Full latitudinal marine atmospheric measurements of iodine monoxide

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Abstract. Iodine compounds destroy ozone (O_3) in the global troposphere and form new aerosols, thereby affecting the global radiative balance. However, few reports have described the latitudinal distribution of atmospheric iodine compounds. This work reports iodine monoxide (IO) measurements over unprecedented sampling areas from Arctic to the Southern Hemisphere and spanning sea surface temperatures (SSTs) of approximately 0°C to 31.5°C. The highest IO concentrations were observed over the Western Pacific warm pool (WPWP), where O_3 minima were also measured. There, negative correlation was found between O_3 and IO mixing ratios at extremely low O_3 concentrations. This correlation is not explained readily by the "O_3-dependent" oceanic fluxes of photolabile inorganic iodine compounds, the dominant source in recent global-scale chemistry-transport models representing iodine chemistry, and rather implies that "O_3-independent" pathways can be similarly important in the WPWP. The O_3-independent fluxes result in a 15% greater O_3 loss than that estimated for O_3-dependent processes alone. The daily O_3 loss rate related to iodine over the WPWP is as high as approximately 2 ppbv despite low O_3 concentrations of ~10 ppbv, with the loss being up to 100% greater than that without iodine. This finding suggests that warming SST driven by climate change may affect the marine atmospheric chemical balance through iodine–ozone chemistry.

1 Introduction

Halogens play an important role in tropospheric and stratospheric chemistry through the catalytic destruction of ozone (O_3), which affects the atmosphere's oxidizing capacity and the radiative balance of the Earth (Alicke et al., 1999; Koenig et al., 2020; Read et al., 2008; Saiz-Lopez et al., 2012; Saiz-Lopez et al., 2014; Simpson et al., 2015). Iodine, in particular, is

30 potentially important in tropospheric chemistry because of its rapid reactions, although its concentration in the troposphere is low compared to that of chlorine and bromine. Iodine also forms aerosol particles; it can thereby affect the global radiative balance (O'Dowd et al., 2002; Sipila et al., 2016; Gómez-Martín et al., 2020; Baccarini et al., 2020; Gómez-Martín et al., 2021).

Because of their low concentrations in the atmosphere, iodine compounds are difficult to quantify. Few reports have attempted to clarify their regiona006C to global-scale sources and roles in atmospheric chemistry (Großmann et al., 2013;

35 Mahajan et al., 2012; Prados-Roman et al., 2015a; Dix et al., 2013; Volkamer et al., 2015). In the past, the primary source of iodine in the troposphere has long been regarded as organic compounds in coastal areas (Davis et al., 1996; Carpenter et al., 2012; Prados-Roman et al., 2015a). However, results of recent studies suggest that iodine compounds over the open ocean are emitted from inorganic sources following O_3 deposition over the ocean surface (Carpenter et al., 2013; Macdonald et al., 2014; Prados-Roman et al., 2015a). The inorganic sources are now regarded as the dominant emission term over the oligotrophic

40 oceans in the global-scale chemistry-transport models representing iodine chemistry (e.g., Saiz-Lopez et al., 2014; Sekiya et al., 2020).

This study specifically examines iodine monoxide (IO) in the marine boundary layer over the open ocean from the wide latitudinal bands. Specifically, we examine processes occurring over the tropical western Pacific, where the global sea surface temperature (SST) reaches a maximum (warm pool) and where O_3 minima have been reported (Rex et al., 2014; Kanaya et al.,

45 2019; Kley et al., 1996). Actually, IO observations in environments with SSTs of >30°C are limited. Observations of IO have been made in the tropics, but only for short time periods with SST > 30°C if any (Großmann et al., 2013; Dix et al., 2013; Prados-Roman et al., 2015a). Although the importance of halogen chemistry as a driver of O_3 losses in this region has been suggested (Großmann et al., 2013; Koenig et al., 2017), this point has yet to be examined in the context of full latitudinal distributions.

50 The initial production of atmospheric inorganic iodine species has not been fully examined in an environment where extremely low O_3 concentrations (<10 ppb) are observed. Over the Atlantic Ocean (in Cape Verde), long-term observations of iodine and ozone have been conducted, but they were in higher O_3 environments of approximately 20 ppbv (Read et al., 2008). We therefore examined IO variations over the tropical western Pacific and their potential contributions to regional O_3 losses, with emphasis on SST as a potential key parameter controlling the initial iodine emissions. The global SST maximum is

55 observed in the tropical western Pacific, but observations reported from earlier studies only took place in the surrounding regions of the maximum (Großmann et al., 2013; Prados-Roman et al., 2015a). Investigation of iodine variations in the tropics is also important for elucidating the stratospheric chemical balance (Koenig et al., 2017) because transport from the troposphere to the stratosphere occurs through the Tropical Tropopause Layer (Takashima et al., 2008; Saiz-Lopez et al., 2015; Koenig et al., 2017; Holton et al., 1995). In fact, it is particularly important over the tropical western Pacific.

60 For this study, using the multi-axis differential optical absorption spectroscopy (MAX–DOAS) remote sensing technique, IO observations were made to quantify IO concentrations over the open ocean, covering the widest latitudinal range ever examined with a single instrument. The technique uses scattered solar radiation at several elevation angles to obtain atmospheric aerosol and gas profile concentrations (Hönninger et al., 2004; Wagner et al., 2004; Wittrock et al., 2004; Sinreich

et al., 2005; Frieß et al., 2006; Kanaya et al., 2014). MAX–DOAS generally measures trace-gas contents over a long light path
(up to 10–20 km) at low elevation angles. The long light path enables the detection of low concentrations of species of interest
at near-surface altitudes. MAX–DOAS is therefore useful for quantifying low-abundance tropospheric trace gases such as IO
over the open ocean.

