, the I atom VMRs derived from the LP-DOAS DL for IO are consistent with the ROFLEX DL (red symbols in Figure 7c). Note that low O$_3$ concentrations result in I atom VMRs comparable to or even larger than those of IO. In order to obtain a variable that can be directly linked to the iodine sources (see below), the MBL-averaged total reactive iodine IO$_3$ is calculated from the sum of the measured MBL-averaged IO and the modeled atomic I (Figure 7d). By considering IO$_3$ rather than IO in correlation studies, the changes in the partitioning between IO and I, determined essentially by O$_3$ and radiation, do not obscure a potential link to other variables.

[41] Other important iodine species such as OIO could not be observed above the LP-DOAS detection limit (Table 1) during the twilight or nighttime targeted measurement periods.

3.3. Iodine Precursors

[42] Indirect evidence from halocarbon flux measurements at CV indicates that inorganic iodine precursors (I$_2$, HOI, ICI, IBr) are the dominant source of reactive iodine in an open ocean environment [Mahajan et al., 2010b]. The halocarbon fluxes measured at CV were not high enough to sustain the daytime IO concentrations observed during the same campaign. Unfortunately, the I$_2$ detection limits of the LP-DOAS and the ROFLEX instruments during the CHARLEX campaign (see Table 1) were too high to enable detection in this environment.

[43] As a result of its photolytic lifetime (~2 days at the equator), which is long compared to the lifetimes of inorganic species such as I$_2$ and HOI, CH$_3$I is not a major precursor of IO, in the MBL. However, CH$_3$I is transported higher up, becoming the major IO source in the free troposphere and the upper troposphere-lower stratosphere region [Ordóñez et al., 2012; Saiz-Lopez et al., 2012b]. High VMRs of CH$_3$I were observed in the 23 air samples (n = 15 single-point daily samples, plus two daily profiles × 4 samples) collected during the months of May and June 2011 at ISB (Figure 7d), with an average CH$_3$I VMR of 1.83 pptv (1.05 pptv standard deviation) and a range of 0.6 to 5.4 pptv (95% of values below 3.14 pptv). The two daily profiles collected did not show any dependence of CH$_3$I on solar radiation.

[44] These VMRs are on average significantly larger and span a wider range than observed throughout 2004 in a previous campaign at SCR-PBM [Yokouchi et al., 2008], where a yearly average of 1.13 pptv (0.37 pptv standard deviation) was observed, with values ranging between 0.53 and 2.55 pptv. The average for the 2004 May–June period was 897
Also the CH$_3$I VMRs reported during the HALOCAST-P cruise pass across the equator in April 2010 (Figure 2b) were smaller (1.2 ± 1.1 pptv) [Mahajan et al., 2012], although overlapping with the range observed during CHARLEX. Only one previous study reports open ocean CH$_3$I VMRs of up to 3 pptv across a region of the southern Atlantic near the Argentinean coast with increased phytoplankton activity and high Chl-α concentrations [Arnold et al., 2010; Lai et al., 2011].

[45] Correlations of gas-phase CH$_3$I with SST [Yokouchi et al., 2008] and Chl-α (or exposure to Chl-α) [Arnold et al., 2010; Lai et al., 2011] have been previously reported. However, the differences in SST (~2°C warmer in 2011) and Chl-α (~20% lower in 2011) as measured by MODIS-A between May–June 2004 and 2011 over the Galápagos area are not in line with the linear relationships of CH$_3$I with these variables previously reported [Yokouchi et al., 2008; Arnold et al., 2010; Lai et al., 2011]. On the other hand, no significant correlation can be observed in the CHARLEX data between CH$_3$I and open ocean box-averaged Chl-α nor with average or age-weighted air mass exposure to Chl-α (up to 5 days exposure).

