Latitudinal gradients in O_3 and CO during INDOEX 1999

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[1]   Measurements of ozone and carbon monoxide (CO) from the INDOEX 1999 experiment show large differences in concentrations of ozone and CO between the Northern Hemisphere and the Southern Hemisphere. These measurements confirm the theory that the Intertropical Convergence Zone (ITCZ) serves as a barrier to mixing over the Indian Ocean, effectively separating the polluted air in the Northern Hemisphere from cleaner air in the Southern Hemisphere. In spite of CO levels similar to those observed off the coast of North America, there is relatively little ozone off the coast of India. The ozone-to-CO ratio in air coming from India is 0.14, lower than 0.3 or 0.4 in air being transported to Bermuda from North America. Diurnal cycles are observed in both CO and ozone. INDOEX data taken onboard the R/V *Ronald H. Brown* show an average diurnal cycle in ozone of 20%, while data from the island of Kaashidhoo in the Republic of Maldives indicate a diurnal variation of 19%, consistent with our analyses of other experiments. Diurnal variations of this magnitude are larger than expected from ozone destruction by conventional HO_x chemistry alone, implying that the sink of ozone in the remote marine boundary layer is likely considerably larger than had been assumed. Additional chemical cycles must be fairly substantial—large enough to rival HO_x chemistry in ozone destruction.   *INDEX TERMS:* 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 9340 Information Related to Geographic Region: Indian Ocean

1.   Introduction

[2]   Carbon monoxide (CO) plays an important role in the chemistry of the troposphere. It is often used as a tracer of anthropogenic pollution, and consumes a large fraction of the OH in the troposphere [*Thompson*, 1992]. As both a primary and secondary pollutant, CO is important on both regional and global scales. In regions with sufficient NO_x, CO also serves to produce ozone and affects global ozone concentrations by its effect on OH and HO_2 concentrations. Observations indicate that CO concentrations in remote portions of the Southern Hemisphere are roughly half the levels observed in the Northern Hemisphere [e.g., *Novelli et al.*, 1998].

[3]   Ozone is a reactive gas that is important throughout the troposphere as both a secondary pollutant and a naturally occurring gas and in the stratosphere where it shields the Earth's surface from harmful ultraviolet radiation. In the troposphere near cities, it is commonly thought of as a pollutant, but throughout the troposphere, it serves an important role in the destruction of hydrocarbons, CO, and other pollutants. Photolysis of ozone and subsequent reaction of atomic oxygen with water serves as the primary source of OH, which initiates many photochemical reaction chains in the Earth's troposphere [e.g., *Finlayson-Pitts and Pitts*, 2000]. Ozone is a lung irritant, and is thought to contribute to the decay of urban buildings and other structures [e.g., *Seinfeld and Pandis*, 1998]. Finally, tropospheric ozone is a greenhouse gas, since it absorbs strongly in the infrared, trapping heat in the lower atmosphere [e.g., *National Research Council*, 1991]. Earlier studies have shown that the remote marine boundary layer represents a net sink for ozone and that ozone exhibits a distinct diurnal cycle there [e.g., *Johnson et al.*, 1990].

[4]   In an earlier view [e.g., *Paluch et al.*, 1992], ozone in the remote marine boundary layer mixes down from the free troposphere; ozone is destroyed by deposition to the surface, and photolysis followed by OH formation.

$$O_3 + hv \rightarrow O_2 + O^1D \tag{1}$$

$$O^1D + H_2O \rightarrow 2\ OH \tag{2}$$
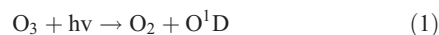
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In this view, the source of ozone is vertical mixing, while the sinks are photochemistry and deposition to the surface. These competing processes result in a diurnal variation in ozone of around 12% [e.g., *Paluch et al.*, 1992; *Dickerson et al.*, 1999] since destruction is only active during the day. A number of recent papers [e.g., *Dickerson et al.*, 1999; *Vogt et al.*, 1999; *McFiggans et al.*, 2000] have suggested that additional processes such as destruction by bromine and iodine as well as photochemical processing of those species on aerosols are likely also significant. Taken together, these additional processes appear capable of destroying roughly the same amount of ozone in the marine boundary layer as the HO_x cycle alone, implying a diurnal cycle in ozone double that previously thought. Additionally, it has been suggested [*de Laat and Lelieveld*, 2000] that ozone in the remote marine boundary layer comes not only from vertical mixing of tropospheric ozone, but also comes from advection from continental sources. If ozone comes from advection, then an air parcel followed outward from the continent should exhibit a staircase profile in its ozone concentration—the result of photochemical destruction during the day and little photochemistry at night. At a remote site, the observed diurnal cycle arises when this staircase pattern is blown past the island. In any view, in situ production of ozone over the Indian Ocean is thought to be minimal, since very little NO_x is present (T. P. Carsey et al., Reactive nitrogen measurements during INDOEX 1999, submitted to *Journal of Geophysical Research*, 2002) [*Rhoads et al.*, 1997] to drive production. An alternative view [*Bremaud et al.*, 1998] holds that variations in mixing between the free troposphere and the marine boundary layer may be responsible for the diurnal variation in ozone.