Multi-platform measurements by MAX–DOAS from aircraft (Koenig et al., 2017; Volkamer et al., 2009) and ships
(Großmann et al., 2013; Takashima et al., 2012; Volkamer et al., 2009) have been developed in recent years. Earlier studies
have retrieved IO concentrations (typically < 1 pptv) in the marine boundary layer over the open ocean from shipboard MAX–
DOAS measurements (Großmann et al., 2013; Mahajan et al., 2012; Prados-Roman et al., 2015a). Since 2008, the Japan
Agency for Marine–Earth Science and Technology (JAMSTEC) has undertaken an unprecedented set of MAX–DOAS
measurements on board the Research Vessels (R/Vs) *Kaiyo*, *Mirai*, and *Kaimei* around the world (Takashima et al., 2012).
This report presents IO and O_3 variations over the open ocean from the Arctic to the Southern hemisphere observed on RV
Mirai between 2014–2018.

2 Methodology

2.1 Iodine monoxide observations from ship-based MAX–DOAS measurements

The shipboard MAX–DOAS apparatus used for this study comprised two main components: an outdoor telescope and an
indoor UV–Vis spectrometer (SP-2358; Acton Research Corp., coupled to a PIXIS-400B back-illuminated CCD detector;
Teledyne Princeton Instruments). These were connected using a 10–14 m long fiber-optic cable (100 µm radius, 60-core or
40-core). The telescope unit was developed jointly by the Japan Agency for Marine–Earth Science and Technology
(JAMSTEC) and PREDE Co. Ltd. (Tokyo, Japan). The movable prism of the telescope unit rotates for elevation angles (ELs)
of 3°, 5°, 10°, 30°, and 90°. The EL is changed every minute to observe scattered sunlight. The target EL is attained by adjusting
the angle of the prism actively, and by considering the angle of the ship's roll (Takashima et al., 2016). The telescope line-of-
sight was off the starboard side of the ship with a field of view of approximately 1.0°. The spectrometer was housed in an
adiabatic plastic box with the temperature held constant at 35°C ± 0.1°C using a temperature controller (KT4; Panasonic Inc.,
Japan). The CCD was cooled to −70°C. The spectrometer was equipped with a 600 line mm⁻¹ grating at 300 nm. The slit width
was 100 µm. The typical exposure time was 0.1–0.2 s.

Spectral data were selected for analysis when the EL was within ±0.5°of the target. Data were analyzed using the DOAS
method (Platt and Stutz, 2008). A nonlinear least-squares spectral fitting procedure was used to derive differential slant column
densities (DSCDs) of the oxygen collision complex (O_2–O_2 or O_4) and IO using the QDOAS software package (Danckaert et
al., 2017), in which absorption cross-section data presented in Table 1 were used. For O_4 and IO retrievals, 425–490 nm and
415–438 nm fitting windows were applied, respectively. Examples of fitting results and the time series of DSCDs are presented
respectively in Figures 1 and 2. The typical fitting error of the IO DSCDs was approximately 1×10^{12} molecules cm⁻², with a
detection limit of approximately 4×10^{12} molecules cm⁻² (2σ).

The Mexican Maxdoas Fit (MMF) retrieval algorithm (Friedrich et al., 2019) was used for retrieval of IO profiles and vertical column densities. MMF applies the optimal estimation method and uses a two-step approach in which the aerosol profile is first retrieved from O_4 DSCDs. Then, the IO profile is retrieved from the IO DSCDs using the earlier retrieved aerosol profile in the forward model. We used VLIDORT (Spurr, 2006) as the forward model in a pseudo-spherical multiple-scattering setting. Only intensity information and its analytically calculated Jacobians were used. No other Stokes parameter was used. MMF was used in logarithmic retrieval space on a retrieval grid of up to 4 km with 200 m layer height.

Both *a priori* profiles were constructed as constant below 500 m with an exponentially decreasing profile above 500 m for aerosol and IO profiles. The *a priori* aerosol optical depth was set as 0.18. The *a priori* IO was set to 2.5×10^{12} molecules cm^{-2}. The Sa matrix for both aerosol and IO retrieval was constructed using the square of 100% of the *a priori* profile on the diagonal and a correlation length of 200 m. For the aerosols, the only retrieved quantity was the partial aerosol optical depth per layer. Therefore, in the forward model, a constant single scattering albedo of 0.95 was used for both retrievals: aerosol and IO. The phase function moments were constructed using the Henyey–Greenstein phase function (Henyey and Greenstein, 1941) with a constant asymmetry factor of 0.72. The surface albedo in the forward models was set as 0.06. The observed IO contents might be a little low compared with those from earlier studies conducted over the open ocean because of inaccuracy of the water–vapor cross-section used in earlier retrievals (Lampel et al., 2015).