[46] All these results seem to suggest a local source of CH$_3$I. Significant correlation between local meteorological parameters (wind speed or direction) or tidal height is not observed either, and therefore influence of local terrestrial or intertidal sources can be discarded. A closer look to the MODIS-A Chl-α fields shows periodically enhanced biological activity in a narrow strip envelop (~10 km wide) along the southern coast of Isabela Island (0.4 ± 0.2 mg m$^{-3}$, max 1.6 mg m$^{-3}$) during the CHARLEX campaign. In fact, recurring phytoplankton blooms are observable in the surf zones off sandy beaches on this island, leaving significant green algal deposits along the shoreline. By contrast, the Chl-α fields show a weaker envelope of biological activity along the southern coast of San Cristóbal (0.27 ± 0.11 mg m$^{-3}$, max 0.8 mg m$^{-3}$). Assuming CH$_3$I is related to Chl-α as a proxy of biological activity, this would explain the observation on San Cristóbal of oceanic CH$_3$I background levels similar to those reported in the HALOCAST-P cruise.

[47] Since the levels of CH$_3$I observed at ISB are relatively high, it is pertinent to determine if they contribute significantly to the inorganic iodine loading in the MBL as determined from the LP-DOAS and MAX-DOAS measurements. The lack of correlation between CH$_3$I and IO$_x$ during the May–June period already indicates that CH$_3$I is not a major source for the IO$_x$ observed. To estimate the contribution of the observed CH$_3$I to the IO$_x$, we used the one-dimensional chemistry transport model, Tropospheric Halogen chemistry Model (THAMO) [Saiz-Lopez et al., 2008]. In the past, this model has been used to study tropical halogen chemistry in the Atlantic MBL [Mahajan et al., 2010b]. The model was constrained with typical concentrations of O$_3$, NO$_x$, and H$_2$O measured at the Galápagos Islands. Vertical mixing was calculated using WS measurements (average of 5 m s$^{-1}$ at 5 m) as detailed by Saiz-Lopez et al. [2008]. We use background CH$_3$I concentrations measured in the open ocean environment during the HALOCAST-P cruise [Mahajan et al., 2012], which peaked at 1 pptv. The model is run until steady state for open ocean conditions, after which the air mass is simulated to pass over a 10 km band of elevated CH$_3$I, 3 pptv, to match the observations at the Galápagos Islands, before arriving at the measurement site. The results show that background CH$_3$I contributes to a maximum of 0.25 pptv of MBL-averaged IO$_x$, which is roughly 30% of the mean MBL-averaged IO$_x$ observed. The presence of localized elevated CH$_3$I does not contribute a large increase in the IO$_x$ due to the long lifetime of CH$_3$I in the MBL (i.e., 6% increase of the background CH$_3$I contribution to IO$_x$ when including a 10 km belt of 3 pptv CH$_3$I at the surface around the Galápagos Islands).

[48] Unfortunately, the long time elapsed between the collection of the samples and their analysis precluded a reliable quantification of other more unstable iodocarbons such as CH$_3$I$_2$. The observation of CH$_3$I$_2$ in a range which can be defined as typically coastal [Saiz-Lopez et al., 2012a] suggests elevated VMRs of these other compounds as well, which could also contribute to the local inorganic iodine loading. An additional discontinuous local source of photolabile iodocarbons and inorganic iodine species would be a possible explanation of the larger variability observed in IO at ISB compared to SCR-PBM (see Figure 7b).

3.4. Short-Term and Seasonal Variability of Reactive Iodine

[49] As a result of the sparse sampling resulting from the application of quality and cloud filters, the MBL-averaged IO data series cannot be used for studying day-to-day or weekly variability. However, the sampling is sufficient for investigating the monthly and seasonal variability of reactive iodine. Note that the MAX-DOAS light path should in principle be free of local effects such as the windscreen created at ISB by the group of islets (Figure 1). Correlation analysis has been carried out between reactive iodine VMR time series and all available in situ and satellite data. In this analysis, we have used time series of Chl-α, CDOM, and SST averaged in a box defined by the coordinates 5.97°–0.97°S × 93.48°–88.48°W (see Figure 2a), where most of the 1 day long back trajectories are contained. A larger box is considered for spatial averaging of salinity data (down to 10°S) to compensate for the poorer sampling provided by ARGO drifting floats.