[5] If ozone in the remote marine boundary layer is brought in by horizontal advection, one might reasonably expect CO to exhibit a diurnal cycle as well, though the cycle would have to be much smaller since CO has a longer lifetime than ozone. Estimates of the CO lifetime range from over a year in the nighttime polar troposphere to perhaps as short as ten days over continents in summer, and are based upon estimates of the concentration of OH. For the cruise track of the *Ronald H. Brown* during INDOEX [e.g., *Holloway et al.*, 2000] the lifetime of CO was approximately 30–50 days (T. Holloway, personal communication). In contrast, a 12% diurnal cycle in ozone implies a lifetime of approximately eight days. The sources of CO in the remote marine boundary layer are more complex than those of ozone, since some CO is created in situ by the destruction of CH_4 and other hydrocarbons.

[6] CO, ozone, and other pollutants exhibit strong gradients at the Intertropical Convergence Zone (ITCZ) [e.g., *Rhoads et al.*, 1997; *Thompson et al.*, 2000]. Strong heating at the surface in the tropics leads to the formation of a band of convection, which, in turn, leads to a broad zone of convergence at the surface and divergence aloft. Transport in both hemispheres is therefore toward the ITCZ at the surface and away from the ITCZ aloft. Since the Southern Hemisphere is generally much cleaner than the Northern Hemisphere, a substantial gradient in ozone, CO, and other pollutants exists at the ITCZ in response to

the dynamics of the ITCZ. The ITCZ therefore serves as a barrier to mixing between the hemispheres. To examine these issues, and to better understand the chemistry of ozone and CO in the remote marine boundary layer, both species were measured from 15 January to 20 February 1999 during the AEROSOLS project [*Bates et al.*, 2002] and from 22 February to 1 April 1999 during the INDOEX project on board the NOAA research vessel the *Ronald H. Brown*. Ozone was also measured at the Kaashidhoo Climatological Observatory (4.97°N, 73.47°E, see *Lobert and Harris* [2002] for a site description) in the Maldives from 14 February 1998 to 1 May 1999. We also present reanalyses of previously published data from the 1995 pre-INDOEX cruise of the Malcolm Baldrige (21 March to 21 April 1995) [*Rhoads et al.*, 1997] the 1996 pre-INDOEX cruise of the Sagar Kanya (4 January to 4 February 1996) [*Lal et al.*, 1998]. All of these studies, except AEROSOLS 1999, were conducted predominantly in the Indian Ocean and sampled both the Southern and Northern Hemispheres. The AEROSOLS project took place largely in the Atlantic Ocean.

2.   Experimental Methods

[7] Measurements were taken on the *Ronald H. Brown* during INDOEX 1999 (22 February to 1 April) and AEROSOLS (leg 2 from 11 to 19 February 1999). The ship track (W. P. Ball et al., Size segregated and bulk aerosol composition: Continental impacts during INDOEX 1999, submitted to *Journal of Geophysical Research*, hereinafter referred to as P. Ball et al., submitted manuscript) is broken up into four legs, as discussed below. Sampling pumps for both the CO and ozone instruments were turned off whenever winds from aft of the ship's beam threatened to introduce stack gas into the sampling lines. This happened once, during a thunderstorm on the third leg of the INDOEX cruise.

[8] Ozone was measured using two unmodified commercial detectors (Thermo Environmental Instruments Model 49) for redundancy. Data from the University of Maryland detector were used first, (the decision was arbitrary) while data from the Pacific Marine Environmental Laboratory (PMEL) detector were used to fill in small gaps in data coverage. The Maryland detector has been compared with standard ozone monitors at the National Institute of Standards and Technology (NIST) (Gaithersburg, Maryland) and found to agree to within less than 1%. The Maryland ozone instrument was housed in a climate-controlled seatainer forward of the ship's stack. To avoid contamination, the sample line inlet was placed atop a tower on the ship's bow, approximately 15 m above the ocean's surface and 9 m above the ship's deck. All measurements were corrected for 7.5% line loss in the 30 m of Teflon tubing that ran from the sampling tower to the seatainer. The portion of the sample line that ran through the seatainer was heated to slightly above ambient temperature to ensure that water vapor would not condense in the sample lines. The zero of the ozone instrument was checked periodically by turning off the pump to verify that the zero had not drifted significantly over the course of the experiment. The PMEL instrument was housed in a similar seatainer nearby. The PMEL inlet