2.2 Zero-dimensional photochemical box model with iodine chemistry

A zero-dimensional photochemical box model (Kanaya et al., 2007a; Kanaya et al., 2007b) based on the Regional Atmospheric Chemistry Mechanism (RACM) (Stockwell et al., 1997) and custom iodine chemistry was updated to include 91 chemical species and 275 reactions (reactions of iodine chemistry added to RACM are presented in Table 3). It was used to simulate the time evolution of mixing ratios of O_3 (initially 18 ppbv) and iodinated species in the boundary layer with assumed height of 500 m over the equatorial Pacific region, where the maximum concentrations of IO and minimum concentrations of O_3 were observed. For O_3, dry deposition at a velocity of 0.04 cm s^{-1} was considered (Pound et al., 2020). Entrainment flux of 1.2×10^8 molecules cm^{-2} s^{-1} was assumed for NO_2, for which the initial mixing ratio was assumed to be 15 pptv. Fluxes of hypoiodous acid (HOI) and I_2 from the ocean surface were estimated (Carpenter et al., 2013) as 8.4×10^7 and 2.6×10^6 molecules cm^{-2} s^{-1}, respectively, at 10 ppbv of O_3, for an aqueous I^- concentration of 74 nM and wind speed of 5 m s^{-1} (8.9×10^7 molecules cm^{-2} s^{-1} as total HOI/I_2 (= HOI + 2I_2) flux). The I^- concentration was referred from the nearest observation data at 12°N and 158°E (Tsunogai and Henmi, 1971). The assumed wind speed was from observations made during MR14-06 cruise over the region. For Case 1a, they were assumed to be linearly dependent on O_3, which is consistent with Carpenter et al. (2013). For Case 1b a 25% reduction of the flux was assumed, potentially because of the presence of sea-surface microlayer or dissolved organic matters (Shaw and Carpenter, 2013; Tinel et al., 2020). The blue band of Figure 3 represents the range of Cases 1a and 1b, representing the case with "O_3-dependent" fluxes. In Cases 2a and 2b, the O_3-dependent flux in Case 1a was reduced to half and compensated by "O_3-independent" inorganic iodine fluxes of 3.3 (or 6.6) $\times 10^7$ molecules cm^{-2} s^{-1} (red band of Figure 3, representing the "quasi-O_3-dependent" case). As a reference, a hypothetical case (Cases 3a and 3b) with

purely "O_3-independent" flux of the magnitude of 9.9 (or 13) $\times 10^7$ molecules cm^{-2} s^{-1} was also tested (orange band of Figure

130   3, representing the "purely O_3-independent" case). The time-dependent simulations continued for five days with evaluation of

the mixing ratio of O_3 and its relation with IO involving daytime averages (0600–1800 ship local time) over the first to fourth

days. Dry deposition velocities of iodine species (I, IO, HI, HOI, OIO, I_2O_2, INO, INO$_2$, IONO$_2$, and I_2) were assumed to be 1

cm s^{-1}.

2.3 Backward trajectory calculation

135   The origins of airmasses over the tropical western Pacific were investigated using five-day backward trajectory calculations

(Takashima et al., 2011) based on meteorological analysis data of the European Centre for Medium-range Weather Forecasts

(ECMWF).

2.4 In situ gas measurements

For measurements of O_3 and CO, ambient air was sampled using approximately 20 m of Teflon tubing (6.35 mm outer

140   diameter) from the bow (Kanaya et al., 2019). To avoid contamination from ship exhaust, 1-min data deviated more than 1σ

of the hourly average were deleted. The O_3 and CO concentrations were measured respectively using UV and infrared

absorptions with O_3 and CO monitors 49C and 48C (Thermo Scientific, USA). O_3 concentrations observed from the R/V *Mirai*

cruises presented in Table 3 are shown in Figure S1.

3 Results and Discussion

145   The IO contents (differential slant column densities (DSCDs) for an elevation angle of 3°) observed from the R/V *Mirai* during

seven research cruises during 2014–2018 are presented in Figure 4. The cruises are presented in Table 3. Although observations

were limited to some seasons and years (e.g., Arctic measurements were limited to the Northern Hemisphere summer), whole

latitudinal bands were covered from 74°N to 67°S, and strong latitudinal variations of IO concentrations were observed, with

a maximum detected clearly in the tropics (10°S – 10°N), but not at higher latitudes in either hemisphere. Over Southeast Asia

150   (near Indonesia), high IO concentrations were sometimes observed near coastal areas. The highest values of up to

approximately 2×10^{13} molecules cm^{-2} (DSCD) were also observed in the tropical western Pacific, with wide variations at

global SST maxima (>30°C). From similar earlier studies (Gómez-Martín et al., 2013; Großmann et al., 2013; Mahajan et al.,

2012) no data obtained under very high SST conditions over a long period were reported. Therefore, our IO observations at

SST maxima (up to 31.5°C) and during more than two weeks represent the most comprehensive measurements of reactive

155   iodine over the tropical Western Pacific warm pool (WPWP).

Specifically regarding IO variations over the tropical western Pacific, we found IO contents (vertical column densities

(VCDs)) of approximately 0.7–1.8 $\times 10^{12}$ molecules cm^{-2} (Figure 5). Five-day backward trajectories indicate that air masses

in this region originated from the open ocean (Figure 5). The carbon monoxide (CO) content was constantly low (60 ppbv,

Figure 6), which is also consistent with an air mass originating from the open ocean. In addition, the chlorophyll content, based

160   on satellite MODIS measurements (NASA Level-3 ver. 2018) in the source region, was also low (Figure 5), implying that any

organic source of iodine is expected to be negligible. The IO data collected over the tropical western Pacific are consistent

with I⁻ variations reported in earlier studies (Chance et al., 2014; Chance et al., 2019; Sherwen et al., 2016), showing an

increase of I⁻ concentration with SST.

