Full latitudinal marine atmospheric measurements of iodine monoxide

Hisahiro Takashima1,2, Yugo Kanaya2, Saki Kato1, Martina M. Friedrich3, Michel Van Roozendael3, Fumikazu Taketani2, Takuma Miyakawa2, Yuichi Komazaki2, Carlos A. Cuevas4, Alfonso Saiz-Lopez4, and Takashi Sekiya2

1Faculty of Science, Fukuoka University, Fukuoka, Japan
2Japan Agency for Marine–Earth Science and Technology (JAMSTEC), Yokohama, Japan
3Belgian Institute for Space Aeronomy (BIRA-IASB), Brussels, Belgium
4Department of Atmospheric Chemistry and Climate, Institute of Physical Chemistry Rosalolano (CSIC), Madrid, Spain

Correspondence: Hisahiro Takashima (hisahiro@fukuoka-u.ac.jp) and Yugo Kanaya (yugo@jamstec.go.jp)

Received: 13 August 2021 – Discussion started: 18 August 2021
Revised: 3 February 2022 – Accepted: 6 February 2022 – Published: 31 March 2022

Abstract. Iodine compounds destroy ozone (O3) 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 taken over unprecedented sampling areas from the Arctic to the Southern Hemisphere and spanning sea surface temperatures (SSTs) of approximately 0 to 31.5 °C. The highest IO concentrations were observed over the Western Pacific warm pool (WPWP), where O3 minima were also measured. There, a negative correlation was found between O3 and IO mixing ratios at extremely low O3 concentrations. This correlation is not explained readily by the O3-dependent oceanic fluxes of photolabile inorganic iodine compounds, which is the dominant source in recent global-scale chemistry transport models representing iodine chemistry. Actually, the correlation rather implies that O3-independent fluxes can be similarly important in the WPWP. The O3-independent fluxes result in a 15 % greater O3 loss than that estimated for O3-dependent processes alone. The daily O3 loss rate related to iodine over the WPWP is as high as approximately 2 ppbv (parts per billion by volume) despite low O3 concentrations of approximately 10 ppbv, with the loss being up to 100 % greater than that without iodine. This finding suggests that warming SST driven by climate change might affect the marine atmospheric chemical balance through iodine–ozone chemistry.

1 Introduction

Halogenes play an important role in tropospheric and stratospheric chemistry through the catalytic destruction of ozone (O3), 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, 2014; Simpson et al., 2015). Iodine, particularly, is 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; He et al., 2021).

Because of their low concentrations in the atmosphere, iodine compounds are difficult to quantify. Few reports have attempted to clarify their regional- to global-scale sources and roles in atmospheric chemistry (Großmann et al., 2013; Mahajan et al., 2012; Prados-Roman et al., 2015; 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; Carpen-
ter et al., 2012; Prados-Roman et al., 2015a). However, the 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., 2015b). The inorganic sources are now regarded as the dominant emission term over the oligotrophic oceans in the global-scale chemistry transport models representing iodine chemistry (e.g., Saiz-Lopez et al., 2014; Sekiya et al., 2020), although the emission process of inorganic iodine is still insufficiently clear in more recent studies (e.g., Inamdar 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., 2019; Kley et al., 1996). Actually, IO observations in environments with SSTs of $>30 \degree C$ are limited. Observations of IO have been made in the tropics but only for short time periods, with SST $>30 \degree C$, 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.

The initial production of atmospheric inorganic iodine species has not been fully examined in an environment where extremely low $O_3$ concentrations ($<10$ ppbv – parts per billion) are observed. Over the Atlantic Ocean (in Cabo Verde), long-term observations of iodine and ozone have been conducted, but they were in higher $O_3$ environments of approximately 20 ppbv (parts per billion by volume; Read et al., 2008). We, therefore, examined IO variations over the tropical Western Pacific and their potential contributions to regional $O_3$ losses, with an emphasis on SST as a potential key parameter controlling the initial iodine emissions. The global SST maximum is observed in the tropical Western Pacific, but observations reported from earlier studies were only taken in the regions surrounding 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.

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 – parts per trillion by volume) 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; Inamdar et al., 2020). 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 as observed on R/V 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, i.e., an outdoor telescope and an indoor UV–Vis spectrometer (SP-2358 coupled to a PIXIS 400B back-illuminated CCD (charge-coupled device) detector; Acton Research Corporation and Teledyne Princeton Instruments, respectively). 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 $35 \degree C \pm 0.1 \degree C$ using a temperature controller (KT4; Panasonic Inc., Japan). The CCD was cooled to $-70 \degree C$. The spectrometer was equipped with a 600 line per millimeter 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), for which the absorption cross section data presented in Table 1 were used. For O$_4$ and IO retrievals, 425–490 and 415–438 nm fitting windows were applied, respectively. Examples of fitting results and the time series of DSCDs are presented, respectively, in Figs. 1 and 2. The typical fitting error of the IO DSCDs was approximately 1 × 10$^{12}$ molec. cm$^{-2}$, with a detection limit of approximately 4 × 10$^{12}$ molec. cm$^{-2}$ (2σ).