Table 1. Summary Statistics for Ozone

Site/Project	Average Ozone, ppbv	Median Ozone, ppbv	Standard Deviation, ppbv	Minimum Ozone, ppbv	Maximum Ozone, ppbv
Ronald H. Brown INDOEX 1999	23	22	12	8	54
Ronald H. Brown AEROSOLS 1999	22	19	9	6	42
Kaashidhoo Island 1998–1999	19	18	7	4	57
Sagar Kanya Pre-INDOEX 1996[a]	28	25	17	7	102
Malcolm Baldrige Pre-INDOEX 1995[b]	13	13	4	6	22

[a] Data from *Lal et al.* [1999].
[b] Data from *Rhoads et al.* [1997].

was on top of a smaller sampling mast on the PMEL seatainer, and connected to the instrument via 8 m of Teflon tubing. The RMS difference between the two instruments was 1.6 ppbv over the course of the experiment. A simple summary of the ozone measurements for INDOEX and three other field experiments is given in Table 1.

[9] CO was measured by a nondispersive infrared monitor, (Thermo Environmental Instruments Model 48, Franklin, Massachusetts) modified [*Dickerson and Delany*, 1988; *Doddridge et al.*, 1994] for greater sensitivity and zeroed for 5 min out of every half hour. The instrument was calibrated by direct measurement of a standard mixture of CO in air, (Matheson Gas Products Inc., Baltimore, Maryland) which was compared directly with a NIST working standard reference material. The detection limit (95% confidence interval) for this instrument, as configured, was 20 parts per billion by volume (ppbv) CO after averaging the signal over one hour. The CO instrument was housed in the climate-controlled interior of the ship. The inlet was located on the port side, aft of the aerosol sampling and ozone sampling inlets, but still well forward of the ship's stack and 11 m above the waterline. Prior to entering the instrument, the sample gas was dried using a Nafion tube dryer (Perma Pure, Inc., Toms River, New Jersey) to avoid condensation of water inside the instrument.

[10] Data for both CO and ozone instruments were recorded every 10 s and averaged over 1 min. The CO data were corrected for zero drift by a linear extrapolation between adjacent zero measurements. Minute averages were then averaged to form hourly averages for both ozone and CO, on which the analyses in this paper are based.

[11] In order to put observations from the various INDOEX platforms on the same scale, side-by-side intercomparisons were conducted between the *Ronald H. Brown*'s sensors and those on the NCAR C-130 aircraft, the Kaashidhoo island site, and the Indian research vessel *Sagar Kanya*. Agreement in measured quantities suggests that analytical techniques are on the same calibration standard, and subject to no (or the same) interferences or contamination. Such intercomparisons also test for perturbations induced by the platforms themselves.

[12] The University of Maryland ozone instrument aboard the *Ronald H. Brown* was calibrated against the NIST standard prior to the cruise. After correcting for line losses and zero drift, all instruments agreed within their

combined uncertainty of 2% or 2 ppbv, whichever is larger. The best fit lines are:

$$[O_3]_{PMEL} = 0.98[O_3]_{UMD} + 1.0 \qquad (r^2 = 0.98) \qquad (3)$$

$$[O_3]_{KCO} = 0.99[O_3]_{UMD} - 0.2 \qquad (r^2 = 0.94) \qquad (4)$$

$$[O_3]_{SK} = 1.06[O_3]_{UMD} + 1.0 \qquad (r^2 = 0.95) \qquad (5)$$

where $[O_3]_{PMEL}$, $[O_3]_{UMD}$, $[O_3]_{KCO}$, $[O_3]_{SK}$ are, respectively, the calibrated hourly averaged output of the PMEL, University of Maryland, Kaashidhoo, and Sagar Kanya ozone detectors in ppbv, and r is the correlation coefficient. During intercomparisons all sensors showed a strong diurnal cycle with maxima before dawn and minima after local solar noon.

[13] Measurements of O₃ and CO made while the C-130 flew by the *Ronald Brown* showed agreement to within 10 ppbv, with the aircraft tending to measure concentrations of ozone that were higher but within the uncertainty of such brief sampling periods. The shipboard and Kaashidhoo CO detectors agreed well for 24-hr averages (200 ppbv on the *Brown*; 195 ppbv on Kaashidhoo); background drift in the Kaashidhoo instrument prevented comparison on finer timescales.

3. Meteorology and Ship Tracks for the *Ronald H. Brown* INDOEX and AEROSOLS Cruises

[14] Back-trajectories were calculated with HYSPLIT4 [*Draxler*, 1988, 1991] using archived analyses from the Medium Range Forecast (MRF) model as input. Data were also obtained from the *Ronald H. Brown*'s anemometers, solar radiometers, and from deck observations made by the ship's crew. From the back-trajectory analyses, several distinct transport regimes were identified: Southern Hemisphere maritime extratropical (SHmX), Southern Hemisphere maritime equatorial (SHmE), Northern Hemisphere maritime equatorial (NHmE), Northern Hemisphere continental tropical (NHcT), and Northern Hemisphere continental extratropical (NHcX). During part of the cruise along the SE coast of India, NHcT air and NHcX air (from aloft) were mixed, and observations made during this period are categorized simply as Northern Hemisphere continental (NHc). The nature of each of these regimes is described in another paper (Ball et al., submitted manuscript) along with a detailed summary of the meteorological conditions. A summary of basic CO concentration statistics is listed in Table 2 for each regime, and a similar table for ozone in Table 3.