For the time series of IO concentrations near the ocean surface (0–200 m height, Figure 7), the values ranged from

165   approximately 0.3–0.8 pptv, with wide variations over a timescale of a few days. The IO concentration near the surface depends

on the shape of the *a priori* profile used for the retrieval, but day-to-day variations near the surface were unaffected by the

choice of profile. Insufficient data were retrieved to document diurnal IO variations accurately. At times, the O_3 concentrations

were generally low (<20 ppbv) and extremely low (<10 ppbv) (Figure 7). One unique finding was that, even under low-O_3

conditions, negative correlation was found between IO and O_3 concentrations in the daily dataset (Figures 3 and 7). Laboratory

170   studies indicate that high O_3 concentrations can cause emission of iodine from ocean to atmosphere (Carpenter et al., 2013;

Macdonald et al., 2014; Sakamoto et al., 2009). This "O_3-dependent" iodine release has been regarded as being more dominant

than other "O_3-independent" types of emission, including photo-labile iodocarbons such as CH_2I_2, CH_2ICl, and their

subsequent photolysis over the open oceans in every global-scale chemistry transport model representing iodine chemistry

(Saiz-Lopez et al., 2014; Sekiya et al., 2020; Sherwen et al., 2016). However, with an "O_3-dependent" HOI/I_2 flux of

175   approximately 9×10^7 molecules cm^{-2} s^{-1} (section 2.2), as expected under an O_3 mixing ratio of approximately 10 ppbv, a

zero-dimensional box model was not able to reproduce the negative correlation found between IO and O_3. Because the initial

HOI/I_2 release flux limited by O_3 in the <12 ppbv mixing-ratio range cannot drive the strong O_3 reduction, the scenario

produced only a positive correlation (Case 1, Figure 3). In contrast, another case in which the "O_3-independent" flux was added

to compensate for the "O_3-dependent" term weakened by a factor of 2 (Case 2, Figure 3) better reproduced the observed trend.

180   The weakened flux might be explained by dissolved organic carbon (Shaw and Carpenter, 2013) or the presence of a sea-

surface microlayer (Tinel et al., 2020) impeding iodine vaporization. The added "O_3-independent" flux is not explainable

solely by flux from photolyses of iodocarbons within the marine boundary layer (approximately 10^7 molecules cm^{-2} s^{-1})

generally assumed in the three-dimensional models (Saiz-Lopez et al., 2014; Sekiya et al., 2020; Sherwen et al., 2016). It

therefore necessitates a survey of missing sources. The third case, with only an "O_3-independent" flux (Case 3, Figure 3) might

185   explain the negative correlation more easily, whereas the total change of the flux type not being simply supported. We therefore

hypothesize that O_3-independent processes are more important than has been represented by recent models. Indeed, a larger

magnitude of organic iodine flux (approximately 7×10^7 molecules cm^{-2} s^{-1}) was reported in the low-latitude Pacific

(Großmann et al., 2013), and would therefore be the most likely cause of the negative correlation. However, that study

(Großmann et al., 2013) relied on assumption of an even larger inorganic iodine emission flux to explain the observed IO

190   concentrations. Therefore, our analysis is the first to suggest that the "O_3-independent" flux can be comparably important to

the "O_3-dependent" flux in this region. Other O_3-independent iodine release mechanisms such as photooxidation of aqueous I⁻

(Watanabe et al., 2019) might also be worth exploring. The modelled net O_3 loss rate due to iodine in Case 2 increased by up

to 100% over that without iodine. The O_3 loss rate in the iodine cycle in Case 2 increased by approximately 15% over that in Case 1 (Table 4).

195   The expectation that a positive correlation between O_3 and IO would occur with O_3-dependent processes over a low O_3 concentration range was also confirmed using three-dimensional global chemistry-transport models including halogen chemistry (Sekiya et al., 2020; Saiz-Lopez et al., 2014) over the tropical western Pacific (Figures S2, S3). An alternative explanation of the observed negative correlation would be the mixing of air masses experiencing different degrees of iodine chemistry. If so, such negative correlation could appear in the chemistry-transport model results. However, this feature was

200   not found and therefore we propose an "O_3-independent" flux. Over the Atlantic, the O_3 mixing ratio rarely reaches these low levels (10 ppbv or less). Therefore such process analyses have not been undertaken there. Under the influence of "O_3-independent" sources, even lower O_3 concentrations would be attainable. Radiative forcing of O_3, as estimated recently with halogen chemistry (Sherwen et al., 2017; Iglesias-Suarez et al., 2020; Saiz-Lopez et al., 2012; Hossaini et al., 2015), might be influenced by the dependence of iodine flux on O_3 concentration, which might play a major role in estimating past and future

205   concentrations of O_3.

The time series of meteorological parameters including wind speed and SST was also investigated, but no clear correlation with O_3 or IO concentration was found on a timescale of a few days (Figure 6). An earlier study (Kanaya et al., 2019) investigating the diurnal variation of O_3 in this area based on a comparison of observational data and a chemical transport model indicated that an as-yet-unidentified O_3 loss might occur over the tropical western Pacific. Our results imply that iodine

210   chemistry plays an important role in O_3 loss in the area of SST maxima, which is regarded as an entry point from the troposphere to stratosphere. Moreover, these results provide insights into the manner by which increasing SST associated with climate change might modify the marine atmospheric chemical balance, which warrants further investigation.

4. Summary

In this study, shipboard multi-axis differential optical absorption spectroscopy (MAX–DOAS), a remote sensing technique, was used during seven research cruises covering the widest latitudinal bands from the Arctic to the Southern Hemisphere as ever made with a single instrument, spanning SSTs of approximately 0°C to 31.5°C, allowing investigation of the variation of IO concentrations. IO was detected at low latitudes. It was particularly abundant over the tropical western Pacific (warm pool), appearing as an "iodine fountain", where SST maxima (>30°C) and O_3 minima are observed.

We report negative correlation between IO and O_3 concentrations over the IO maximum, even under extremely low O_3 conditions, which few earlier studies have demonstrated. This correlation is not explained easily by the O_3-dependent oceanic fluxes of photolabile inorganic iodine compounds adopted for recent simulation studies. Our findings rather imply that "O_3-independent" pathways which release iodine compounds from the ocean are also important. Iodine input to the atmosphere from the ocean surface is greater in areas of higher SST, leading to an "iodine fountain" in the Western Pacific warm pool because the I^- concentration in the ocean surface is likely to be higher in these areas. This higher concentration might contribute to more pronounced O_3 destruction over the Western Pacific warm pool than estimated earlier. Warming SSTs associated with

climate change can change the atmospheric chemical balance through halogen chemistry, warranting further quantitative investigation.