The Mexican MAX-DOAS Fit (MMF) retrieval algorithm (Friedrich et al., 2019) was used for the retrieval of IO profiles and vertical column densities. The version of MMF used in this study is the same as used in Friěß et al. (2019) and Tirpitz et al. (2021) but with adjusted a priori and variance–covariance matrix settings to fit for IO retrieval. 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 (v.2.7; 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 a 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, to examine near-surface areas specifically. The a priori aerosol optical depth was set as 0.18. The a priori IO vertical column density (VCD) was

---

**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.
set to $2.5 \times 10^{12}$ molec. cm$^{-2}$. The a priori covariance matrix $S_a$ 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, i.e., 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. Here, the single scattering albedo, asymmetry factor, and surface albedo were used, similar to the work presented by Großmann et al. (2013). The degrees of freedom (DOF) for the IO retrieval for MR14-06 (leg1) were 1–1.4. Typical averaging kernels for IO are presented in Fig. S1 in the Supplement. It is also noteworthy that the observed IO contents might be a little low compared to 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, b), 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 an 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). An entrainment flux of $1.2 \times 10^8$ molec. cm$^{-2}$ s$^{-1}$ was assumed for NO$_2$, for which the initial mixing ratio was assumed to be 15 pptv. Fluxes of hypiodous acid (HOI) and I$_2$ from the ocean surface were estimated, respectively (Carpenter et al., 2013), as $8.4 \times 10^7$ and $2.6 \times 10^6$ molec. cm$^{-2}$ s$^{-1}$ at 10 ppbv of O$_3$, for an aqueous I$^-$ concentration of 74 nM and wind speed of 5 m s$^{-1}$ ($8.9 \times 10^7$ molec. 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$^\circ$ N and 158$^\circ$ E (Tsunogai and Henmi, 1971). The assumed wind speed was from observations made during MR14-06 cruise over the region. For Case 1a, the fluxes were assumed to be linearly dependent on O$_3$, which is consistent with Carpenter et al. (2013). For Case 1b, a 25% reduction in the flux was assumed, potentially because of the presence of a sea surface microlayer or dissolved organic matter (Hayase et al., 2010, 2012; Shaw and Carpenter, 2013; Tinel et al., 2020). The blue band of Fig. 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) $\times 10^7$ molec. cm$^{-2}$ s$^{-1}$ (red band of Fig. 3, which represents the quasi-O$_3$-dependent case). As a reference, a hypothetical case (Cases 3a and 3b) with a purely O$_3$-independent flux of the magnitude of 9.9 (or 13) $\times 10^7$ molec. cm$^{-2}$ s$^{-1}$ was also tested (orange band of Fig. 3, which represents the purely O$_3$-independent case). The time-dependent simulations continued for 5 d, with the evaluation of the mixing ratio of O$_3$ and its relation with IO involving daytime averages (06:00–18:00 ship local time) over the first to fourth days. Dry deposition velocities of iodine species (I, IO, HI, HOI, I$_2$O$_2$, INO, INO$_2$, IONO$_2$, and I$_2$) were assumed to be 1 cm s$^{-1}$.

### 2.3 Backward trajectory calculation

The origins of air masses over the tropical Western Pacific were investigated using 5 d 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
Table 2. Reactions of iodine chemistry added to RACM.

