Sink mechanism for significantly low level of ozone over the Arabian Sea during monsoon

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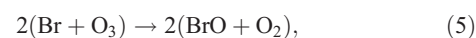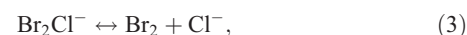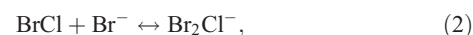
[1] Measurement of surface ozone over the Arabian Sea during the southwest monsoon season (June–September) of 2002 has shown an unusually low level of ozone with an overall average of 9 nmol/mol. Such a low level of ozone could not be explained by simulations using a three-dimensional chemistry transport model, Model for Ozone and Related Tracers (MOZART), which accounts for the known processes of advective transport and includes a standard photochemical mechanism. Thus, for the Arabian Sea region, we propose for the first time that destruction of ozone by reactive halides released from sea salt aerosols is the sink mechanism which played a crucial role in ensuring the significantly low ozone level over the Arabian Sea. Theoretical calculations constrained by observations have shown that, on average, ozone losses due to catalytic action of halogens and due to photolysis plus chemical reaction amount to 2.15 nmol mol^{-1}d^{-1} and 4.64 nmol mol^{-1}d^{-1}, respectively.

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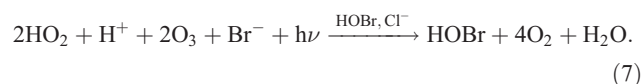
1. Introduction

[2] Considerable attention has been given to investigate the sources of reactive halogen radicals, the mechanisms for their release from sea salt aerosol and to ensure the role of reactive halogens in the chemistry of Marine Boundary Layer (MBL) and in the boundary layer of the polar regions [*Dickerson et al.*, 1999; *Finlayson-Pitts*, 1993; *von Glasow et al.*, 2004; *Graedel and Keene*, 1995; *James et al.*, 2008; *McKeen and Liu*, 1993; *Parrish et al.*, 1993; *Saiz-Lopez et al.*, 2007; *Sander et al.*, 2003, 2006; *Wingenter et al.*, 1996; *Yang et al.*, 2005]. Known sources for reactive halogens include anthropogenic halons, methyl halides (both from natural and anthropogenic activity) and a set of halocarbons emitted naturally from the ocean (i.e., from algae and phytoplankton). Also, the reactive halogens are generated either by catalytic reaction involving NO$_x$ [*Pszenny et al.*, 1993; *Singh et al.*, 1996; *Zetzsch and Behnke*, 1992] or by an autocatalytic mechanism involving release of reactive halogens from sea salt aerosols [*Mozurkewich*, 1995; *Sander and Crutzen*, 1996; *Vogt et al.*, 1996]. According to the autocatalytic mechanism, the bromine present in the marine boundary layer is oxidized initially into hypobromous acid, HOBr, which is further scavenged by sea salt aerosol. Since chlorine to bromine ratio in seawater is very high (~700), HOBr reacts with Cl$^-$ to produce BrCl. A substantial fraction of the BrCl reacts with Br$^-$ leading finally to active Br atom. Active Br atom reacts with O$_3$

molecule and reduces it to O$_2$ molecule. Different steps in the ultimate reaction are as follows:

$$HOBr + Cl^- + H^+ \leftrightarrow BrCl + H_2O, \tag{1}$$

$$BrCl + Br^- \leftrightarrow Br_2Cl^-, \tag{2}$$

$$Br_2Cl^- \leftrightarrow Br_2 + Cl^-, \tag{3}$$

$$Br_2 + h\nu \rightarrow 2Br, \tag{4}$$

$$2(Br + O_3) \rightarrow 2(BrO + O_2), \tag{5}$$

$$2(BrO + HO_2) \rightarrow 2(HOBr + O_2), \tag{6}$$

yielding net

$$2HO_2 + H^+ + 2O_3 + Br^- + h\nu \xrightarrow{\text{HOBr, Cl}^-} HOBr + 4O_2 + H_2O. \tag{7}$$

Observational study with model calculation has also shown that these reactive halogens provide a destruction mechanism for ozone in the marine boundary layer [*Vogt et al.*, 1996; *Sander and Crutzen*, 1996; *Barrie et al.*, 1988; *Bottenheim et al.*, 1990].

[3] Dry deposition of boundary layer ozone to the Arabian Sea surface is understood to be another ozone loss mechanism of concern. The MOZART simulates aerodynamic resistance, gas-phase film resistance, and aqueous phase film resistance to estimate ozone deposition

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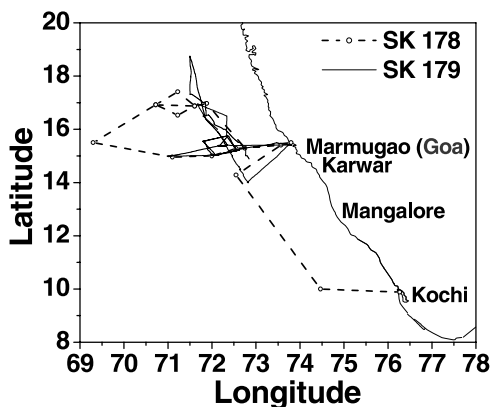
Figure 1. Cruise track of ORV *Sagar Kanya* during ARMEX 2002.

over the Arabian Sea [*Seinfeld and Pandis*, 1998]. This is similar to what has been assumed in the present deposition mechanism. However, the mechanism adopted in the present work slightly differs from that simulated by the MOZART in relation to the chemical process involved in affecting gas-phase and aqueous phase film resistances. The implication which is not simulated by the model is reduction in the gas phase and the aqueous phase film resistances caused by destruction of ozone by activated halogen species. *Chang et al.* [2004] have used this fact and have estimated dry deposition velocity of ozone for different ranges of wind speed over the marine region. He has shown that deposition of ozone is enhanced owing to decrease in these resistances. Alternatively, it may be said that net downward flux of ozone is increased on increase in the turbulence while the surface concentration of ozone remains less owing to destruction of ozone by the active halogens in the gas and aqueous phase film layers bordering the sea surface. Consequently, the deposition of ozone is enhanced.