[50] In order to investigate variability on the shorter time scales (5 to 60 days), the ancillary and reactive iodine daily average datasets have been filtered by applying a fast Fourier transform (FFT) band-pass filter with 0.2 day$^{-1}$ and 0.0167 day$^{-1}$ higher and lower cutoff frequencies, respectively. In this way, the short-term variability present in the remaining IO contiguous data points and the seasonal cycle are removed. Pearson correlation coefficients for the band-pass filtered data have been calculated for the entire period of measurement as well as for the two measurement sites separately. The only significant correlation of the high-pass filtered IO data observed during the entire measurement period are with satellite SST ($R = 0.30$, $p = 0.001$) and with air $T$. A similar although less significant correlation with SST and air $T$ is also found for IO$_x$. This changes when each site is investigated separately. For ISB, no significant correlation is found for IO. However for SCR-PBM (Figure 9a), a significant correlation is found between IO and SST ($R = 0.48$, $p = 0.001$) and with air temperature ($R = 0.51$, $p < 0.001$). This correlation is also strong for the high-pass filtered IO$_x$. The higher variability of IO at ISB may be a consequence of a more variable mixing of the
boundary layer or due to intermittent emissions of very short lived iodocarbons (e.g., CH$_2$I$_2$) from the belt of enhanced productivity around the island.

[51] Time series of average and weighted exposure to Chl-$\alpha$ and CDOM along 5 day back trajectories do not improve the lack of correlation between reactive iodine and spatially averaged Chl-$\alpha$ and CDOM in short time scales. Correlation between CH$_3$I and Chl-$\alpha$ exposure was reported in a previous study [Arnold et al., 2010]. Assuming that in the eastern Pacific the CH$_3$I emission regime was indeed related to the Chl-$\alpha$ field, such lack of correlation between IO$_x$ and Chl-$\alpha$ exposure is consistent with the minor contribution of CH$_3$I to IO$_x$ estimated above. On the other hand, the Chl-$\alpha$ fields are in general rather homogeneous along the air mass trajectories and only have substantially enhanced values in the Pacific upwelling region, generally more than 6 days upwind of the Galápagos Islands.

[52] For investigating the month-to-month and seasonal cycle, a low-pass FFT filter is applied (0.0167 day$^{-1}$ cutoff frequency) to the daily average time series. Pearson correlation coefficients of the low-pass filtered IO and IO$_x$ data are shown in Figures 9b, 9c, and 9d. The complete IO VMR time series smoothed in this way is anticorrelated to radiation ($R = -0.65$, $p < 0.001$) and Chl-$\alpha$ ($R = -0.35$, $p < 0.001$) and correlates positively with salinity ($R = 0.50$, $p < 0.001$) (Figure 9b). IO$_x$ is strongly anticorrelated to O$_3$, which may be regarded as a trivial consequence of using O$_3$ to derive this variable, although it should be noted that such anticorrelation results only from the low IO VMRs and O$_3$ observed at this location. If O$_3$ VMR was larger than 25 ppb, the calculated I atom VMR would be negligible, and IO$_x$ (~IO) would not be correlated to O$_3$ (e.g., at CV). However, IO$_x$ is not strongly correlated either to RH or to SST as would be expected from the strong correlation between the former variables and O$_3$. The anticorrelations of IO$_x$ to Chl-$\alpha$ and to CDOM are also remarkable. Looking only at the ISB site data (Figure 9c), IO$_x$ is anticorrelated with the O$_3$ cycle, showing correlation with RH and wind direction (both covary with O$_3$). The IO correlation with salinity and the anticorrelation with radiation and Chl-$\alpha$ become stronger for the ISB period compared to the full time series, and a strong positive correlation with WS appears ($R = 0.74$, $p < 0.001$) (WS and radiation are anticorrelated in ISB, Figure 3c). A negative correlation of IO and SST is also significant at ISB. The most remarkable correlation in the SCR-PBM period (Figure 9d) is the anticorrelation between O$_3$ and IO ($R = -0.83$, $p < 0.001$). In this period, IO$_x$ and IO grow in parallel with a continuous decay of the O$_3$ concentration and are positively correlated to SST and anticorrelated to Chl-$\alpha$ and CDOM. Note that radiation is not available for most of the SCR-PBM period and that salinity does not change significantly.