| Reactants | Products | $A$ (cm$^3$ molec.$^{-1}$ s$^{-1}$) | $E_a/R$ (K) | Reference |
|-----------|----------|----------------------------------|-------------|-----------|
| I + O$_3$ | IO + O$_2$ | $2.10 \times 10^{-11}$ | 830 | Atkinson et al. (2007), Sherwen et al. (2016) |
| I + HO$_2$ | HI + O$_2$ | $1.50 \times 10^{-11}$ | 1090 | Atkinson et al. (2007), Sherwen et al. (2016) |
| IO + NO | I + NO$_2$ | $7.15 \times 10^{-12}$ | -300 | Atkinson et al. (2007), Sherwen et al. (2016) |
| IO + HO$_2$ | HOI + O$_2$ | $1.40 \times 10^{-11}$ | -540 | Atkinson et al. (2007), Sherwen et al. (2016) |
| IO + IO | 0.43IO + 0.71I + 0.43I$_2$O$_2$ | $9.60 \times 10^{-11}$ | 0 | Stutz et al. (1999) |
| OH + HI | I + H$_2$O | $1.60 \times 10^{-11}$ | -440 | Atkinson et al. (2007), Sherwen et al. (2016) |
| HOI + OH | IO + H$_2$O | $5.00 \times 10^{-12}$ | 0 | Riffault et al. (2005), Sherwen et al. (2016) |
| I + NO$_3$ | IO + NO$_2$ | $4.50 \times 10^{-10}$ | 0 | Chambers et al. (1992), McFiggans et al. (2000) |
| IO + CH$_2$O$_2$ | 0.25I + 0.254HCHO + 0.25HO$_2$ + 0.75HOI + 0.746ORA + 0.009H$_2$O$_2$ | $1.00 \times 10^{-11}$ | 0 | Stutz et al. (1999) |
| IO + hv | I + O$_3$ | | | Harwood et al. (1997), Kanaya et al. (2007b) |
| HOI + hv | I + OH | | | Rowley et al. (1999), Kanaya et al. (2007b) |
| INO$_2$ + hv | 0.5I + 0.5NO$_2$ + 0.5I + 0.5NO | | | Sander et al. (2011), McFiggans et al. (2000), Kanaya et al. (2007b) |
| IONO$_2$ + hv | 0.5IO + 0.5NO$_2$ + 0.5I + 0.5NO$_3$ | | | Sander et al. (2011), McFiggans et al. (2000), Kanaya et al. (2007b) |
| OIO + OH | HOI + O$_2$ | $7.00 \times 10^{-12}$ | 0 | Von Glasow (2000), Kanaya et al. (2007b) |
| I$_2$O$_2$ + hv | I + OIO | | | Davis et al. (1996), Kanaya et al. (2007b) |
| I + NO$_2$ (+M) | INO$_2$ (+M) | $5.40 \times 10^{-12}$ | 0 | Alicke et al. (1999), Atkinson et al. (2007), Kanaya et al. (2003) |
| INO$_2$ | I + NO$_2$ | $9.94 \times 10^{-17}$ | 11 859 | McFiggans et al. (2000), Sherwen et al. (2016) |
| IO + NO$_2$ (+M) | IONO$_2$ (+M) | $3.70 \times 10^{-12}$ | 0 | Alicke et al. (1999), Atkinson et al. (2007), Kanaya et al. (2003) |
| IONO$_2$ | IO + NO$_2$ | $2.10 \times 10^{-15}$ | 13 670 | Kaltsoyannis and Plane (2008), Sherwen et al. (2016) |
| I + NO (+M) | INO (+M) | $4.10 \times 10^{-13}$ | 0 | Alicke et al. (1999), Atkinson et al. (2007), Kanaya et al. (2003) |
| INO | I + NO | $1.40 \times 10^{-1}$ | 0 | Alicke et al. (1999), Atkinson et al. (2007), Kanaya et al. (2003) |
| OIO + NO | IO + NO$_2$ | $1.10 \times 10^{-12}$ | -542 | Atkinson et al. (2007), Sherwen et al. (2016) |
| IO + ISOP | 0.25I + 0.132MACR + 0.855OLT + 0.25HO$_2$ + 0.179HCHO + 0.75HOI + 0.075H$_2$O$_2$ + 0.9OH | $1.00 \times 10^{-11}$ | 0 | Analogous to Stutz et al. (1999), Kanaya et al. (2007b) |
| Br$_2$ + hv | I | | | Seery and Britton (1964), Kanaya et al. (2007b) |
| OIO + hv | I + O$_2$ | | | McFiggans et al. (2000), Kanaya et al. (2007c) |
| I$_2$ + OH | HOI + I | $2.10 \times 10^{-10}$ | | Atkinson et al. (2007), Sherwen et al. (2016) |
| I$_2$ + NO$_3$ | I + IONO$_2$ | $1.50 \times 10^{-12}$ | | Atkinson et al. (2007), Sherwen et al. (2016) |
| I$_2$ + hv | 2I | | | Tellinghuisen (1973), Alicke et al. (1999) |
| IO + OIO | I$_2$O$_3$ | $1.5 \times 10^{-10}$ | | Gómez Martín et al. (2007), Sherwen et al. (2016) |
| OIO + OIO | I$_2$O$_4$ | $1.5 \times 10^{-10}$ | | Gómez Martín et al. (2007), Sherwen et al. (2016) |
| I$_2$O$_2$ | OIO + I | 1.13 | | Kaltsoyannis and Plane (2008), Galvez et al. (2013), Gómez Martín and Plane (2009), Saiz-Lopez et al. (2016) |
| I$_2$O$_2$ | IO + IO | $0.00532$ | | Kaltsoyannis and Plane (2008), Galvez et al. (2013), Gómez Martín and Plane (2009), Saiz-Lopez et al. (2016) |
| I$_2$O$_4$ | OIO + OIO | $0.0879$ | | Kaltsoyannis and Plane (2008), Gómez Martín and Plane (2009), Saiz-Lopez et al. (2016) |
| HOI + NO$_3$ | IO + HNO$_3$ | $2.7 \times 10^{-12} \times (300/K)^{2.66}$ | | Saiz-Lopez et al. (2016) |
| I$_2$O$_3$ + hv | IO + OIO | | | Saiz-Lopez et al. (2014, 2016) |
| I$_2$O$_4$ + hv | OIO + OIO | | | Saiz-Lopez et al. (2014, 2016) |
Table 3. Research cruises of the R/V Mirai that generated the data used for this study.

| Cruise       | Period               | Area                                      |
|--------------|----------------------|-------------------------------------------|
| MR14-06 (leg 1) | 8 Nov–3 Dec 2014    | Western Pacific; tropics                   |
| MR15-04      | 6–21 Nov 2015        | Western Pacific; eastern Indian Ocean      |
| MR15-05 (leg 2) | 14–24 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; eastern Indian Ocean |

(diameter) from the bow (Kanaya et al., 2019). To avoid contamination from ship exhaust, 1 min data that deviated more than $\sigma$ from the hourly discrete average were deleted. The typical magnitude of $\sigma$ over the remote ocean was approximately 0.1–0.5 ppbv. 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). The O$_3$ instrument was calibrated twice per year in the laboratory, before and after deployment, using a primary standard O$_3$ generator. The CO instrument was calibrated on board twice per year, on embarking and disembarking of the instrument, using a premixed standard gas. The reproducibility of the calibration was to within 1 % for O$_3$ and 3 % for CO (Kanaya et al., 2019). The O$_3$ concentrations observed from R/V Mirai cruises, presented in Table 3, are shown in Fig. S2.

3 Results and discussion

The IO contents (differential slant column densities (DSCDs) for an elevation angle of 3°) observed from R/V Mirai during seven research cruises during 2014–2018 are presented in Fig. 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 in 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 (near Indonesia), high IO concentrations were sometimes observed near coastal areas. The highest values of up to approximately $2 \times 10^{13}$ molec. cm$^{-2}$ (DSCD) were also observed in the tropical Western Pacific, with wide variations in 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 2 weeks, represent the most comprehensive measurements of reactive iodine over the tropical Western Pacific warm pool (WPWP).

Specifically regarding IO variations over the tropical Western Pacific, we found IO VCDs of approximately $0.7$–$1.8 \times 10^{12}$ molec. cm$^{-2}$ (Fig. 5). The 5 d backward trajectories indicate that air masses in this region originated from the open ocean (Fig. 5). The carbon monoxide (CO) content was constantly low (60 ppbv; Fig. 6), which is also consistent with an air mass originating from the open ocean. In addition, the chlorophyll content, based on satellite MODIS measurements (MODIS-Aqua, MODISA, Level 3 version 2018) in the source region, was also low (Fig. 5), implying that any organic source of iodine can be expected to be negligible (although we also must consider abiotic organic source and mesotrophic conditions; Jones et al., 2010). The IO data collected over the tropical Western Pacific are consistent with I$^-$ variations reported in earlier studies (Chance et al., 2014, 2019; Sherwen et al., 2016), indicating an increase in I$^-$ concentration with SST.