[4] The objective of the present study is to investigate, through measurements and model simulation; average level of ozone and of its precursor gases like NO_x and CO over the Arabian Sea during monsoon season and to delineate the significant mechanisms ensuring the level of ozone over the region.

[5] The study is based on shipborne measurement of ozone, sea salt in TSP (total suspended particles), wet deposition flux of sea salt and weather parameters over the Arabian Sea during the Arabian Sea Monsoon Experiment (ARMEX) 2002. It also includes model simulation of surface ozone, NO_x and CO over the Arabian Sea for the period of ARMEX 2002. The ship arranged for the cruise during ARMEX 2002 was ORV (Ocean Research Vessel) *Sagar Kanya*. The cruise was divided into two legs (SK-178 and SK-179) spread over a period constituting most of the monsoon season in India (Figure 1). Leg 1 started at Kochi port (9.57°N, 76.16°E) on 21 June 2002 and ended at Goa port (15.24°N, 73.47°E) on 15 July 2002. Leg 2 started at Goa port on 17 July 2002 and ended at the same location on 16 August 2002.

2. Measurement and Analysis

[6] Surface ozone was monitored daily (except on a few bad weather occasions) from 0800 IST (0230 UTC)

to 2000 IST (1430 UTC) at a height of about 20 m asl over the Arabian Sea during 25 June to 13 August 2002. It was monitored at an interval of 5 min by UV-photometric ozone analyzer (Thermo Environmental Model 49, USA) using absorption wavelength 0.254 μm. The analyzer was calibrated by the built-in ozonator (ozone generator) using pure zero grade air. Error range of the instrument is ±1 nmol mol^{-1}. Meteorological parameters like temperature and humidity were measured with the help of automatic weather monitor. Data for sea salt in TSP were obtained by collecting TSP on board the ship with the help of a high-volume sampler, extracting the sample and analyzing them for major cations like Na$^+$, K$^+$, Ca^{2+} and Mg^{2+} by atomic absorption spectrometer (Perkin Elmer, 373 USA) and for major anions like Cl$^-$, SO$_4^{2-}$ and NO$_3^-$ by ion chromatograph (DIONEX-100, USA). Data for different chemical ions collected in this way were subjected to ion balance check and Na$^+$/Cl$^-$ molar ratio check which were statistically within the acceptable limit of variations.

[7] Sea salt concentrations were estimated by adding the concentrations of Na$^+$ and Cl$^-$ assuming that nearly all Na$^+$ and Cl$^-$ are in the form of NaCl molecule. Although it is a rather overestimation, it gives at least an approximate quantitative characterization of the presence of sea salt in the TSP. For estimating wet deposition flux of sea salt, rainwater samples were collected on event basis [*Momin et al.*, 2005] and were analyzed for major chemical ions. On the basis of these measurements, wet deposition flux was estimated as

$$F_{\text{sea salt}} = \frac{[\text{Na} + \text{Cl}] \times L}{A_{b_c}}, \qquad (8)$$

where $F_{\text{sea salt}}$ represents wet deposition flux of sea salt (μg/m^2), [Na + Cl] is concentration of sea salt (μg/L), L is amount of collected rainwater sample (liter), and A_{bc} is cross-section area of the funnel of bulk collector (m^2).