3.1. AEROSOLS Second Leg: 11–19 February

[15] The ship went from Cape Town, South Africa, to Mauritius in the Southern Indian Ocean. The air was clean throughout this leg of the cruise except for brief periods on 12 and 13 February. On the 12th, ozone briefly surged to double what it had been previously (Figure 1) as the back-trajectories indicate stagnant conditions near the South African coast. On the 13th, back-trajectories near the surface briefly swing close to the South African coast before the ship headed out to sea at 0000 UTC on the 14th, which

Table 2. Summary Statistics for CO for the *Ronald H. Brown* INDOEX Cruise and Leg 2 of the AEROSOLS Cruise by Meteorological Regime

Meteorological Regime	Average CO (ppbv)	Median CO (ppbv)	Standard Deviation (ppbv)	Minimum CO (ppbv)	Maximum CO (ppbv)
SHmX	51	49	8	39	83
SHmE	54	52	10	39	104
NHcT	152	145	31	91	212
NHcX	130	131	7	114	142
NHc	122	124	14	85	154
NHmT	94	94	16	53	131
All	103	108	46	39	212

is exhibited in a brief surge in CO mixing ratios (Figure 2). On 16 February, back trajectories begin to change from being long trajectories of extratropical origin to shorter ones of equatorial origin. By late on the 17th, the change is complete, and the air mass is clearly equatorial in origin. In accordance with the shift from SHmX air mass to the SHmE air mass, ozone levels also drop from a peak of 26 ppbv early on the 16th to a low of 7 ppb late on the 17th (UTC).

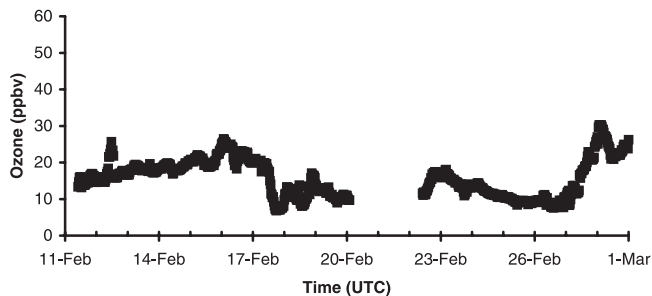### 3.2. INDOEX First Leg: 22 February to 1 March

[16] The ship went from Mauritius to Male', the capital of the Maldives, just north of the Equator. The air was clean at the start of this leg, since all back-trajectories (Ball et al., submitted manuscript) came from the middle of the Indian Ocean or possibly from Australia more than six days previously. Late on 26 February, the ship began crossing into Northern Hemisphere air, as CO increased by a factor of three, ozone by a factor of four, and visibility dropped noticeably, all over the course of 2 days (Figures 1 and 2). On this leg, the transition from Southern Hemisphere air to Northern Hemisphere air was quite sharp, indicating that the ITCZ serves as a barrier to mixing, effectively keeping Northern Hemisphere air separate from Southern Hemisphere air.

3.3. INDOEX Second Leg: 4–23 March

[17] The ship first went north to 19°N, the approximate latitude of Mumbai, India (formerly Bombay) and conducted an intercomparison with the Indian ship Sagar Kanya. The ship then followed the direction of transport, heading due south, before turning east for two days, and

Table 3. Summary Statistics for Ozone for the *Ronald H. Brown* INDOEX Cruise and Leg 2 of the AEROSOLS Cruise by Meteorological Regime

Meteorological Regime	Average Ozone (ppbv)	Median Ozone (ppbv)	Standard Deviation (ppbv)	Average Diurnal Cycle
SHmX	19	19	2.8	12%
SHmE	13	12	3.7	23%
NHcT	24	24	8.2	27%
NHcX	42	44	6.9	17%
NHc	28	30	7.6	15%
NHmT	15	12	6.5	19%
All	22	19	10.7	21%

Figure 1. Ozone for Leg 2 of AEROSOLS and Leg 1 of INDOEX on board the *Ronald H. Brown*: From Cape Town, South Africa to Mauritius to Male', Maldives in the Indian Ocean. Two transitions are evident: from an extratropical air mass (SHmX) to an equatorial one (SHmE) on 17 February and from the Southern Hemisphere (SHmE) to the Northern Hemisphere (NHmE) on 27 February.

then heading due south again until reaching the far southern extent of the journey at 12.7°S, south of the ITCZ. The ship then returned to the Maldives. CO and ozone measurements for Leg 2 of INDOEX are presented in Figures 3 and 4.