For the time series of IO concentrations near the ocean surface (0–200 m height; Fig. 7), the values were 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 re-
H. Takashima et al.: Full latitudinal marine atmospheric measurements of iodine monoxide

Figure 5. Daily median tropospheric IO vertical column densities (VCDs; molec. cm$^{-2}$) observed from R/V Mirai during 16 November to 2 December 2014 and chlorophyll a concentrations observed via satellite (MODIS). Blue crosses and lines represent 5 d backward trajectories.

The observed trend. 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 the photolysis of iodocarbons within the marine boundary layer (approximately 10$^7$ molec. cm$^{-2}$ s$^{-1}$) generally assumed in the three-dimensional models (Saiz-Lopez et al., 2014; Sekiya et al., 2020; Sherwen et al., 2016). While indirectly considering the global total fluxes of CH$_2$I$_X$ ($X$ = I, Br, and Cl), as described by Ordóñez et al. (2012) in these model simulations, the chl-a-based parameterization reduced the fluxes to too low a level over this oceanic region. It, therefore, necessitates a survey of missing sources. We might not need a brand new flux mechanism but, rather, a good parameterization of the traditional organoiodine fluxes (including their photolysis) over the region.

The third case, with only an O$_3$-independent flux (Case 3; Fig. 3) might explain the negative correlation more easily, whereas the total change of the flux type is simply not being 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 $\times$ 10$^7$ molec. 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 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

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 ($^\circ$C).
The expectation that a positive correlation between O\textsubscript{3} and IO would occur with O\textsubscript{3}-dependent processes over a low O\textsubscript{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 (Figs. S3, S4). An alternative explanation for the observed negative correlation would be the mixing of air masses with different degrees of iodine chemistry. If so, such a negative correlation could appear in the chemistry transport model results. However, this feature was not found. Therefore, we propose an O\textsubscript{3}-independent flux. Over the Atlantic, the O\textsubscript{3} mixing ratio rarely reaches these low levels (10 ppbv or fewer). Therefore, such process analyses have not been undertaken there. Under the influence of O\textsubscript{3}-independent sources, even lower O\textsubscript{3} concentrations would be attainable. Radiative forcing of O\textsubscript{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\textsubscript{3} concentration, which might play a major role in estimating past and future concentrations of O\textsubscript{3}.

Table 4. Net and process-specific O\textsubscript{3} loss rates in three cases at an O\textsubscript{3} concentration of 10 ppbv, as calculated using the box model.

| Case          | IO loss (ppbv) | net loss (ppbv d\textsuperscript{-1}) | HO\textsubscript{2}/O\textsubscript{3} cycle loss (ppbv d\textsuperscript{-1}) | Iodine cycle loss (ppbv d\textsuperscript{-1}) |
|---------------|---------------|--------------------------------------|---------------------------------------------------------------------------------|-----------------------------------------------|
| Without iodine| 0             | -1.06                                | -1.64                                                                            | 0                                             |
| Case 1        | 0.553–0.741   | -1.85 to -2.08                       | -1.62                                                                            | -0.519 to -0.720                              |
| Case 2        | 0.611–0.851   | -1.92 to -2.21                       | -1.62                                                                            | -0.579 to -0.844                              |
| Case 3        | 0.723–0.960   | -2.05 to -2.34                       | -1.62                                                                            | -0.700 to -0.967                              |

The time series of meteorological parameters including wind speed and SST was also investigated, but a clear correlation, such as that shown by O\textsubscript{3} and IO, was not observed in the correlation with O\textsubscript{3} or IO concentrations on a timescale of a few days (Fig. 6). The correlation coefficient between SST and IO was found to be 0.39, that between SST and O\textsubscript{3} was -0.51, and that between wind speed and IO was -0.45. In addition, that between wind speed and O\textsubscript{3} was 0.59. It is noteworthy that the correlation coefficient between IO and O\textsubscript{3} was -0.75, which is much higher than others and, therefore, is the dominant feature. An earlier study (Kanaya et al., 2019) investigating the diurnal variation of O\textsubscript{3} in this area based on a comparison of observational data and a chemical transport model indicated that an as-yet-unidentified O\textsubscript{3} loss might occur over the tropical Western Pacific. Our results imply that iodine chemistry plays an important role in O\textsubscript{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. Results of recent studies indicate a roughly threefold increase in iodine since the 1950s, with at least 50 % attributed to anthropogenic O\textsubscript{3} (Cuevas et al., 2018; Legrand et al., 2018; Zhao et al., 2019). If half of the inorganic flux were O\textsubscript{3}-independent, as suggested by Case 2, then either some other cause should be sought or the change in O\textsubscript{3}-dependent fluxes to produce the observed change is even more dramatic than previously thought. Further investigation of these points is necessary.

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, ever made with a single instrument, spanning SSTs of approximately 0 to 31.5 °C and allowing the investigation of the variation of IO concentrations. It was particularly abundant over the tropical Western Pacific (warm pool), appearing as an iodine fountain, where SST maxima (> 30 °C) and O\textsubscript{3} minima are observed.
This report describes negative correlation between IO and O3 concentrations over the IO maximum, even under extremely low O3 conditions, which few earlier studies have demonstrated. This correlation is not explained easily by the O3-dependent oceanic fluxes of photolabile inorganic iodine compounds adopted for recent simulation studies. Our findings rather imply that O3-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 O3 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.