3. Model Description

[8] The model used in the present study is MOZART-2 chemical transport model [*Horowitz et al.*, 2003]. It provides the distribution of 63 chemical compounds, including ozone and ozone precursors, at a horizontal resolution of ~1.8 degree in longitude and latitude, and on 31 vertical levels extending from the surface to approximately the 10-hPa pressure level. Present result is taken at the level 20 m asl, the model's third pressure level from the ground. The model is able to resolve vertical gradient at this level reasonably well as also demonstrated and widely used by earlier worker [*Beig and Ali*, 2006; *Beig and Brasseur*, 2006]. A few vertical levels starting from the lowest level considered in the model are 7 m, 16 m, 20 m, 29 m, 52 m, etc. The emissions due to various sectors used in the model for 2002 are taken similar to the work by *Beig and Brasseur* [2006]. The emissions due to fossil fuel combustion, agricultural burning, biofuel, etc., are taken from the recent estimates made under the project entitled "Precursors of Ozone and their Effect on the Troposphere (POET)" [*Olivier et al.*, 2003]. In the adopted emission inventory, total global NO_x and CO emissions are taken as 126,122 Gg NO_2/a and 1,044,200 Gg CO/a, respectively. The regional
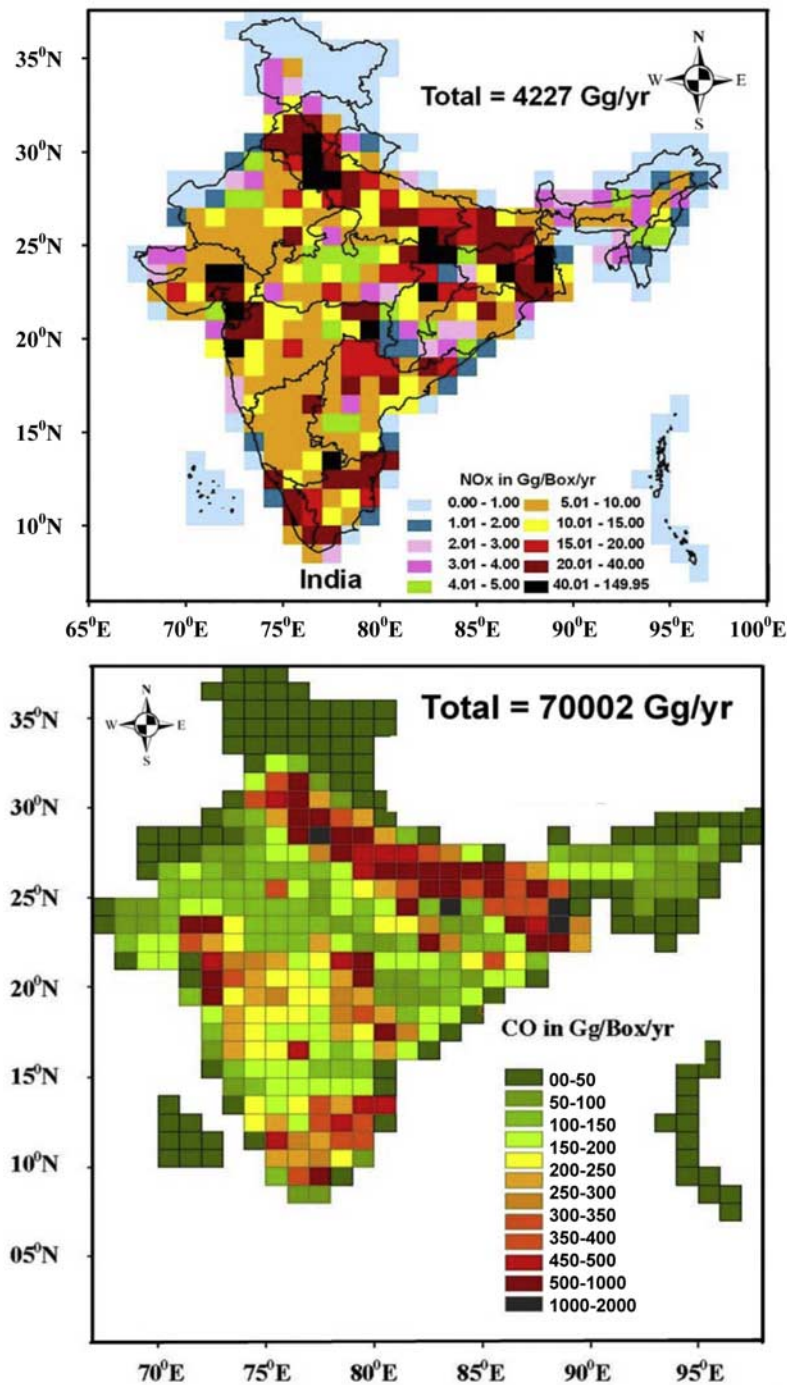
Figure 2. Regional total (bottom) CO and (top) NO$_2$ emissions in Indian geographical region.

total NO$_x$ and CO emissions in Indian geographical region are shown in Figure 2. Figure 2 has around 390 cells of 1° × 1° sizes covering the Indian geographical region in each plot. The total emissions from all sources in the Indian region are found to be approximately 4227 Gg NO$_2$/a and 70,002 Gg CO/a. Figure 2 (top) shows that the maximum NO$_x$ emission is from Indo-Gangetic region which is spread in northeast regions of India. The contribution of coal sources is found to be the highest contributor which amounts to about 44% of the total NO$_x$ emissions in India. The second largest contribution is provided by fossil fuel

combustion which is increasing rapidly owing to increase in vehicular traffic. Biofuel burning also contributes to the NO$_x$ emissions. The location of emission hot spots in Figure 2 correlates with the location of mega cities, emphasizing the contribution of emissions through transport sector and thermal power plants.

[9] Figure 2 (bottom) shows that the largest CO emissions are found to occur in the Indo-Gangetic plane. The location of emission hot spots seems to correlate with the densely populated rural areas, emphasizing the contribution of rural biofuel emissions through fuel wood
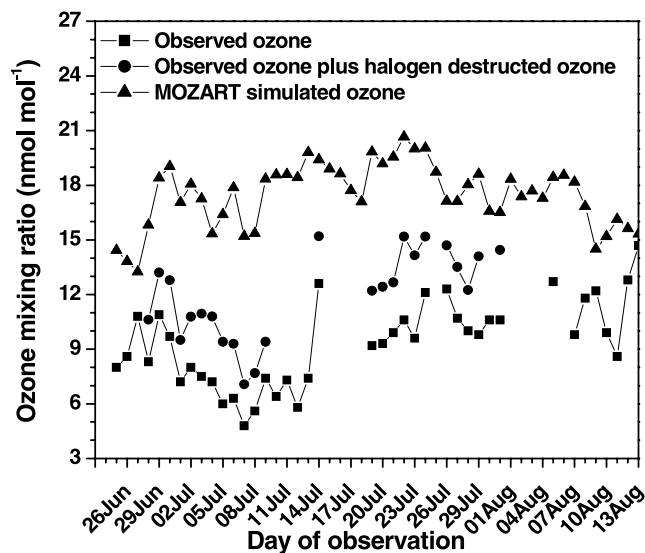
Figure 3. Observed and MOZART simulated daily average ozone over the Arabian Sea during ARMEX 2002 along the cruise track of ORV *Sagar Kanya*, SK-78 and SK-79 (circles indicate sum of observed ozone mixing ratio and that destroyed by halogens).

burning, etc. Relatively low values are seen over western part of India in spite of the fact that this area has significantly large rural population. The extreme north Indian states show minimum emission due to lower population density, limited agriculture and less vehicular proliferation due to undulating topography. The highest contribution in CO emission comes from biofuel emission amounting to more than 50%. The highest contribution for this source is found to be from the southern Indian states where several high emission areas are noticed. Contribution from rural sector is also high from northeast coastal areas. However, urban sector contribution is not much from these states excepting few big cities. However, overall urban contribution by biofuel is much less than that of rural sector. The VOC emissions adopted in the present work are provided by the POET project and details are provided by *Olivier et al.* [2003]. The emissions of some of the organic compounds like C_2H_6 is found to be as small as 0.488 Tg C/a but expected to increase in future, primarily owing to the increasing contribution of the transport sector. Meteorological data used in the model simulations are from ECMWF analysis for 2002 [*Beig and Brasseur*, 2006]. It may be noted that the model cannot resolve the gradient within a particular grid box (1.8 × 1.8 degrees) but it obviously resolves the gradient from one grid box to another. Also, the model cannot be run for finer resolution as this version of model is set for ~1.8 degrees resolution for optimum accuracy. On account of uncertainty in the emission estimates, error is introduced in the simulated mixing ratio of ozone and the other species, but it is likely to be less than 2−5% [*Beig and Brasseur*, 2006].