[53] The significant correlations of reactive iodine species with different atmospheric and oceanic variables and the fact that many of these variables are themselves mutually correlated (see section 3.1) make an assessment of the possible emission mechanisms of iodine precursors difficult. Moreover, the different correlations found during the ISB and SCR-PBM periods (see Figures 9c and 9d), especially regarding SST and salinity, point to an emission mechanism depending on multiple factors. The monthly averages plotted in Figure 10 indicate that while IO and IO$_x$ show a seasonal trend, it is not completely coupled to the SST seasonal variation. A positive correlation between IO and IO$_x$ and SST such as the one observed at SCR-PBM is in line with an enhanced sea-to-air emission of reactive iodine precursors or an increasing rate of production of these compounds with higher SST. However, at ISB, no significant correlation of IO$_x$ with SST is observed, and a negative correlation between SST and IO. Monthly changes of salinity and radiation are observed in that period correlated to a change in IO and IO$_x$, which could be a reason for the apparent decoupling from SST. The minimum IO in February–April is well matched by the maximum in radiation and the minimum in salinity. Higher radiation would shift the I-IO steady state toward I, increase the rate of formation of IO$_x$ from the photolysis of iodine precursors, and perhaps accelerate the production rates of these. A decrease in salinity on the other hand could be associated to a reduction of iodide ($\Gamma^-$) availability in seawater, which could decrease the iodide-dependent emission rates of iodine precursors (chiefly I$_2$ and HOI) [Carpenter et al., 2013]. The eastern Pacific equatorial salinity front shifts south from January to June (Figure 10 shows the salinity variation south of the Galápagos Archipelago throughout 2011) as a result of cessation of equatorial upwelling, advection of low salinity water from

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**Figure 9.** Pearson correlation coefficients between IO and IO$_x$ and meteorological and ocean variables. (a) High-pass filtered data series at Puerto Baquerizo Moreno on San Cristóbal Island (SCR-PBM). (b) Low-pass filtered data for the full dataset. (c) Low-pass filtered data at ISB. (d) Low-pass filtered data at SCR-PBM. The thick lines indicate the 99% ($p = 0.01$) confidence boundaries.
the Northern Hemisphere, and possibly local rainfall [Pak and Zaneveld, 1974; Donguy and Henin, 1980]. Shutting down upwelling could enhance iodate (IO$_3^-$) reduction to I$^-$ close to the surface [Truesdale et al., 2000; Truesdale and Bailey, 2002], thus enhancing iodine emission to the MBL. If this was the dominating effect, it would result in anticorrelation between IO$_3^-$ and salinity. Horizontal advection of water with lower I$^-$ on the other hand, fits well with the correlation observed, since such water is also characterized by its lower salinity. Measurements of seawater I$_x$ in this region are scarce and to our knowledge only data collected during the cruise 2/76 of R.R.S. Shackleton in May 1976 has been published [Elderfield and Truesdale, 1980]. This dataset shows that I$_x$ is nearly a factor of two higher in the Peruvian current than in the surface tropical water reaching the Galapagos Islands in the warm season.

[55] An interesting result of the correlation analysis is the significant linear anticorrelation of IO$_3^-$ and IO$_x$, with CDOM and Chl-a (Figure 9b), which persists when both measurement periods are analyzed separately. This suggests an inhibiting role of biological activity, although it must be noted that high Chl-a and CDOM are associated with upwelling of cold waters, and in fact they are seasonally anticorrelated to SST (to which IO$_3^-$ is positively correlated), which means that the aforementioned anticorrelation could be noncausal. In any case, a mechanism where the availability of dissolved organic matter or Chl-a is important [Reeser et al., 2008; Jammoul et al., 2009] (see also [Saiz-Lopez et al., 2012a]) would also be unlikely to dominate here.

3.5. Comparison With Satellite Observations and Other Ground and Ship-Based Measurements in Tropical Latitudes

[56] The results obtained in the present study are consistent with the recently reported latitudinal distribution of IO across the eastern Pacific during the HaloCAST-P study in April 2010 [Mahajan et al., 2012], showing a low iodine load in the MBL, linearly correlated to SST and salinity but with a small slope and anticorrelated to Chl-a. At the equatorial crossing point during the cruise, the MBL-averaged IO VMR was 0.4 ± 0.2 pptv (IO$_3^-$ = 0.7 ± 0.2 pptv) (note that the higher values reported by [Mahajan et al., 2012] are 200 m VMRs), which compares well to the April monthly average and maximum at Galápagos of 0.33 ± 0.17 pptv (IO$_3^-$ = 0.7 ± 0.4 pptv) and 0.57 pptv (IO$_x$ = 1.2 pptv), respectively. The corresponding values of salinity and SST were higher along the cruise track in April 2010 than the April 2011 average at Galápagos (Figure 7).