Data availability. MAX-DOAS data are available by contacting the corresponding authors. Other data are available at the following sites (DARWIN): MR14-06 (leg 1; https://doi.org/10.17596/0001862, JAMSTEC, 2015); MR15-04 (https://doi.org/10.17596/0001975, JAMSTEC, 2016a); MR15-05 (leg 2; https://doi.org/10.17596/0002030, JAMSTEC, 2016b); MR16-06 (https://doi.org/10.17596/0001870, JAMSTEC, 2016c); MR16-09 (leg 3; https://doi.org/10.17596/0000262, JAMSTEC, 2017a); MR17-05C (https://doi.org/10.17596/0001879, JAMSTEC, 2017b); MR17-08 (leg 1; https://doi.org/10.17596/0001881, JAMSTEC, 2018a); MR17-08 (leg 2; https://doi.org/10.17596/0001882, JAMSTEC, 2018b).

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/acp-22-4005-2022-supplement.

Author contributions. HT designed the study, conducted shipboard MAX–DOAS observations and analyses, and wrote the paper. YugK proposed the research concept, supported the MAX–DOAS observations, and conducted O3/CO observations and 0-D box model calculations. KS supported the observations and analysis. MF conducted the retrieval of IO profiles and IO VCDs. MV supported the MAX–DOAS observations. CAC, ASL, and TS conducted a simulation using a global chemical model. All co-authors provided comments to improve the paper.

Competing interests. At least one of the (co-)authors is a member of the editorial board of Atmospheric Chemistry and Physics. The peer-review process was guided by an independent editor, and the authors also have no other competing interests to declare.

Disclaimer. Publisher’s note: Copernicus Publications remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Acknowledgements. We thank Kirstin Krüger, Yousuke Yamashita, and Keiichiro Hara, for their useful comments. We thank Robert Spurr, for the free use of the VLIBORT radiative transfer code package. We also thank the two anonymous reviewers, for their constructive comments. DOAS analysis involved the QDOAS software. We used MODIS chlorophyll a, OI SST, and ECMWF meteorological data. Figures were produced using the GFD Dennou Library.

Financial support. This study was supported by the KAKENHI (grant nos. 16KK0017 and 21H04933), and by the ArCS (Arctic Challenge for Sustainability; grant no. JPMXD130000000) of the Ministry of Education, Culture, Sports, Science, and Technology of Japan. This study has also received funding from the European Research Council Executive Agency under the European Union’s Horizon 2020 Research and Innovation programme (grant no. ERC-2016-COG 726349; CLIMAHA). This study was also supported, in part, by funding from Fukuoka University (grant no. 197103).

Review statement. This paper was edited by Steven Brown and reviewed by two anonymous referees.

References

Alicke, B., Hebestreit, K., Stutz, J., and Platt, U.: Iodine oxide in the marine boundary layer, Nature, 397, 572–573, https://doi.org/10.1038/17508, 1999.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hansson, H. C., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume III – gas phase reactions of inorganic halogens, Atmos. Chem. Phys., 7, 981–1191, https://doi.org/10.5194/acp-7-981-2007, 2007.

Baccarini, A., Karlsson, L., Drommen, J., Duplessis, P., Pullers, J., Brooks, I. M., Saiz-Lopez, A., Salter, M., Tjernstrom, M., Balkensperger, U., Zieger, P., and Schmale, J.: Frequent new particle formation over the high Arctic pack ice by enhanced iodine emissions, Nat. Commun., 11, 4924, https://doi.org/10.1038/s41467-020-18551-0, 2020.

Bogumil, K., Orphal, J., and Burrows, J. P.: Temperature-dependent absorption cross-sections of O3, NO2, and other atmospheric trace gases measured using the SCIAMACHY spectrometer, Proceedings of the ERS-Envisat Symposium, October 2000, Goteborg, Sweden, 2000.

Carpenter, L. J., Archer, S. D., and Beale, R.: Ocean-atmosphere trace gas exchange, Chem. Soc. Rev., 41, 6473–6506, https://doi.org/10.1039/c2cs35121h, 2012.