4. Results and Discussion

[10] Day to day variation of simulated boundary layer ozone as well as measured ozone over the region of cruise

track in the Arabian Sea for a period from 25 June to 13 August 2002 is shown in Figure 3. It is found that simulated ozone mixing ratio is low with an average value of ~17 nmol mol^{-1} and varying between ~13 nmol mol^{-1} and ~21 nmol mol^{-1}. Mixing ratios of NO$_x$ and CO as shown in Figure 4 are also low and vary in the range 90–350 pmol mol^{-1} and 50–80 nmol mol^{-1}, respectively, over the region of cruise track. The reason for low mixing ratio of ozone, NO$_x$ and CO over the Arabian Sea lies mainly in the dynamics involved in the prevailing synoptic weather system. During the monsoon season air over the Arabian Sea is purely of marine origin blowing from the Arabian Sea toward the west coast of India. So, transport of ozone precursors mainly from the continental source region of Indo-Gangetic Plains [*Ali et al.*, 2004; *Beig and Ali*, 2006] to the Arabian Sea region is completely ceased. Consequently, the region records less mixing ratio of ozone precursor gases like NO$_x$ and CO during monsoon resulting in a net photochemical loss of ozone. However, lower insolation due to cloudiness over the Arabian Sea for most of the period of the day tends to slow down the loss. Also,
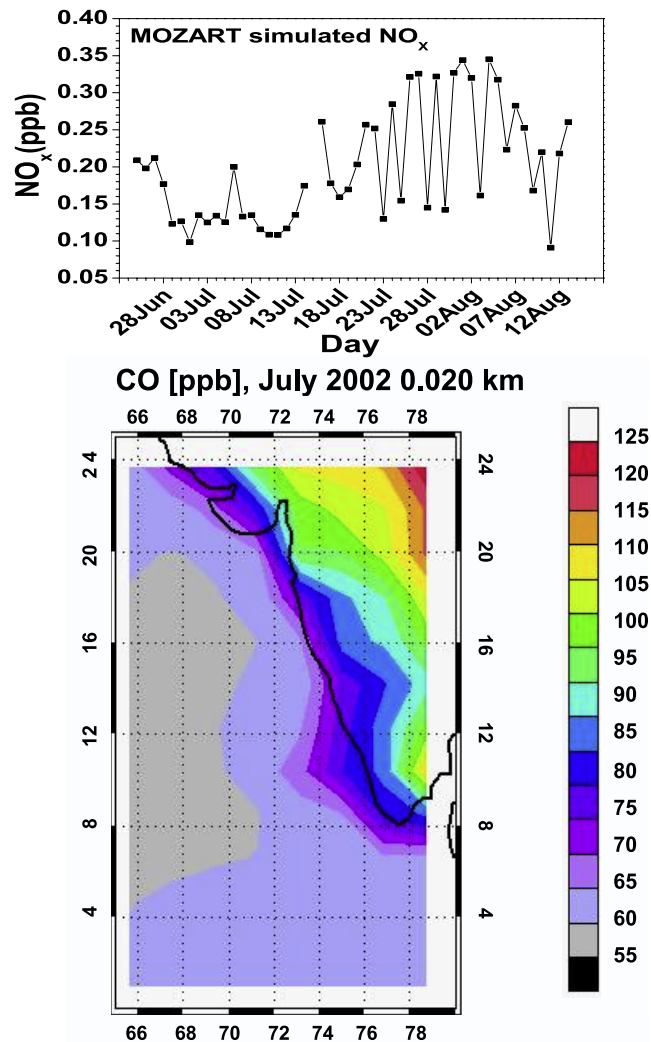