[57] In an attempt to derive a source function of physical oceanic parameters providing a spatial and temporal description of IO$_3^-$ in the eastern Pacific, a composite of the IO$_3^-$ HaloCAST-P and CHARLEX 1000 m VMRs datasets has been constructed by merging the daily averages obtained during the cruise (~4° were covered in 1 day) and the monthly averages obtained from the ground-based campaign. Strong linear correlation is found between this composite and SST ($R = 0.77$, $p < 0.001$), giving a slope of 0.035 ± 0.005 pptv °C$^{-1}$. Strong correlation between SST and IO itself is also observed. Adding a linear term dependent on salinity to the model does not contribute significantly to explain the variability in IO or IO$_3^-$, while this exercise provides evidence of a general link between ocean physical variables and the reactive iodine loading and shows that SST accounts for a large fraction of the IO$_3^-$ variability, it must be considered as semiquantitative, since IO$_3^-$ is derived in part from model calculations and, in the case of the HaloCAST-P data, calculated O$_3$ from a global model is also used to derive it from the IO observations (O$_3$ measurements were not available during the cruise). Note also that iodine emissions are likely to be dependent on the partitioning of iodine into I$^-$ [Carpenter et al., 2013], which is in principle independent of salinity. Thus, while salinity would account for very small changes of total iodine concentration in sea water (dilution) or would be a marker for mixing of different water masses with characteristic iodine content, it would not account for the latitudinal variation of I$^-$ in the ocean surface. In fact, the latitudinal dependence of IO$_3^-$ reported by [Mahajan et al., 2012] matches remarkably well the latitudinal variation.
of $\Gamma^-$ in the Pacific and the Atlantic Oceans [Tsunogai and Henni, 1971; Truesdale et al., 2000].

Previous LP-DOAS IO measurements in the tropical Atlantic (CV) from November 2006 to June 2007 [Read et al., 2008] with the same instrument as used in the present study are higher than the LP-DOAS detection limit and the MAX-DOAS measurements reported here ([IO] = 1.4 ± 0.8 pptv and [IO$_3$] = 1.7 pptv in CV compared to [IO] = 0.44 ± 0.16 pptv and [IO$_3$] = 0.8 ± 0.3 pptv in Galápagos). Although as pointed out before, the MAX-DOAS measurements in this study are not directly comparable to surface LP-DOAS measurements, the LP-DOAS in Galápagos did not make any positive detection over the average 0.9 pptv DL. In the tropical Atlantic, most of the IO appears in the form of IO due to much higher O$_3$ VMRs, and no clear seasonal cycle was observed beyond the instrumental uncertainty. During the November 2006 to June 2007 period, SST seasonal variation at CV was significantly narrower (19–24°C) than in Galápagos during the CHARLEX campaign (19–28°C), and salinity was significantly higher at CV, with values of 36.4 ± 0.4 psu, which could explain the higher, nearly constant IO$_3$. CDOM was significantly larger north (prevailing wind origin) of CV than south of Galápagos, but the strong seasonal change of CDOM at CV was not correlated to any IO$_3$ seasonality. Chl-α north of the CV archipelago was significantly lower than in the Galápagos Islands during the CHARLEX study.