Carpenter, L. J., MacDonald, S. M., Shaw, M. D., Kumar, R., Saunders, R. W., Partipan, R., Wilson, J., and Plane, J. M. C.: Atmospheric iodine levels influenced by sea sur-
face emissions of inorganic iodine, Nat. Geosci., 6, 108–111, https://doi.org/10.1038/ngeo1687, 2013.
Chambers, R. M., Heard, A. C., and Wayne, R. P.: Inorganic gas-phase reactions of the nitrate radical – I$_2$+ NO$_3$ and I + NO$_3$, J. Phys. Chem., 96, 3321–3331, 1992.
Chance, R., Baker, A. R., Carpenter, L., and Jickells, T. D.: The distribution of iodide at the sea surface, Environ. Sci.-Proc. Imp., 16, 1841–1859, https://doi.org/10.1039/c4em00139g, 2014.
Chance, R. J., Tinel, L., Sherwen, T., Baker, A. R., Bell, T., Brindle, J., Campos, M., Croot, P., Ducklow, H., Peng, H., Hopkins, F., Hoogakker, B., Hughes, C., Jickells, T. D., Loades, D., Macaya, D. A. R., Mahajan, A. S., Malin, G., Phillips, D., Roberts, I., Roy, R., Sarkar, A., Sinha, A. K., Song, X., Winkelbauer, H., Wuttig, K., Yang, M., Peng, Z., and Carpenter, L. J.: Global sea-surface iodide observations, 1967–2018, Sci. Data, 6, 268, https://doi.org/10.1038/s41597-019-0288-y, 2019.
Cuevas, C. A., Maffezzoli, N., Corella, J. P., Spolaor, A., Vallonga, P., Kjaer, H. A., Simonsen, M., Wistrup, M., Vinther, B., Horvat, C., Fernandez, R. P., Kinnison, D., Lamarque, J. F., Barbante, C., and Saiz-Lopez, A.: Rapid increase in atmospheric iodine levels in the North Atlantic since the mid-20th century, Nat. Commun., 9, 1452, https://doi.org/10.1038/s41467-018-03756-1, 2018.
Danckaert, T., Fayt, C., Van Roozendael, M., De Smedt, I., Leto- dez, R. P., Gilfedder, B. S., Weller, R., Baker, A. R., Droste, E., and Lai, S.: Spatial and temporal variability of iodine in aerosol, J. Geophys. Res.-Atmos., 126, e2020JD034410, https://doi.org/10.1029/2020JD034410, 2021.
Großmann, K., Frieß, U., Peters, E., Wittrock, F., Lampel, J., Yilmaz, S., Tschritter, J., Sommariva, R., von Glasow, R., Quack, B., Krüger, K., Pfeilsticker, K., and Platt, U.: Iodine monoxide in the Western Pacific marine boundary layer, Atmos. Chem. Phys., 13, 3363–3378, https://doi.org/10.5194/acp-13-3363-2013, 2013.
Harwood, M. H., Burkholder, J. B., Hunter, M., Fox, R. W., and Ravishankara, A. R.: Absorption cross sections and self-reaction kinetics of the IO radical, J. Phys. Chem., 101, 853–863, 1997.
Hayase, S., Yabushita, A., Kawasaki, M., Enami, S., Hoffmann, M. R., and Colussi, A. J.: Heterogeneous Reaction of Gaseous Ozone with Aqueous Iodide in the Presence of Aqueous Organic Species, J. Phys. Chem. A., 114, 6016–6021, https://doi.org/10.1021/jp101985F, 2010.
Hayase, S., Yabushita, A., Kawasaki, M.: Iodine Emission in the Presence of Humic Substances at the Water’s Surface, J. Phys. Chem. A., 116, 5779–5783, https://doi.org/10.1021/jp2048234, 2012.
He, X. C., Tham, Y. J., Dada, L., Wang, M. Y., Finkenzeller, H., Stolzenburg, D., Iyer, S., Simon, M., Kuren, A., Shen, J. L., Rorup, B., Rissmann, M., Schobesberger, S., Babiloni, R., Wang, D. S., Koenig, T. K., Jokinen, T., Sarnela, N., Beck, L. J., Almeida, I., Amanatidis, S., Amorim, A., Ataei, F., Barbari, A., Bertozzi, B., Bianchi, F., Brikke, S., Caudillo, L., Chen, D. X., Chiu, R., Chua, W. B., Dias, A., Ding, A. J., Domnen, J., Duplissy, J., El Haddad, I., Carracedo, L. G., Granzi, M., Hansel, A., Heinritzi, M., Hofbauer, V., Juminen, H., Kangasluoma, J., Kemppainen, D., Kim, C., Kong, W. M., Kreczmer, J. E., Kvasch, A., Laitinen, T., Lamkaddam, H., Lee, C. P., Lehtipalo, K., Leiminger, M., Li, Z. J., Makhmutov, V., Manninen, H. E., Marie, G., Frang, R., Martel, S., Mauldin, R. L., Mentler, B., Mohler, O., Muller, T., Nie, W., Omela, A., Petaja, T., Pfeifer, J., Philippov, M., Ranjithkumar, A., Saiz-
Kaltsoyannis, N. and Plane, J. M. C.: Quantum chemical calculations on a selection of iodine-containing species (IO, OIO, \(\text{IO}_2\), \(\text{I}_2\text{O}_3\), \(\text{I}_2\text{O}_4\) and \(\text{I}_2\text{O}_5\)) of importance in the atmosphere, Phys. Chem. Chem. Phys., 10, 1723–1733, 2008.

Kanaya, Y., Kajii, Y., and Akimoto, H.: Solar actinic flux and photochemical fraction determinations by radiometers and a radiative transfer model at Rishiri Island: comparisons, cloud effects, and detection of an aerosol plume from Russian forest fires, Atmos. Environ., 37, 2463–2475, https://doi.org/10.1016/S1352-2310(03)00183-3, 2003.

Kanaya, Y., Cao, R. Q., Akimoto, H., Fukuda, M., Komazaki, Y., Yokouchi, Y., Koike, M., Tamimoto, H., Takegawa, N., and Kondo, Y.: Urban photochemistry in central Tokyo: 1. Observed and modeled OH and \(\text{HO}_2\) radical concentrations during the winter and summer of 2004, J. Geophys. Res.-Atmos., 112, D21312, https://doi.org/10.1029/2007jd008670, 2007a.

Kanaya, Y., Tamimoto, H., Matsumoto, J., Furutani, H., Hashimoto, S., Komazaki, Y., Tanaka, S., Yokouchi, Y., Kato, S., Kajii, Y., and Akimoto, H.: Diurnal variations in \(\text{H}_2\text{O}_2\), \(\text{O}_3\), \(\text{PAN}\), \(\text{HNO}_3\) and aldehyde concentrations and \(\text{NO}/\text{NO}_2\) ratios at Rishiri Island, Japan: Potential influence from iodine chemistry, Sci. Total Environ., 376, 185–197, https://doi.org/10.1016/j.scitotenv.2007.01.073, 2007b.

Kanaya, Y., Cao, R. Q., Kato, S. G., Miyakawa, Y. K., Kajii, Y., Tamimoto, H., Yokouchi, Y., Mochida, M., Kawamura, K., and Akimoto, H.: Chemistry of OH and \(\text{HO}_2\) radicals observed at Rishiri Island, Japan, in September 2003: Missing daytime sink of \(\text{HO}_2\) and positive nighttime correlations with monoterpene, J. Geophys. Res.-Atmos., 112, D11308, https://doi.org/10.1029/2006jd007987, 2007c.