Figure 4. (top) Time series of daily average value of NO$_x$ over the Arabian Sea during ARMEX 2002 and (bottom) average spatial variation of CO during July 2002.
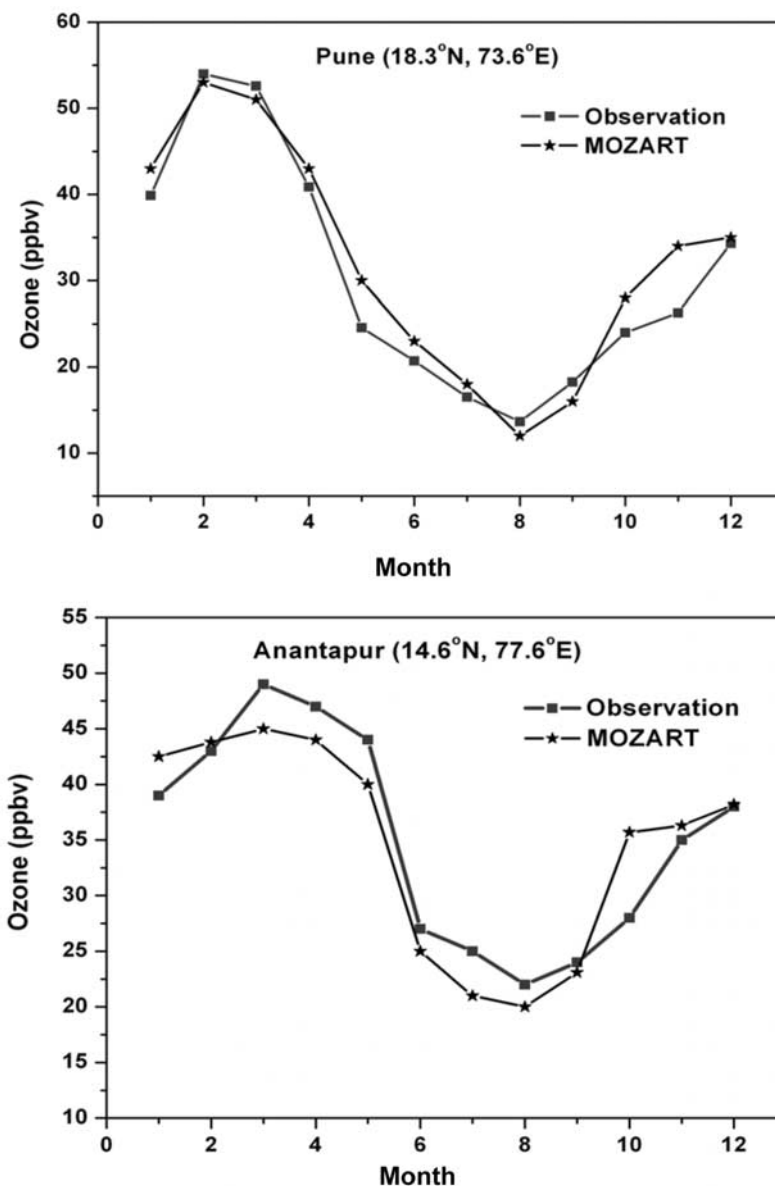
Figure 5. Comparison of calculated seasonal cycle for ozone with MOZART simulation in two regions of India.

the possibility of transport of ozone from land areas to sea is negligibly small as the prevailing southwesterly wind over the region during this season blow from sea to land.

[11] Daily average mixing ratio of ozone measured over the region of cruise track varies in the range $\sim5-15$ nmol mol^{-1} with an overall average value of 9 nmol mol^{-1}. When measured and simulated values of ozone are compared on day-by-day basis, observed ozone is $\sim28-69\%$ lower in about 90% of cases. It is pertinent to mention that the simulated and the observed ozone concentration data used for comparison are correlated in time and space both. Thus the above discrepancy may be caused by errors in simulating either marine boundary layer (MBL) height, meteorology and/or chemical sources and sinks.

[12] It may be noted that observed MBL height varied between 1.93 and 3.28 km in about 83% of cases [Morwal, 2005] with an average height of 2.63 km, whereas model simulated MBL height varied between 2 and 3 km during

the period of observation. Model and observed MBL heights are well correlated with correlation coefficient (r) equal to 0.95 (significant at better than 0.1% level). Vertical structure of the MBL at an Arabian Sea location (16°94′N, 71°20′E) showed that inversion layer persisted at around 800 hPa ($\sim$2 km) nearly on all the occasions during first stationary ship position (30 June to 10 July 2002). However, at the second stationary position of the ship (15°38′N, 72°18′E) during 22 July to 5 August 2002, inversion layer shifted a little upward with weakening of the inversion strength. On the other hand, inversion layer was not observed during the disturbed weather conditions on a few occasions. Various meteorological parameters showed prominent diurnal variations. The offshore trough did not affect the vertical structure of the atmospheric boundary layer. Consequently, the possibility that the observed anomaly in the ozone level might have been due to difference between model and observed MBL heights is ruled out.

[13] A comparison of the modeled result on the surface volume mixing ratio of ozone with that of observed data obtained from two different stations located in the western and the southern part of India is made to examine the model capability to reproduce the seasonal cycle over the landmass area. The simulated seasonal cycle for ozone is compared with values measured [*Beig et al.*, 2007] at a location in the western part of India, Pune (18.3°N, 73.6°E) as shown in Figure 5 (top). A seasonal maximum of ozone is observed during spring and is well captured by the model. During winter to spring period, northeasterly winds prevail over Pune which help in transporting pollutant rich air from the regions in the route where anthropogenic emissions are high. So the long-range/regional transport of pollutants can have a significant contribution toward the spring maximum of ozone at Pune as simulated by the model. The influence of long-range/regional transport is perceived to be more as compared to local photochemical production on the observed spring maximum of ozone at Pune. A seasonal minimum is observed during the period from June to September and is very well reproduced by the model. This minimum can be attributed partly to the influences of the southwest monsoon circulation during this period which brings clean marine air containing low concentrations of ozone toward the Indian subcontinent. During the monsoon period, the influence of the local photochemistry on the observed seasonal minimum at Pune seems to be negligible as compared to the southwest monsoon circulation driven transport which play a major role in redistributing the pollutants. The simulated seasonal cycle of ozone is also compared with the observed values [*Ahammed et al.*, 2006] at a southern Indian location, Anantapur (14.6°N, 77.7°E) as shown in Figure 5 (bottom). The agreement between observed data and model is reasonably good. The seasonal cycle at this station is very well reproduced by the model. The magnitude of the model results is well within the 2-sigma standard deviation of the observed data. The maximum concentration of ozone is found to be in the period from March to April. However, the model underestimates the observed values during these months. The minimum values of ozone are observed in the monsoon months (July−August) which are also simulated by the model. The low values of ozone during the monsoon months can be attributed to the southwest monsoon circulation which helps in transporting cleaner air from the marine regions toward the Indian landmass. Also, sunshine period gets reduced owing to cloudy condition which leads to lower photochemical production of ozone during this period. The above comparison indicates that the model is able to reproduce the observations reasonably well over the landmass and hence observed high values of ozone over the oceans discussed in this article are most likely to be due to missing sink mechanism rather than model deficiencies.