[18] From 11 to 16 March, analysis of the back trajectories revealed that the direction of transport at 500 m (Ball et al., submitted manuscript) was straight from north to south. In this period, the ship traveled due south for 11 and 12 March, then east on 13 and 14 March, before turning more southerly again on 15 and 16 March. The ship's speed was very nearly the same as the wind speed over the entire period. The two downwind periods (11–12 and 15–16 March) are therefore approximate Lagrangian experiments surrounding one period of cross-flow travel for contrast.

[19] On 19 March at 1400 UTC, the ship reached 12.7°S, the farthest southern extent of this leg. Back-trajectories seem to indicate that the ship never quite reached Southern Hemispheric air, but CO, ozone, and other in situ measurements indicate that from 19 March at 0700 UTC until 20 March at 1100 UTC the ship dipped briefly into Southern Hemisphere air that had not recently passed over a continent. Substantial cloudiness was present
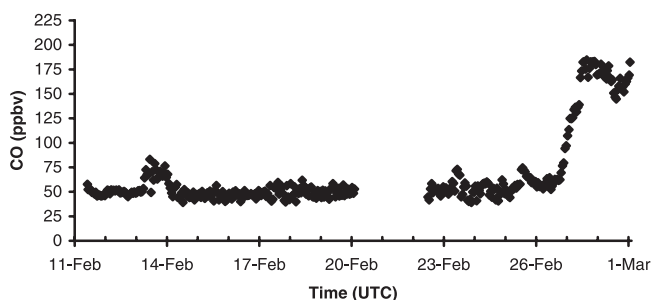
Figure 2. CO for Leg 2 of AEROSOLS and Leg 1 of INDOEX on board the *Ronald H. Brown*: From Cape Town, South Africa to Mauritius to Male', Maldives in the Indian Ocean. The small rise in CO on 13 February occurred as back-trajectories briefly came from the South African coast. The transition from clean Southern Hemisphere air (SHmE) to more polluted Northern Hemisphere air (NHmE) is clearly seen on 27 February.
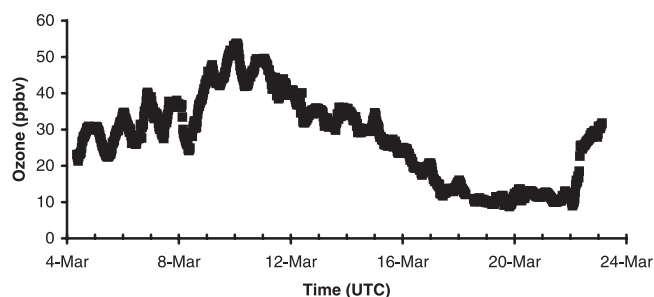
Figure 3. Ozone for Leg 2 of the *Ronald H. Brown* INDOEX cruise: From Male', Maldives, north to the latitude of Mumbai, India, then south to 12.7°S and back to Male'. Peak ozone concentrations around 10 March occurred when the ship encountered extratropical air from the Northern Hemisphere (NHcX). From 11 to 16 March, the ship followed the same air mass from north to south (see text), making an approximate Lagrangian experiment. Low ozone levels on and around 19 March reflect a brief trip into maritime equatorial air (NHmE and SHmE) before returning to more continental air at the end of the leg.

throughout the return from 12.7°S. Throughout this leg, the ITCZ was much more diffuse than for the first leg of the voyage.

3.4. INDOEX Third Leg: 26–30 March

[20] On this leg, the ship's track (Ball et al., submitted manuscript) went up into the Bay of Bengal, finishing near 11°N and 85°E. The flow was mostly from Southern India and Sri Lanka for the start of this leg and came from the east later on. A substantial thunderstorm was directly over or near the ship on 28 March from 0000 UTC to 1200 UTC, leading to gusty winds, which at times exceeded 15 m/s, and precipitation rates of up to 70 mm/hr. During the thunderstorm, some CO and ozone data had to be removed from the data set due to contamination by the ship's stack gas. Ozone
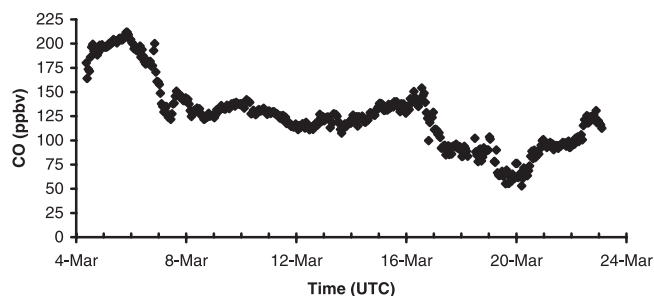