Table 1: Cross-sections of iodine monoxide (IO) and O_4 differential slant column densities used for this study

	Component	Reference
IO	NO$_2$	Vandaele et al. (1998)
	O$_3$	Bogumil et al. (2000)
	H$_2$O	HITEMP* (Rothman et al., 2013)
	IO	Gómez-Martín et al. (2005)
O$_4$	NO$_2$	Vandaele et al. (1998)
	O$_3$	Bogumil et al. (2000)
	H$_2$O	HITEMP (Rothman et al., 2013)
	O$_4$	Thalman and Volkamer (2013)

* Correction factors from Lampel et al. (2015) were applied.

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Table 2: Reactions of iodine chemistry added to RACM

Reactants	Products	A (cm^3 molecule^{-1} s^{-1})	Ea/R (K)	Reference
I + O$_3$	IO + O$_2$	2.10×10^{-11}	830	Sherwen et al. (2016)
I + HO$_2$	HI + O$_2$	1.50×10^{-11}	1090	Sherwen et al. (2016)
IO + NO	I + NO$_2$	7.15×10^{-12}	−300	Sherwen et al. (2016)
IO + HO$_2$	HOI + O$_2$	1.40×10^{-11}	−540	Sherwen et al. (2016)
IO + IO	0.43OIO + 0.71I + 0.43I$_2$O$_2$	9.60×10^{-11}	0	Stutz et al. (1999)
OH + HI	I + H$_2$O	1.60×10^{-11}	−440	Sherwen et al. (2016)
HOI + OH	IO + H$_2$O	5.00×10^{-12}	0	Sherwen et al. (2016)
I + NO$_3$	IO + NO$_2$	4.50×10^{-10}	0	Mcfiggans et al. (2000)
IO + CH$_3$O$_2$	0.25I + 0.254HCHO + 0.25HO$_2$ + 0.75HOI + 0.746ORA1 + 0.004H$_2$O$_2$	1.00×10^{-11}	0	Stutz et al. (1999)
IO + hv	I + O$_3$			Kanaya et al. (2007b)
HOI + hv	I + OH			Kanaya et al. (2007b)
INO$_2$ + hv	0.5I + 0.5NO$_2$ + 0.5IO + 0.5NO			Kanaya et al. (2007b)
IONO$_2$ + hv	0.5IO + 0.5NO$_2$ + 0.5I + 0.5NO$_3$			Kanaya et al. (2007b)

OIO + OH	HOI + O_2	7.00×10^{-12}	0	Kanaya et al. (2007b)
I_2O_2 + hv	I + OIO			Kanaya et al. (2007b)
I + NO_2 (+M)	INO_2 (+ M)	5.40×10^{-12}	0	Kanaya et al. (2003)
INO_2	I + NO_2	$9.94 \times 10^{+17}$	11859	Sherwen et al. (2016)
IO + NO_2 (+M)	$IONO_2$ (+ M)	3.70×10^{-12}	0	Kanaya et al. (2003)
$IONO_2$	IO + NO_2	$2.10 \times 10^{+15}$	13670	Sherwen et al. (2016)
I + NO (+M)	INO (+ M)	4.10×10^{-13}	0	Kanaya et al. (2003)
INO	I + NO	1.40×10^{-1}	0	Kanaya et al. (2003)
OIO + NO	IO + NO_2	1.10×10^{-12}	−542	Sherwen et al. (2016)
IO + ISOP	0.25I + 0.132MACR + 0.855OLT + 0.25HO_2 + 0.179HCHO + 0.75HOI + 0.075H_2O_2 + 0.9OH	1.00×10^{-11}	0	Kanaya et al. (2007b)
IBr + hv	I			Kanaya et al. (2007b)
OIO + hv	I + O_2			Kanaya et al. (2007c)
I_2 + OH	HOI + I	2.10×10^{-10}		Sherwen et al. (2016)
I_2 + NO_3	I + $IONO_2$	1.50×10^{-12}		Sherwen et al. (2016)
I_2 + hv	2I			Alicke et al. (1999)
IO + OIO	I_2O_3	1.5×10^{-10}		Sherwen et al. (2016)
OIO + OIO	I_2O_4	1.5×10^{-10}		Sherwen et al. (2016)
I_2O_2	OIO + I	1.13		Saiz-Lopez et al. (2016)
I_2O_2	IO + IO	0.00532		Saiz-Lopez et al. (2016)
I_2O_4	OIO + OIO	0.0879		Saiz-Lopez et al. (2016)
HOI + NO_3	IO + HNO_3	$2.7 \times 10^{-12} \times (300/T)^{2.66}$		Saiz-Lopez et al. (2016)
I_2O_3 + hv	IO + OIO			Saiz-Lopez et al. (2016)
I_2O_4 + hv	OIO + OIO			Saiz-Lopez et al. (2016)

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Table 3: Research cruises of the R/V *Mirai* that generated data used for this study

Cruise	Period	Area
MR14-06 (leg 1)	8 Nov – 3 Dec, 2014	Western Pacific, Tropics
MR15-04	6 Nov – 21 Nov, 2015	Western Pacific, East Indian Ocean
MR15-05 (leg 2)	14 Jan – 24 Jan, 2016	Western Pacific
MR16-06	24 Aug – 4 Oct, 2016	Arctic Ocean, Bering Sea, North Pacific
MR16-09 (leg 3)	8 Feb – 3 Mar, 2017	Southern Ocean