High IO slant columns from satellite observations (single pixel monthly averages up to 8 × 10$^{12}$ molecule cm$^{-2}$ monthly averages, DL = 3–7 × 10$^{12}$ molecule cm$^{-2}$) over the eastern Pacific during 2005 have been reported [Schönhardt et al., 2008]. An important caveat to these observations is the poor signal-to-noise ratio of the retrieval and therefore a high sensitivity to the fit settings, which led the authors of this work to recommend treating the results with caution. A more thorough discussion of these observations was presented by Schönhardt [2009], who reported a time series from 2005 to 2007 of spatially averaged (5°N–10°S, 80°W–100°W) and daily averaged IO columns. The average IO column for this period is about 3 × 10$^{12}$ molecule cm$^{-2}$ (4 × 10$^{12}$ molecule cm$^{-2}$ 1σ standard deviation, 8 × 10$^{12}$ molecule cm$^{-2}$ maximum), with monthly averages ranging from 2 × 10$^{12}$ molecule cm$^{-2}$ to 4 × 10$^{12}$ molecule cm$^{-2}$ (no significant seasonal variation can be discerned). Assuming a unit air mass factor, the slant column is equal to the vertical column, and with a box profile height of 1 km, a 3 × 10$^{12}$ molecule cm$^{-2}$ vertical column converts to 1.4 pptv. This is about a factor of 2 larger than the highest MBL-averaged IO VMRs reported here and 3 times larger than the highest IO monthly averaged MBL VMRs derived from MAX-DOAS in the present study (~0.5 pptv). If IO was concentrated in the lowermost 100 m, then the average VMR would be 14 pptv across the 5°N–10°S, 80°W–100°W box according to the satellite observations, contrasting with the 0.9 pptv LP-DOAS detection limit. Since IO most likely shows a profile decreasing with height in the MBL [Mahajan et al., 2010b], a 3 × 10$^{12}$ molecule cm$^{-2}$ satellite vertical column would correspond to a surface VMR much larger than 1.4 pptv. In addition, the results of the HaloCAST-P cruise [Mahajan et al., 2012] reveal a spatial distribution of IO inconsistent with the published satellite maps. Therefore, the field measurements of IO from the present study are not consistent with the satellite observations over the eastern Pacific. However, it should be remembered that the satellite measurements would also be sensitive to IO located higher up in the free troposphere.

### 3.6. Impact of Halogens on Ozone Depletion and New Particle Formation

SCR-PBM can be considered as a background rural area. The closest road to the site and the seaport are located about 160 m and 400 m away, respectively, nearly always downwind of the inlet, and both of them had a small impact over the samples. Particles related to rural activity from 6:00 to 18:00 local time can possibly contribute to the background aerosol levels. New particle formation events peaking at ~3500 particles cm$^{-3}$ (3–9 nm) and ~5000 particles cm$^{-3}$ (>3 nm) were observed at SCR-PBM. When correlated to radiation and wind direction, higher particle numbers were seen when the wind was coming from the SE, i.e., the air masses passed over the densely wooded southern slopes of the island, and much smaller when the wind blew from the south and southwest, passing over a much narrower barren strip of land. The absence of photolytic particle formation at the SCR-LBR site when sampling oceanic air masses suggests that the observations at SCR-PBM were most probably caused by secondary organic aerosol formed by organic emissions from the local vegetation or other local emissions. The coastal particle measurements at SCR-LBR were independent of solar radiation, wind direction, and the rest of meteorological variables, with average total particle numbers of 400–500 particles cm$^{-3}$ typical of a coastal clean environment [Brechtle et al., 1998; Heintzenberg et al., 2000]. No indication of new particle formation could be discerned in the data. According to [Mahajan et al., 2010b], more than 7 pptv of IO would be required to form a few hundred new particles of 20 nm diameter if the background aerosol surface area is 10$^{-7}$ cm$^2$, whereas the simultaneous MAX-DOAS measurements indicated IO VMRs an order of magnitude smaller.

We have used the model THAMO (see above) constrained by observations of O$_3$, NO, and meteorological variables in order to estimate the impact of the observed halogen loading on MBL O$_3$ depletion. Two O$_3$ scenarios are considered: (i) 25 ppbv (cold season) and (ii) 8 ppbv (warm season). For each of these scenarios, runs for different IO$_3$ loadings spanning the range of observations in Galápagos have been carried out to determine the corresponding daily O$_3$ destruction rates, which are shown in Figure 11. In all cases, the BrO$_3$ loading (0.5 pptv BrO$_3$, corresponding to the LP-DOAS detection limit) is fixed. Since the reactions of halogen oxides catalytically destroy O$_3$, photochemical destruction rates are higher for higher halogen oxide VMRs, i.e., for higher O$_3$ VMRs. On the other hand, the MBL-averaged reactive iodine loading has also a seasonal cycle, such that the maximum IO$_3$ occurs for the lowest O$_3$. Therefore, the halogen-driven MBL-averaged O$_3$ loss keeps approximately within the same range throughout the year, e.g., for 25 ppbv of O$_3$ and 0.75 pptv of IO$_3$, 0.6 ppbv day$^{-1}$ of O$_3$ are destroyed, while for 8 ppbv of O$_3$ and 1.25 pptv of IO$_3$, 0.5 ppbv day$^{-1}$ of O$_3$ are destroyed (note that this is 2.4% and 6.3%, respectively, of the absolute O$_3$ concentration in each case). In the cold season (September–October 2010, 25 ppbv O$_3$) 1.25 ppbv day$^{-1}$ is destroyed by HO$_x$. 