Figure 4. CO for Leg 2 of the *Ronald H. Brown* INDOEX cruise: From Male', Maldives, north to the latitude of Mumbai, India, then South to 12.7°S and back to Male'. High levels of CO early on this leg are the result of transport directly from Sri Lanka and the southern tip of India (NHcT). CO levels then remain steady as the ship sampled air that had been over the ocean for some time or (from 9 to 17 March) air that was transported from the free troposphere (NHc and NHcX). The transition to tropical (NHmT) air is evident on 17 March, as is the brief transition to Southern Hemisphere air (SHmE) on 19 March.
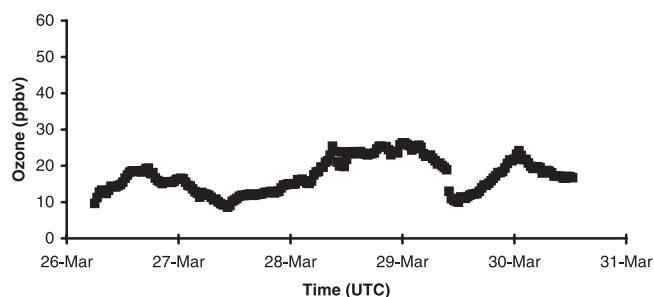

Figure 5. Ozone for Leg 3 of the *Ronald H. Brown* INDOEX cruise: From Male' in the Maldives east to the Bay of Bengal. The ship went into the Bay of Bengal on this leg and encountered Northern Hemisphere continental air (NHcT). A thunderstorm on 28 March resulted in the brief erratic pattern in that day's ozone levels.

and CO concentrations for Leg 3 of INDOEX are presented in Figures 5 and 6.

4. Analysis

[21] *Dickerson et al.* [1999] examined the diurnal variation in average ozone concentrations to test for ozone losses beyond those due to HO$_x$ chemistry. They binned ozone concentrations by time of day and took average values for each time bin. This approach tends to smooth out diurnal cycles in any pollutant because the exact shape of the diurnal variation does not remain constant from day to day; on some days, the minimum may be shifted by a couple hours relative to others. To better quantify ozone's diurnal variation, we have taken the difference between a 6-hour running mean and a 24-hour running mean of ozone to be a measure of diurnal variability. The 24-hour running mean smoothes out most variations on a timescale shorter than 24 hours, whereas the 6 hour mean only reduces the amplitude of a 24-hour sine wave by 10%, while smoothing out shorter-scale variations. The difference between the two is therefore a measure of the deviation of the ozone concentration from the 24-hour mean. The minimum of that difference is then subtracted from the maximum to obtain the diurnal change in ozone. We have further limited the time window for the maximum ozone to be between 2
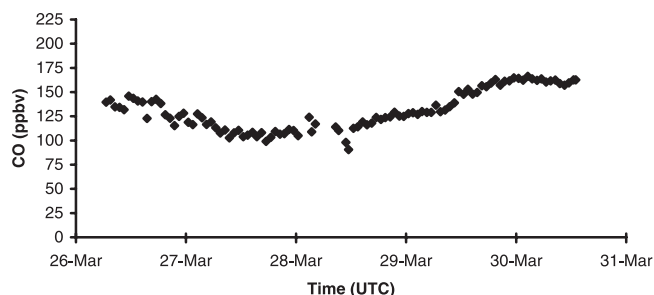

Figure 6. CO for Leg 3 of the *Ronald H. Brown* INDOEX cruise: From Male' in the Maldives east to the Bay of Bengal. The influence of Northern Hemisphere continental air (NHcT) is shown by consistently elevated levels of CO throughout this leg. The small gap in data on 28 March is due to a thunderstorm centered over the ship.

Table 4. Diurnal Variation Statistics for Ozone

Site/Project	Average Diurnal Variation	Median Diurnal Variation	Standard Deviation
Ronald H. Brown INDOEX 1999	20%	19%	15%
Ronald H. Brown AEROSOLS 1999	21%	17%	18%
Kaashidhoo Climate Observatory 1998–1999	19%	18%	12%
Sagar Kanya Pre-INDOEX 1996	14%	13%	14%
Malcolm Baldrige Pre-INDOEX 1995	27%	27%	17%

Table 5. Diurnal Variations and Loss Rates for Ozone During Lagrangian Experiments

Day (UTC) of 1999	Ozone Loss Rate From Regression	Diurnal Variation in Ozone	Daily Average Ozone (ppbv)
11 March	17%/day	11%	43
12 March		14%	36
13 March[a]	–	12%	33
14 March[a]		16%	32
15 March	23%/day	17%	27
16 March		18%	21

[a] The ship headed perpendicular to the direction of transport on 13 and 14 March.

AM and 9 AM local time (LST) and the minimum to be between noon and 7 PM LST so that variations in ozone not due to photochemistry are less likely to be included. A 10% correction is then applied to account for the smoothing of the diurnal cycle caused by taking a 6-hour average. The results are summarized in Table 4 for INDOEX and three other field projects. The diurnal variations are broken down by meteorological regime in Table 3.