MR17-05C	25 Aug – 29 Sep, 2017	Arctic Ocean, Bering Sea, North Pacific
MR17-08	22 Nov, 2017 – 17 Jan 2018	Western Pacific, East Indian Ocean

Table 4. Net and process-specific O_3 loss rates in three cases at an O_3 concentration of 10 ppbv, as calculated by the box model

	IO [ppbv]	net loss [ppbv d^{-1}]	HOx/Ox cycle loss [ppbv d^{-1}]	Iodine cycle loss [ppbv d^{-1}]
w.o. iodine	0	−1.06	−1.64	0
Case 1	0.553–0.741	−1.85 – −2.08	−1.62	−0.519 – −0.720
Case 2	0.611–0.851	−1.92 – −2.21	−1.62	−0.579 – −0.844
Case 3	0.723–0.960	−2.05 – −2.34	−1.62	−0.700 – −0.967

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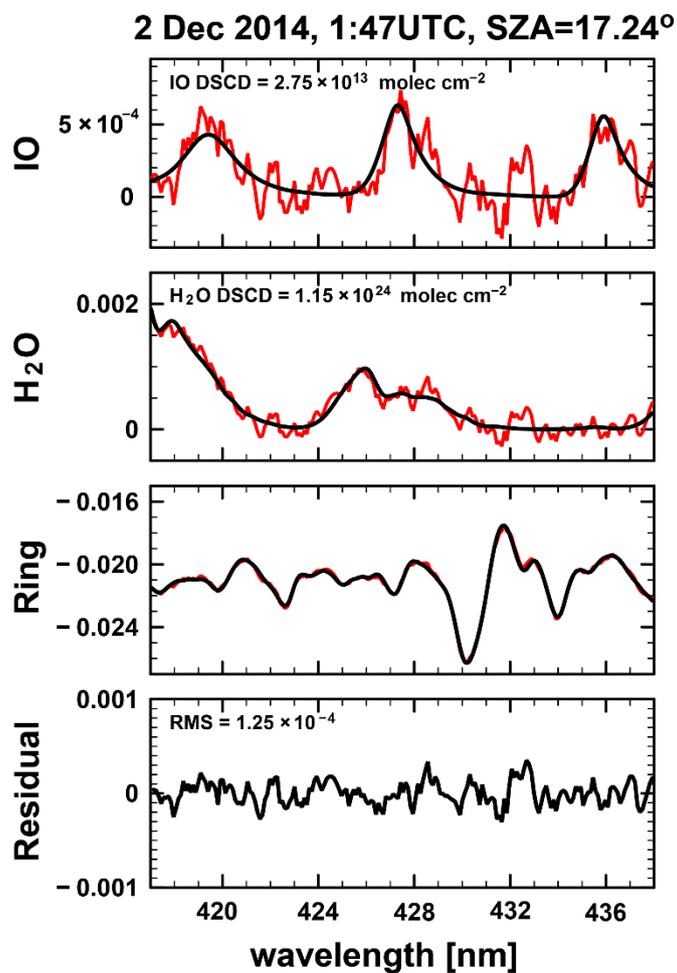
Figure 1: Nonlinear least-squares spectral fitting results for IO concentrations observed on 2 December 2014. The top two panels show fitting for IO and H$_2$O. Black lines represent the cross-section scaled to the spectrum (red) determined by differential optical absorption spectroscopy. The lower two panels show the Ring-effect contribution and the residual spectrum.

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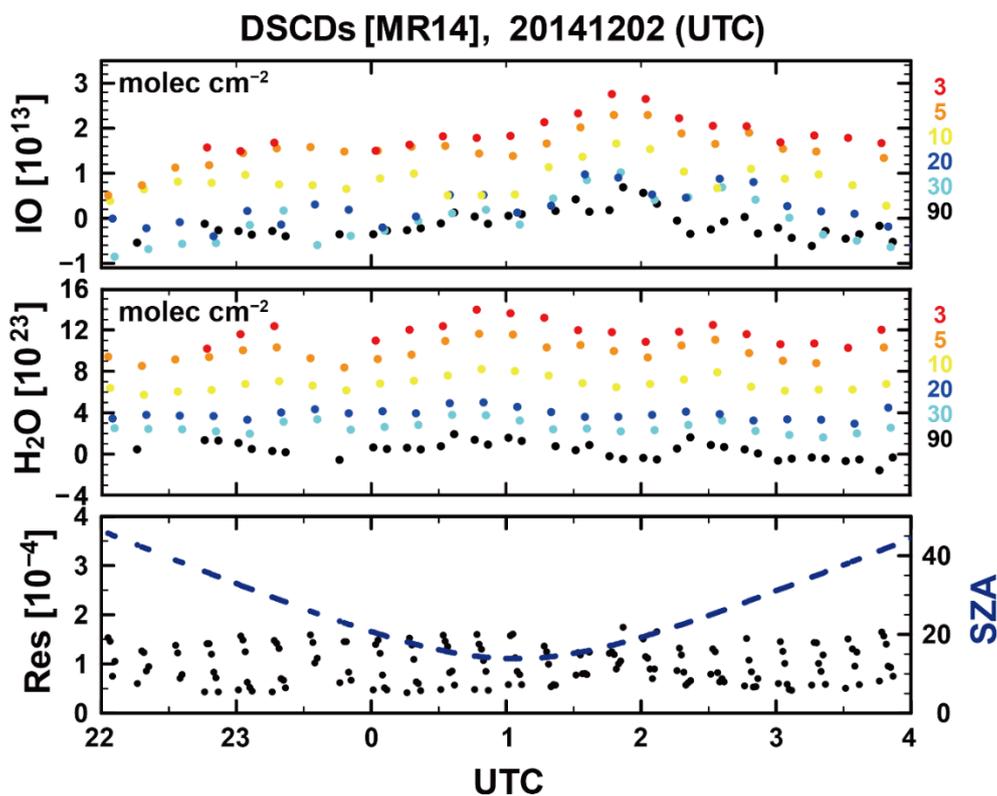
Figure. 2: Time series of IO and H_2O differential slant column densities (DSCDs) for elevation angles of 3°, 5°, 10°, 20°, 30°, and 90°; RMS residual; and the solar zenith angle observed on 1–2 December 2014 over the tropical western Pacific.