[14] The mechanisms simulated by MOZART-2 chemical transport model mainly involve ozone photochemistry, its advective and convective transport process and its standard deposition mechanism. Thus the observed result indicates that there is prominence of some other mechanisms, particularly sink mechanisms, than adopted in the model simulation which cause such a low level of ozone over the Arabian Sea.

[15] Figure 6 includes regression plots of observed ozone mixing ratio on temperature, relative humidity and on sea salt concentration in TSP on the basis of their daily average values. It may be noted that during the observation period there were some occasions when ozone and sea salt were not measured owing to some technical problem. As such, the number of points appearing in the regression plot between ozone and other parameters are less than the actual number of days of observational period. Figure 6 also shows time series of wet deposition flux of TSP, wind speed and wind direction during the period of observation. Regression analysis between ozone and temperature indicates that ozone has inverse relationship with temperature showing correlation coefficient r = −0.576 (significant at better than 0.1 percent). This indicates a regime of net photochemical loss of ozone and as the temperature increases the loss speeds up. Relative Humidity (RH) shows positive relationship with ozone. However, the result of correlation coefficient of ozone with RH is not significant at 5%. Thus, for the Arabian Sea region, we hereby propose for the first time two sink mechanisms, (1) enhanced surface deposition of ozone facilitated by increased marine surface reactivity due to more surface content of halogens and (2) destruction of ozone by reactive halides, which might have been dominant over the Arabian Sea during the monsoon season.

[16] The Arabian Sea surface was highly turbulent during most of the observational period because of the occurrence of semipermanent offshore trough and the daily average wind speed ranged between 8.2 and 15.1 m/s with an overall average value of 10.4 m/s (Figure 6). Using dry deposition velocity equal to 0.04 cm/s as given by *Chang et al.* [2004] for the range of wind speed as observed during ARMEX 2002, average dry deposition flux of ozone is found to be 8.8×10^9 molec cm^{-2} s^{-1} varying in the range 4.7×10^9 to 14.5×10^9 molec cm^{-2} s^{-1}. Using data for daily average height values of the MBL [*Morwal*, 2005] during ARMEX 2002, estimation of the loss of boundary layer ozone by deposition mechanism is made in the unit of nmol mol^{-1}d^{-1}. It is found that ozone loss by this mechanism is slow with an average value of 0.12 nmol mol^{-1}d^{-1} and varying in the range 0.08−0.16 nmol mol^{-1}d^{-1}. This mechanism contributes, on average, to nearly 1.5% of the total ozone loss by sea salt destruction, photolysis, chemical reaction and deposition to the sea surface. Dry deposition velocity of ozone in the standard model configuration over the Arabian Sea is considered as 0.025 cm/s. As such, the estimated ozone deposition rate is nearly 60% more than that given by the model.

[17] Evidence for the role of sea salt in destruction of ozone molecules is further obtained by investigating the relationship between ozone mixing ratio and sea salt concentration in TSP during the observational period. It is found that boundary layer ozone level is well anticorrelated with sea salt concentration in TSP (correlation coefficient, R = −0.543, significant at 0.4%). Regression equation between them is given as

$$\text{Ozone (nmol mol}^{-1}) = 14.904 - 0.975 \text{ Sea salt } (\mu g/m^3). \quad (9)$$

The above analysis suggests that sea salt may be playing a role in the destruction of boundary layer ozone over the Arabian Sea.
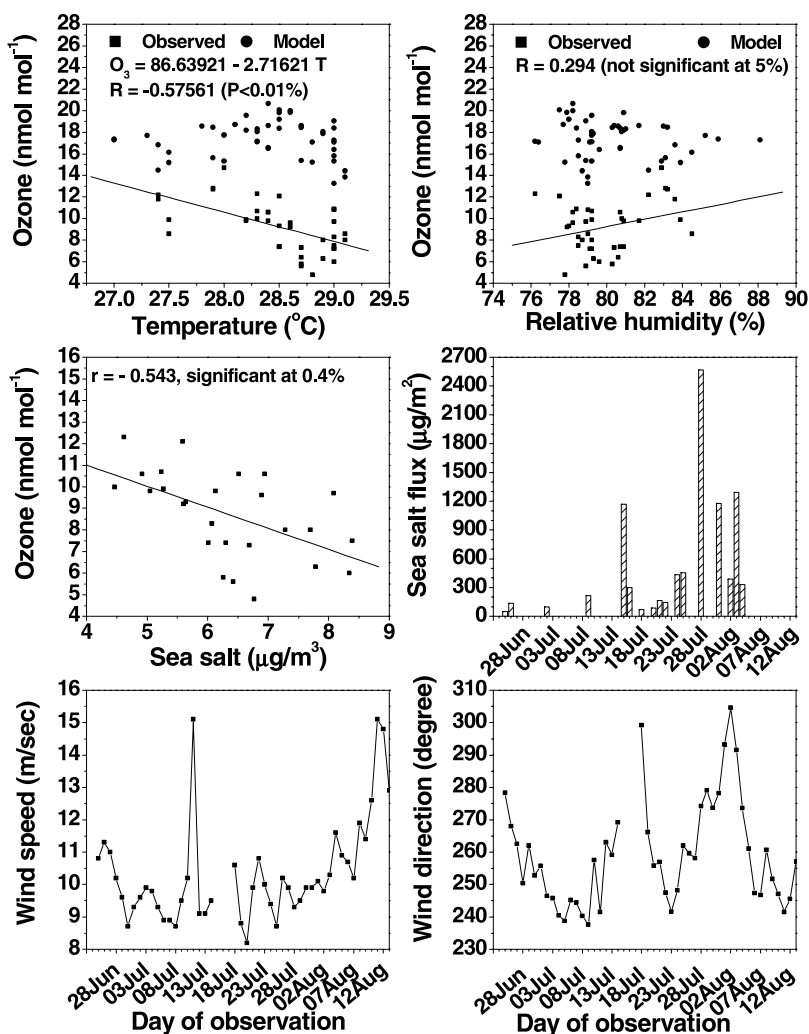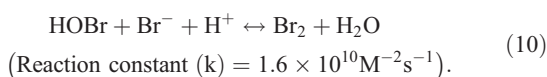
Figure 6. Regression plot of ozone on temperature and relative humidity and variation of daily mean concentration of sea salt in TSP, wet deposition flux of sea salt, wind speed, and wind direction over the Arabian Sea during ARMEX 2002.