Kanaya, Y., Irie, H., Takashima, H., Ibukuchi, H., Akimoto, H., Sudo, K., Gu, M., Chong, J., Kim, Y. J., Lee, H., Li, A., Si, F., Xu, J., Xie, P.-H., Liu, W.-Q., Dzhola, A., Postylyakov, O., Ivanov, V., Grechko, E., Terpugova, S., and Panchenko, M.: Long-term MAX-DOAS network observations of \(\text{NO}_2\) in Russia and Asia (MADRAS) during the period 2007–2012: instrument calibration, elucidation of climatology, and comparisons with OMI satellite observations and global model simulations, Atmos. Chem. Phys., 14, 7909–7927, https://doi.org/10.5194/acp-14-7909-2014, 2014.

Kanaya, Y., Miyazaki, K., Taketani, F., Miyakawa, T., Takashima, H., Komazaki, Y., Pan, X., Kato, S., Sudo, K., Sekiya, T., Inoue, J., Sato, K., and Oshima, K.: Ozone and carbon monoxide observations over open oceans on R/V "Mirai" from 67° S to 75° N during 2012 to 2017: testing global chemical reanalysis in terms of Arctic processes, low ozone levels at low latitudes, and pollution transport, Atmos. Chem. Phys., 19, 7233–7254, https://doi.org/10.5194/acp-19-7233-2019, 2019.

Kley, D., Crutzen, P. J., Smit, H. G. J., Vomel, H., Oltmans, S. J., Grassl, H., and Ramanathan, V.: Observations of near-zero ozone concentrations over the convective Pacific: Effects on air chemistry, Science, 274, 230–233, https://doi.org/10.1126/science.274.5285.230, 1996.

Koenig, T. K., Volkamer, R., Baidar, S., Dix, B., Wang, S., Anderson, D. C., Salawitch, R. J., Wales, P. A., Cuevas, C. A., Fernandez, R. P., Saiz-Lopez, A., Evans, M. J., Sherwen, T., Jacob, D. J., Schmidt, J., Kinnison, D., Lamarque, J.-F., Apel, E. C., Bresch, J. C., Campos, T., Flocke, F. M., Hall, S. R., Homonichl, S. B., Hornbrook, R., Jensen, J. B., Lueb, R., Montzka, D. D., Pan, L. L., Reeves, J. M., Schauffler, S. M., Ullmann, K., Weinheimer, A. J., Atlas, E. L., Donets, V., Navarro, M. A., Riemer,
chemistry of iodine, Atmos. Chem. Phys., 16, 15593–15604, https://doi.org/10.5194/acp-16-15593-2016, 2016.

Sakamoto, Y., Yabushita, A., Kawasaki, M., and Enami, S.: Direct emission of I₂ molecule and IO radical from the heterogeneous reactions of gaseous ozone with aqueous potassium iodide solution, J. Phys. Chem. A, 113, 7707–7713, https://doi.org/10.1021/jp903486u, 2009.

Sander, S. P., Friedl, R. R., Abbatt, J. P. D., Barker, J. R., Burkholder, J. B., Golden, D. M., Kolb, C. E., Kurylo, M. J., Moortgat, G. K., Wine, P. H., Huie, R. E., and Orkin, V. L.: Chemical kinetics and photochemical data for use in atmospheric studies, Evaluation Number 17, Tech. rep., NASA Jet Propulsion Laboratory, 2011.

Seery, D. J. and Britton, D.: The continuous absorption spectra of chlorine, bromine, bromine chloride, iodine chloride, and iodine bromide, J. Phys. Chem., 68, 2263–2266, 1964.

Sekiya, T., Kanaya, Y., Sudo, K., Taketani, F., Iwamoto, Y., Aita, M. N., Yamamoto, A., and Kawamoto, K.: Global Bromine- and Iodine-Mediated Tropospheric Ozone Loss Estimated Using the CHASER Chemical Transport Model, Sola, 16, 220–227, https://doi.org/10.2151/sola.2020-037, 2020.

Shaw, M. D. and Carpenter, L. J.: Modification of Ozone Deposition and I-2 Emissions at the Air-Aqueous Interface by Dissolved Organic Carbon of Marine Origin, Environ. Sci. Technol., 47, 10947–10954, https://doi.org/10.1021/acs.est.0c01459, 2013.

Sherwen, T., Schmidt, J. A., Evans, M. J., Carpenter, L. J., Großmann, K., Eastham, S. D., Jacob, D. J., Dix, B., Koenig, T. K., Sinreich, R., Orkven, I., Volkamer, R., Saiz-Lopez, A., Prados-Roman, C., Mahajan, A. S., and Ordóñez, C.: Global impacts of tropospheric halogenics (Cl, Br, I) on oxidants and composition in GEOChem. Atmos. Chem. Phys., 16, 12239–12271, https://doi.org/10.5194/acp-16-12239-2016, 2016.

Sherwen, T., Evans, M. J., Carpenter, L. J., Schmidt, J. A., and Mickley, L. J.: Halogen chemistry reduces tropospheric O₃ radiative forcing, Atmos. Chem. Phys., 17, 1557–1569, https://doi.org/10.5194/acp-17-1557-2017, 2017.

Simpson, W. R., Brown, S. S., Saiz-Lopez, A., Thornton, J. A., and von Glasow, R.: Tropospheric Halogen Chemistry: Sources, Cycling, and Impacts, Chem. Rev., 115, 4035–4062, https://doi.org/10.1021/acs.chemrev.1c00124, 2015.