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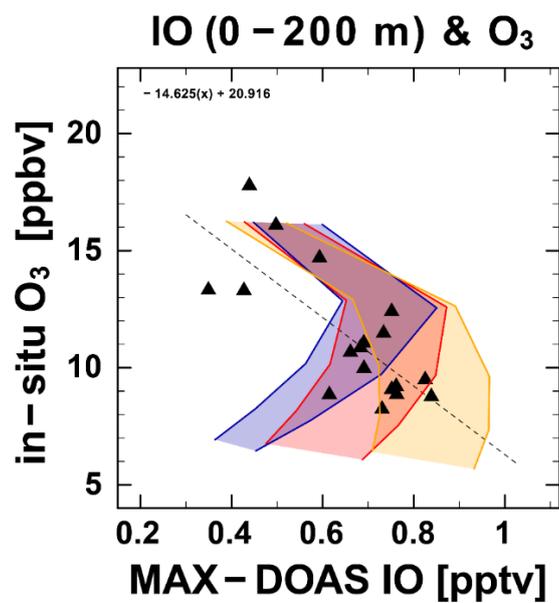
Figure 3: Daily median IO mixing ratio for 0–200 m (pptv) concentrations observed by MAX–DOAS versus daily median *in situ* ozone mixing ratio (ppbv). Results of box-model simulations with "O_3-dependent" (Case 1), "quasi-O_3-dependent" (Case 2), and "pure O_3 independent" (Case 3) emission fluxes of iodine compounds are superimposed respectively as blue-, red-, and orange-shaded areas.
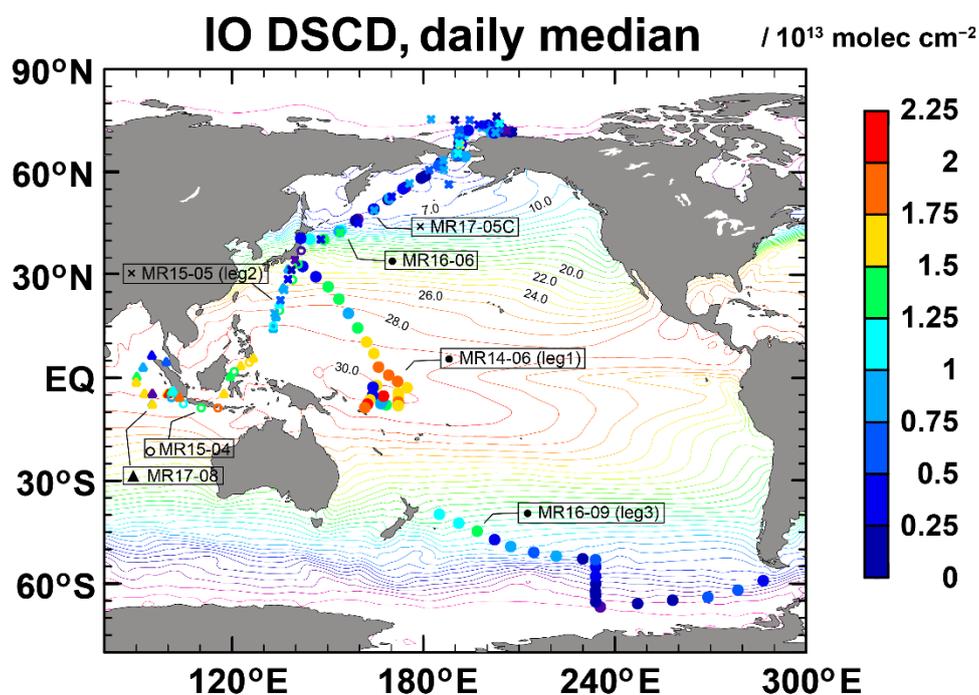
Figure 4: Daily median IO content (differential slant column densities (DSCD) for an elevation angle of 3°; molecules cm^{-2}) observed from
240   the R/V *Mirai* during 2014–2018. Color contours represent the optimum interpolated SST averaged for 2014–2018.
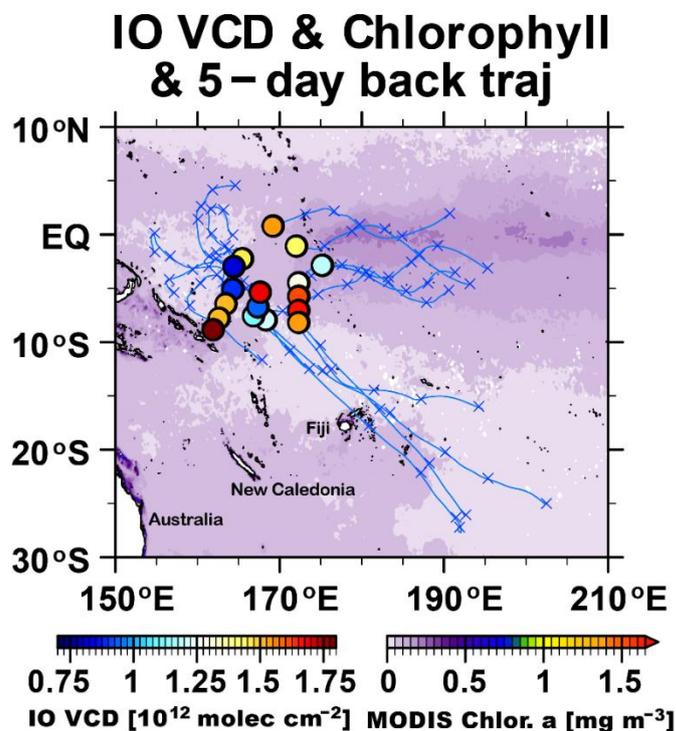
Figure 5: Daily median tropospheric IO vertical column densities (VCDs, molecules cm^{-2}) observed from the R/V *Mirai* during 16 November to 2 December 2014 and chlorophyll-a concentrations observed via satellite (MODIS). Blue crosses and lines represent five-day backward trajectories.
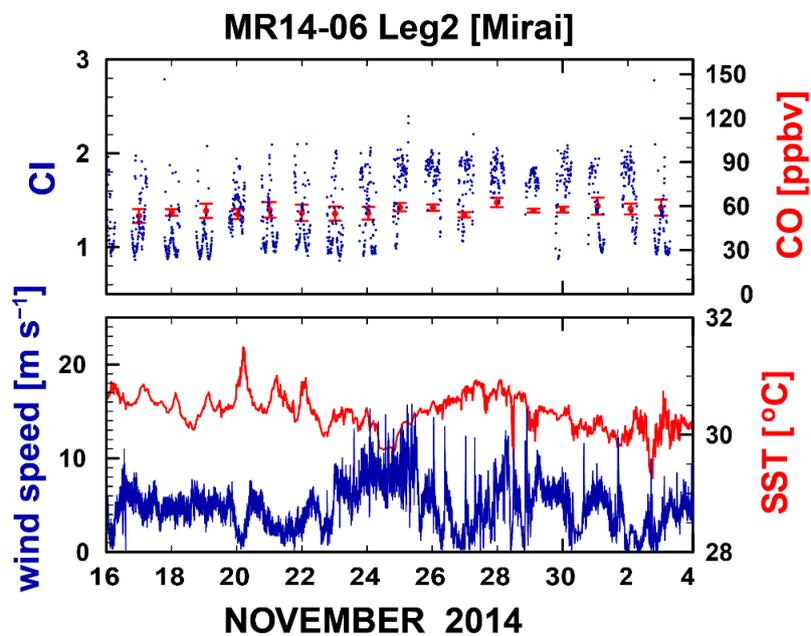
Figure 6: Time series of the CO mixing ratio [ppbv], color index (CI; defined as the ratio of the measured intensities at the two wavelengths of 500 and 380 nm (Takashima et al., 2009)), wind speed (m s^{-1}), and SST (°C).