[18] On the basis of the above evidence of the role of reactive halogens in destroying boundary layer ozone, calculation of the loss of ozone over the Arabian Sea due to reactive halogens is made. The calculation employs the proposed autocatalytic mechanism which critically depends on the rate of reaction (1). The rate constant of the forward reaction (1) used in the present calculation is that used by *Vogt et al.* [1996] ($k_1 \geq 5.6 \times 10^9$ M^{-2} s^{-1}) which is obtained by using an equilibrium constant (K_{eq}) equal to 5.6×10^4 M^{-2} for reaction (1) as used by *Wang et al.* [1994]. Reaction (1) is of the same order of magnitude as that of the comparable reaction of HOBr with Br$^-$ [*Eigen and Kustin*, 1962] which gives rise to Br$_2$ as shown below:

$$HOBr + Br^- + H^+ \leftrightarrow Br_2 + H_2O$$
$$\left(\text{Reaction constant (k)} = 1.6 \times 10^{10} M^{-2} s^{-1}\right). \quad (10)$$

However, the above reaction is potentially important for bromine cycling on sulphate aerosol [*Fan and Jacob*, 1992] and for autocatalytic bromine release from sea salt aerosol [*Mozurkewich*, 1995; *Sander and Crutzen*, 1996]. On account of large [Cl$^-$]/[Br$^-$] ratio in seawater the forward reaction (1) is more important than the forward reaction (10). The calculation of ozone loss utilizing the autocatalytic reaction mechanism involves a constant mixing ratio of HOBr (13 pmol mol^{-1}, a steady state value given by *Vogt et al.* [1996] for 14 model days) for every day computation, daily measured average concentration of Cl$^-$, daily measured average mixing ratio of ozone and an average pH value of aerosol equal to 6.74. Since the calculation involves daily average value of some of the observed chemical species along with model simulated steady state average mixing ratio of some of the species, the rate of production of intermediate species in the process is assumed to be an average rate for the day and there is no need of performing iteration in the computation. Rate of production of the chemical species involving reversible reaction in the reaction mechanism is computed at equilibrium state.

[19] Calculations based on the proposed mechanism of ozone destruction in the marine boundary layer by reactive halogens released from sea salt reveal that average ozone loss rate during monsoon season was 2.15 nmol mol^{-1}d^{-1}
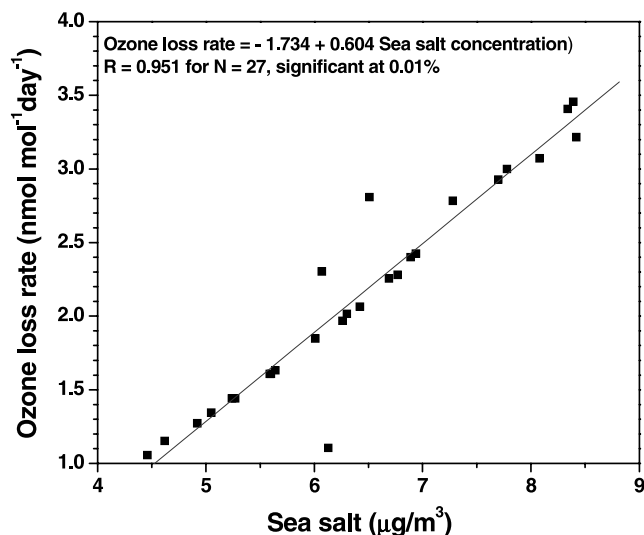
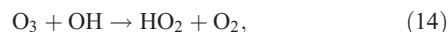**Figure 7.** Dependence of ozone loss rate on concentration of sea salt over the Arabian Sea during ARMEX 2002.

and it varied between 1.06 nmol mol^{-1}d^{-1} and 3.46 nmol mol^{-1}d^{-1} depending upon the abundances of sea salt in the marine boundary layer and of observed ozone (reaction constants are taken from *Sander and Crutzen* [1996]). Contribution from this mechanism to the model overestimation is found to vary between 18.4 and 65.1% of the overestimation with an average value of ~35%. It is also found from the calculation that average concentration of Br released from sea salt over the Arabian Sea during the observational period is 1.83 pmol mol^{-1} and varies in the range 1.3–2.4 pmol mol^{-1}. Average rates of release of Br and BrO come to be 0.88 × 10^{-5} pmol mol^{-1} s^{-1} and 0.19 pmol mol^{-1} s^{-1}, respectively; their ranges of variation are 0.43 × 10^{-5} to 1.4 × 10^{-5} pmol mol^{-1}s^{-1} and 0.11–0.39 pmol mol^{-1} s^{-1}, respectively. Ozone loss rate is found to be nearly linearly dependent on the sea salt abundance. The correlation coefficient (R) between ozone loss rate and sea salt concentration is 0.951 (significant at 0.01%). Their relationship can be expressed by following equation:

$$\text{Ozone loss rate } (\text{nmol mol}^{-1}\text{d}^{-1})$$
$$= -1.734 + 0.604 \text{ Sea salt conc.} (\mu\text{g/m}^3). \quad (11)$$

Regression plot showing nearly linear relationship between ozone loss rate and concentration of sea salt is shown in Figure 7. The negative intercept and zero loss rates at nonzero sea salt as appearing in the relation imply that ozone destruction by this mechanism needs certain threshold concentration of sea salt to start with the ozone destruction reaction. This threshold concentration of sea salt may vary depending on the temperature. On an average, the threshold concentration of sea salt is found here to be 2.88 μg/m^3. However, it is emphasized that there is a need for more observational investigation and also of laboratory simulation in this regard. This is because regression analysis provides only an approximate relationship, and not one-to-one mapping, between the two variables. The general range of sea salt concentration and the ozone mixing ratio over which this linear relationship will be applicable is difficult

to ascertain. However, the above relation can be applied to estimate approximate ozone loss over the whole gamut of observed sea salt concentration (4.06–8.42 μg/m^3) over the Arabian Sea during monsoon season.