[22] As mentioned before, the period of 11–16 March contains two downwind (Lagrangian) experiments and a cross-flow experiment. The ozone profile (Figure 7) shows two periods of steadily decreasing ozone surrounding an interim period of diurnal variations in ozone that are typical of an island site. During the two downwind periods, a linear fit was used to determine the rate of ozone destruction (Table 5). In doing this, the regression was only performed over whole days in an effort to eliminate any dependence on the starting and stopping times of the regression. Picking the starting and stopping times in the regression is by far the largest source of uncertainty in this estimate, giving an estimated uncertainty of ± 5% (of the ozone present) in the destruction rate. The diurnal variation in ozone about a 24-hour running mean was also determined using the methods described previously. The precision of the CO instrument was not sufficient over this period to allow for a similar analysis of CO destruction. Over this period, CO concentrations rise. Since nonmethane hydrocarbon measurements
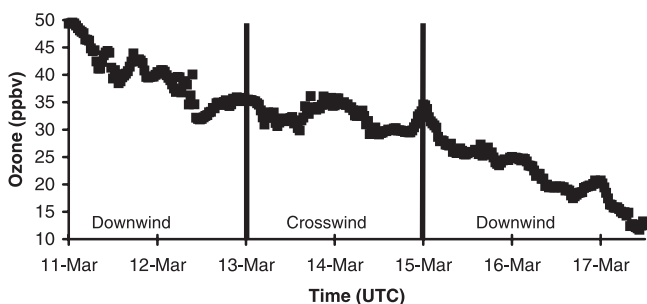
[*Muehle et al.*, 2002] show a few ppbv of nonmethane hydrocarbons present at the beginning of this period, and only 20% remaining at the end of the period, it appears likely that part of the rise in CO is due to oxidation of nonmethane hydrocarbons. Additionally, some CO may be mixing down from the free troposphere.

[23] The ozone data from the Kaashidhoo Climatological Observatory were segregated according to transport regime (Table 6). The regimes are identical to those used by *Lobert and Harris* [2002]. Briefly, the regimes were determined by clustering back-trajectories into nine categories. Brief descriptions of the categories are listed in Table 6; further details are available in the work of *Lobert and Harris* [2002]. Back trajectories were generated using an isentropic trajectory model from NOAA/CMDL [*Harris and Kahl*, 1994] with ECMWF model data.

5. Discussion

[24] The strong gradients in both CO and ozone at the ITCZ indicate that the ITCZ serves as a barrier to mixing between the Northern Hemisphere and the Southern Hemisphere. Nowhere is this separation more clearly demonstrated than in the ITCZ crossing of the first leg of the *Ronald H. Brown*'s INDOEX voyage, where ozone rises by a factor of two and CO rises by a factor of three over the course of only two days.

[25] There is surprisingly little ozone in the air off the coast of India. Measurements at a site in Bermuda, off the coast of North America, show similar levels of CO, but ozone around 55 ppbv on average [*Moody et al.*, 1995;

Figure 7. Ozone for Lagrangian experiments on Leg 2 of the *Ronald H. Brown* INDOEX cruise. On 11–12 and 15–16 March, the ship was traveling with the direction of transport from the Indian subcontinent. From 13 to 14 March, the ship traveled across the direction of flow. At all times, the ship's speed was approximately the same as the wind speed.

Table 6. Ozone Levels by Transport Regime for Kaashidhoo Climatological Observatory

	Transport Regime	Average Ozone (ppbv)	Median Ozone (ppbv)	Ozone Standard Deviation (ppbv)
1	SE Asia	20	21	4.5
2	Distant India, Bay of Bengal, Sri Lanka	27	27	6.0
3	Nearby India	25	23	6.1
4	Arabian Sea	21	21	6.9
5	Local	15	15	7.3
6	Horn of Africa	15	13	6.5
7	Somali Basin	16	16	3.6
8	Remote Indian Ocean	15	14	4.0
9	South Indian Ocean	17	17	4.4

Dickerson et al., 1995]. In air coming from tropical South or Southeast Asia, the maximum ozone was 44 ppbv, and on average only 24 ppbv. The highest ozone mixing ratio observed from the *Ronald H. Brown* during INDOEX was 54 ppbv, and that was in subsiding free tropospheric air from the extratropics (the NHcX regime). On average, that same air mass contained only 42 ppbv ozone. This NHcX regime showed the highest hydrocarbon concentrations [*Muehle et al.*, 2002] and nitrate to sulfate ratios (Ball et al., submitted manuscript).

[26] In mid latitudes, one generally finds a slope of about 0.3 to 0.4 O_3/CO [*Dickerson et al.*, 1995; *Parrish et al.*, 1998] but in polluted air masses from India the slope was only 0.14, indicating less efficient ozone production. Results from Kaashidhoo were similar, with an O_3/CO ratio of 0.16 in air coming from India. The lack of photochemical ozone production may be due to the high initial VOC/NO_x ratio or absorption of ultraviolet radiation by absorbing aerosol [*Dickerson et al.*, 1997; *Lelieveld et al.*, 2001] (Ball et al., submitted manuscript). Rapid removal of ozone in the marine boundary layer may also play a role, but high concentrations of ozone are rarely observed, even in urban Indian environments [e.g., *Pandey et al.*, 1992; *Khemani et al.*, 1995; *Lal et al.*, 2000].