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photochemistry according to the model. Thus, ~30% of the total O₃ loss (1.85 ppbv day⁻¹) is caused by halogens. The annual average contribution of halogens to O₃ depletion in CV is larger by nearly a factor of 2 (56%). Finally, the annual average O₃ loss rate due to halogens in CV (1.8 ppbv day⁻¹, ~7% of average total O₃) is a factor 3.5 larger than in Galápagos (~0.5 ppbv day⁻¹, ~5% of average total O₃). Note that since BrO could not be detected over the 0.5 pptv DL, the calculated O₃ depletion rates due to halogens in Galápagos are upper limits.

4. Conclusions

[62] The results of the long-term CHARLEX ground-based field study, together with the recently reported spatial distribution of IO obtained during the HaloCAST-P cruise, show consistently low concentrations of reactive iodine species in the eastern Pacific MBL. Both the low levels and the spatial distribution observed indicate that the recent satellite detection of IO over this region is inconsistent with the iodine loading in the MBL. This does not necessarily mean that the satellite retrievals are incorrect, since a distribution higher up in the free troposphere cannot yet be ruled out and such a possibility is currently being investigated.

[63] Emission of iodine compounds is most likely dependent on multiple factors. Reactive iodine in the MBL is antecorrelated with Chl-α and CDOM, thus suggesting that biological activity plays a minor role in the dominant emission mechanism or indeed acts as an inhibiting factor for iodine sources rather than being related to a production mechanism. A seasonal cycle can be observed in IOₓ, which is best explained by multilinear correlation with SST and salinity. Positive correlation with SST is indicative of enhanced phase transfer of iodine source gases from the ocean to the atmosphere. Correlation with salinity (possibly a proxy for iodide concentration in seawater in the equatorial eastern Pacific) is suggestive of an abiotic mechanism limited by availability on iodide in seawater. In general, the correlations observed in this study are in agreement with the ones observed in the HaloCAST-P cruise [Mahajan et al., 2012].

[64] Higher than background CH₃I VMRs at the ISB site (~2 pptv average) are consistent with frequently enhanced biological activity around the coast of the Isabela Island. Such local emissions would not contribute significantly to the observed reactive iodine loading, although the contribution of the background CH₃I (~1 pptv measured in the HaloCAST-P cruise in 2010 [Mahajan et al., 2012] and in SCR-PBM in 2004 [Yokouchi et al., 2008]) to IOₓ is not negligible (~30%).

[65] The absence of substantial photolytic O₃ loss during most of the campaign and the absence of particle formation events attributable to open ocean sources are consistent with low halogen concentration in the tropical Pacific Ocean. With the observed levels of IO and BrO, a maximum of 30% of the daily photochemical loss of O₃ can be attributed to iodine and bromine chemistry, and nucleation of iodine oxides would be insignificant. The picture emerging from the CHARLEX and HaloCAST-P campaigns and other cruises in the eastern and western Pacific [Peters et al., 2011; Volkamer et al., 2011] is of unexpectedly low reactive iodine loading in the tropical Pacific O3 MBL, insufficient for substantial O₃ depletion and particle formation. In the tropical Atlantic [Read et al., 2008; Mahajan et al., 2010b] (and possibly also in the tropical Indian ocean [Oetjen, 2009]), higher levels of iodine and bromine have a more significant combined impact on MBL O₃ depletion but are not sufficient for particle formation either. These converging pieces of evidence indicate that iodine chemistry is, contrary to the starting hypothesis of our two campaigns, unlikely to have significant effects on new particle formation in the present-day tropical MBL, while the impact on surface ozone can be more or less significant depending on the regional MBL halogen loading. Future work should also concentrate on free troposphere studies, where a relatively low loading of iodine has been shown to efficiently deplete ozone [Saiz-Lopez et al., 2012b] and could have a more significant climatic impact.

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