Sinreich, R., Frieß, U., Wagner, T., and Platt, U.: Multi axis differential optical absorption spectroscopy (MAX-DOAS) of gas and aerosol distributions, Faraday Discuss., 130, 153–164; https://doi.org/10.1039/b419274p, 2005.

Sipila, M., Samela, N., Jokinen, T., Henschel, H., Junninen, H., Kontkanen, J., Richters, S., Kangasluoma, J., Franchin, A., Perakyla, O., Rissanen, M. P., Ehn, M., Vehkamaki, H., Kurten, T., Berndt, T., Petaja, T., Worsnop, D., Ceburnis, D., Kerminen, V. M., Kulmala, M., and O’Dowd, C.: Molecular-scan evidence of aerosol particle formation via sequential addition of HIO₃, Nature, 537, 532–534, https://doi.org/10.1038/nature19314, 2016.

Spurr, R. J. D.: VLIBORT: A linearized pseudo-spherical vector discrete ordinate radiative transfer code for forward model and retrieval studies in multilayer multiple scattering media. J. Quant. Spectrosc. Ra., 102, 316–342, https://doi.org/10.1016/j.jspsr.2006.05.005, 2006.

Stockwell, W. R., Kirchner, F., Kuhn, M., and Seefeld, S.: A new mechanism for regional atmospheric chemistry modeling. J. Geophys. Res.-Atmos., 102, 25847–25879, https://doi.org/10.1029/97jd008849, 1997.

Stutz, J., Hebestreit, K., Aliche, B., and Platt, U.: Chemistry of halogen oxides in the troposphere: Comparison of model calculations with recent field data, J. Atmos. Chem., 34, 65–85, https://doi.org/10.1023/A:1006245802825, 1999.

Takashima, H., Shiotani, M., Fujiwara, M., Nishi, N., and Hasebe, F.: Ozone and Aerosol observations at Christmas Island (2 degrees N, 157 degrees W) in the equatorial Pacific, J. Geophys. Res.-Atmos., 113, D10112, https://doi.org/10.1029/2007jd009374, 2008.

Takashima, H., Irie, H., Kanaya, Y., Shimizu, A., Aoki, K., and Akimoto, H.: Atmospheric aerosol variations at Okinawa Island in Japan observed by MAX-DOAS using a new cloud-screening method, J. Geophys. Res.-Atmos., 114, D18213, https://doi.org/10.1029/2009jd011939, 2009.

Takashima, H., Irie, H., Kanaya, Y., and Akimoto, H.: Enhanced NO₂ at Okinawa Island, Japan caused by rapid air-mass transport from China as observed by MAX-DOAS, Atmos. Environ., 45, 2593–2597, https://doi.org/10.1016/j.atmosenv.2010.10.055, 2011.

Takashima, H., Irie, H., Kanaya, Y., and Syamsudin, F.: NO₂ observations over the western Pacific and Indian Ocean by MAX-DOAS on Kaiyo, a Japanese research vessel, Atmos. Meas. Tech., 5, 2351–2360, https://doi.org/10.5194/amt-5-2351-2012, 2012.

Takashima, H., Kanaya, Y., and Taketani, F.: Downsizing of a ship-borne MAX-DOAS instrument, JAMSTEC Report of Research and Development, 23, 34–40, https://doi.org/10.5918/jamstcr.23.34, 2016.

Tellinghuisen, J.: Resolution of the visible-infrared absorption spectrum of I₂ into three contributing transitions, J. Chem. Phys., 58, 2821–2834, 1973.

Thalman, R. and Volkamer, R.: Temperature dependent absorption cross-sections of O₂-O₂ collision pairs between 340 and 630 nm and at atmospherically relevant pressure, Phys. Chem. Chem. Phys., 15, 15371–15381, https://doi.org/10.1039/c3cp50968k, 2013.

Tinel, L., Adams, T. J., Hollis, L. D. J., Bridger, A. J. M., Chance, R. J., Ward, M. W., Ball, S. M., and Carpenter, L. J.: Influence of the Sea Surface Microlayer on Oceanic Iodine Emissions, Environ. Sci. Technol., 54, 13228–13237, https://doi.org/10.1021/acs.est.0c02736, 2020.

Tirpitz, J.-L., Frieß, U., Hendrick, F., Alberti, C., Allwart, M., Apituley, A., Bais, A., Beirle, S., Bermingham, S., Bousch, T., Bruchkowski, I., Cede, A., Chan, K. L., den Hoed, M., Donner, S., Drosoglou, T., Fayt, C., Friedrich, M. M., Frumau, A., Gast, L., Gilgen, C., Gomez-Martín, L., Hao, N., Hensen, A., Henzing, B., Herrmans, C., Jin, J., Krehl, K., Kuhn, J., Lampel, J., Li, A., Liu, C., Liu, H., Ma, J., Merlaut, A., Peters, E., Pinardi, G., Pitsers, A., Platt, U., Puentedura, O., Richter, A., Schmitt, S., Spinei, E., Stein Zweers, D., Strong, K., Swart, D., Tack, F., Tiefengraber, M., van der Hoff, R., van Roorzendaal, M., Vlemmix, T., Vonk, J., Wagner, T., Wang, Y., Wang, Z., Wenig, M., Wiegner, M., Wittrock, F., Xie, P., Xing, C., Xu, J., Yela, M., Zhang, C., and Zhao, X.: Intercomparison of MAX-DOAS vertical profile retrieval algorithms: studies on field data from the CINDI-2 campaign, Atmos. Meas. Tech., 14, 1–35, https://doi.org/10.5194/amt-14-2021-2021.
Atmos. Chem. Phys., 22, 4005–4018, 2022
https://doi.org/10.5194/acp-22-4005-2022