[27] In the conventional view of ozone photochemistry, the dominant source of ozone in the remote marine boundary layer is mixing down from the upper troposphere, and the bulk of ozone destruction takes place in the formation of OH from O^1D attacking water vapor. This will only account for a maximum diurnal cycle of around 12% of the average ozone level for that day [e.g., *Paluch et al.*, 1992; *Dickerson et al.*, 1999]. In contrast, the average diurnal cycle is over 19% for the INDOEX data and every project surveyed in this paper except the data from the Sagar Kanya in 1996. Since conventional chemistry appears inadequate to account for the observed diurnal cycle, others have proposed that an additional source of ozone destruction must exist [e.g., *Dickerson et al.*, 1999]. Several studies have suggested that free halogens may be present at sufficient concentrations in the marine boundary layer to destroy an amount of ozone comparable to that destroyed by HO_x chemistry alone. At present, it appears that destruction by bromine [e.g., *Dickerson et al.*, 1999; *Foster et al.*, 2001] and iodine [e.g., *Allan et al.*, 2000; *McFiggans et al.*, 2000] along with their interactions in the gas phase and in aerosols might supply the required photochemical sink.

[28] *de Laat and Lelieveld* [2000] suggest that the diurnal cycle can come from advection and destruction of ozone. This hypothesis is supported by our data set. In the Lagrangian experiment discussed previously, we found that when the ship traveled at right angles to the direction of transport, we observed a distinct diurnal cycle about a steady median value. This result is similar to that observed at an island site, since the ship is at a constant distance from the continental source. When the ship followed an air mass downwind, a steady decrease in ozone was observed in addition to a diurnal cycle in ozone, consistent with de Laat and Lelieveld's hypothesis. The rates of destruction implied by the downwind legs of the ship's voyage are consistent with the magnitude of the average diurnal variation seen on those days and on the days in between, as one would expect from a staircase ozone profile.

[29] De Laat and Lelieveld's hypothesis suggests that ozone should be minimal in air parcels that have been out over the ocean for over several days. Using the destruction rates deduced in the first and second Lagrangian experiments, one gets 17% and 7% of the original ozone remaining after ten days, respectively. Since this implies very low values for the remote oceans, the INDOEX data suggest that some mixing of free tropospheric ozone from above must still be present, though it may not be the dominant source. If the advection hypothesis is correct, CO should also show a diurnal cycle, albeit a much smaller one. This cycle would likely be masked by variations in CO due to changes in air mass origin and altered by in situ production of CO from CH_4 and hydrocarbon destruction. Furthermore, data from individual days cannot be analyzed using this technique, since the precision of the instrument is far less than that needed to detect such a small change. If data are averaged for the entire cruise, the diurnal variation in the average CO level is approximately 4%, with the minimum CO at midday. This implies a CO lifetime of roughly 25 d. Though this estimate has considerable uncertainty it is in line with predictions [*Holloway et al.*, 2000] of 30–50 days determined from a global chemical transport model simulation for the area covered by the *Ronald H. Brown* during INDOEX.

6. Conclusions

[30] CO and ozone were measured on the *Ronald H. Brown* and on the island of Kaashidhoo in the Maldives. Similar measurements from other experiments have also been used to augment the measurements presented in this paper.

[31] The diurnal cycle observed in ozone was too large to be accounted for using HO_x-only chemistry. It appears that additional chemical reactions will have to be considered (most likely those involving halogens, with iodine and bromine of particular concern) to account for the destruction of ozone in the marine boundary layer. The amount of ozone destruction in parts of the remote marine boundary layer is therefore likely double what was thought previously, using HO_x-only chemistry. Doubling the size of a major sink of ozone clearly has large implications in the global ozone budget for the troposphere. A small diurnal cycle was also observed in CO measurements on board the ship, in agreement with a lifetime of approximately 25 days for in the remote marine boundary layer over the Indian Ocean.

[32] Considering the concentrations of CO and other pollutants present, there is relatively little ozone off the coast of India. On average, the levels of ozone appear to be roughly half those observed in Bermuda off the coast of North America.

[33] Measurements of CO indicate a clear difference between the Northern Hemisphere and Southern Hemisphere, with concentrations in the Northern Hemisphere two to three times higher than those encountered in the Southern Hemisphere. Similarly, measurements of ozone indicate a difference of a factor of two between the clean Southern Hemisphere and the relatively polluted Northern Hemisphere. A strong gradient is also observed at the ITCZ, indicating that the ITCZ serves as a barrier to mixing

between the Northern Hemisphere and the Southern Hemisphere.

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