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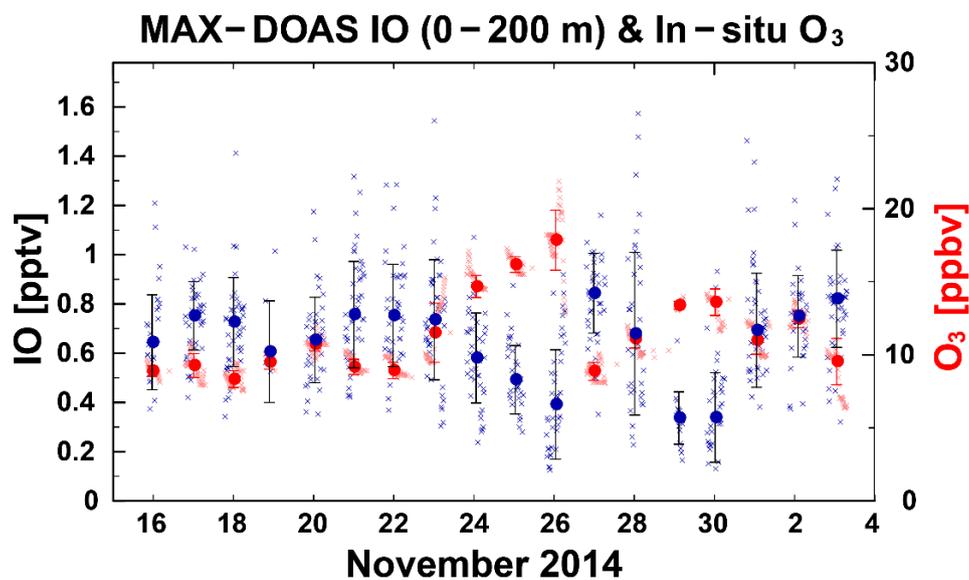
Figure 7: Time series of IO mixing ratio for 0–200 m (blue, pptv) observed by MAX–DOAS, and *in situ* O$_3$ mixing ratio (red, ppbv). Circles and horizontal bars respectively represent the daily median and one standard deviation.

250

Author contributions

HT designed the study, conducted shipboard MAX–DOAS observations and analyses, and wrote the manuscript. YKa proposed the research concept, supported the MAX–DOAS observations, and conducted O_3/CO observations and 0-D box
255   model calculations. KS supported the observations and analysis. MF conducted the retrieval of IO profiles and IO VCDs. MV supported the DOAS analysis. FT, TM, and YKo supported the MAX–DOAS observations. CAC, AS-L, and TS conducted a simulation using a global chemical model. All co-authors provided comments to improve the manuscript.

Supplement

Supporting information accompanies this paper.

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