[20] Ozone losses by photolysis and chemical reaction are also estimated from observations in order to compare them with the ozone loss by sea salt destruction mechanism. Chemical equations involved in these calculations are

$$O_3 \rightarrow O('D) + O_2, \quad (12)$$

$$H_2O + O('D) \rightarrow 2OH, \quad (13)$$

$$O_3 + OH \rightarrow HO_2 + O_2, \quad (14)$$

$$HO_2 + O_3 \rightarrow OH + 2O_2. \quad (15)$$

Equation (12) represents photolysis of ozone giving rise to electronically excited singlet oxygen atom. A small fraction (10%) of the produced singlet oxygen atom is assumed to react with water vapor at one atmospheric pressure and room temperature. It is mentioned that water vapor (H$_2$O) data used in the estimation of ozone loss by chemical reaction are those computed from ARMEX 2002 Humidity Mixing Ratio Data [*Morwal*, 2005]. Estimated water vapor mixing ratio is found to vary between 1.85% and 2.1% during the course of observation. The method used in the computation of ozone loss by photolysis and chemical reactions and production of hydroxyl radical (equations (12)–(15)) is described elsewhere in detail [*Buckley and Birks*, 1995]. Presence of such level of water vapor mixing ratio produces, on average, ~2.12 × 10^{10} molec s^{-1} hydroxyl radical during day hours which is equivalent to 0.861nmol mol^{-1} s^{-1}. Average concentration of hydroxyl radical over the Arabian Sea is not calculated in order to avoid complication in the computation. Calculation of ozone loss via equation (15) employs HO$_2$ concentration value equal to 2 × 10^8 molec cm^{-3}, a maximum concentration value determined by *Hard et al.* [1992] for a site characterized by clean marine air. Rate constants for photolysis of O$_3$ and Br$_2$ and for chemical reactions represented by equations (13)–(15) are taken from *Sander and Crutzen* [1996]. When ozone loss by sea salt destruction mechanism is compared with the total ozone loss (i.e., sum of ozone losses due to catalytic action of halogens, photolysis, chemical reaction and deposition to the sea surface) it amounts, on average, to ~31.5% of the total loss and varies in the range ~15–51% over the period of observation. Thus, ozone destruction by reactive halogens from sea salt manifests one of the major ozone sink mechanisms over the Arabian Sea during monsoon season. Comparison of the slope of equation (9) and (11) reveals that average lifetime of ozone over the Arabian Sea is about 2 days which is less than its estimated usual lifetime of 10–12 days. This may be due to the presence of additional ozone destruction mechanisms. It may be noted that the estimated additional loss of ozone due to sea salt destruction does not seem to be large enough to correct

model overestimation completely, but certainly it improves the result.

[21] The proposed ozone destruction mechanism may not be so effective for ozone loss during the other seasons owing to less availability of surface layer sea salt during those periods. It may be noted that average ozone losses due to photolysis, chemical reaction and deposition to the sea surface are around 56%, 11% and 1.5%, respectively. Consequently, photochemical sink mechanism is dominant over the sea salt destruction mechanism even during monsoon season, but the sea salt ozone destruction mechanism is playing significant role in this season to bring the ozone level down.

[22] A special feature seen in the variation of observed ozone (Figure 3) is that it became minimum (5 nmol mol^{-1}) during 1–13 July 2002 and varied between 5 nmol mol^{-1} and 8 nmol mol^{-1} with an average value around ~7 nmol mol^{-1}. On the other hand, during the period prior to and after it, the range of variations were 8–11 nmol mol^{-1} and 9–15 nmol mol^{-1} and the average mixing ratios were about 30% and 40% more, respectively. The explanation of the result follows that, during 1–13 July 2002, approaching winds were nearly southwesterly which were purely of marine origin containing aerosol mostly (about 85%) constituted by sea salt. It may be noted that average sea salt concentration during 1–13 July was 7.024 $\mu g/m^3$. After 13 July, there was massive removal of sea salt through rain occurring on a number of occasions. The per-event wet deposition of sea salt was found to range from 69.5 to 2567.5 $\mu g/m^2$ with an average value of 687.2 $\mu g/m^2$ spread over 12 days as shown in Figure 6. Wet deposition caused reduction of sea salt aerosols in the boundary layer and the average sea salt concentration during the period after 13 July was reduced to 5.474 $\mu g/m^3$. Thus, average sea salt concentrations in TSP were more by 1.55 $\mu g/m^3$ during 1–13 July than those recorded during the other observational periods. Theoretical calculations based on our proposed hypothesis indicate that the observed elevation in sea salt concentration during 1–13 July caused an increase in ozone loss rate of 0.56 nmol mol^{-1}/d which brought ozone level to its minimum value. Average ozone mixing ratio revealed by the model during 1–13 July is 17.4 nmol mol^{-1} and afterward it is 17.8 nmol mol^{-1}. Thus, there is little change in the average mixing ratio of model ozone over the entire period of observation. This is a clear indication that incorporation of the proposed mechanism in the model will provide an improvement over the present model results. On the basis of the present work and other available publications, it is also emphasized that the mechanism of ozone loss by reactive halogens may be considered in the model studies of ozone only when some particular regions and/or seasons are selected under the study. Also, halogen chemistry in the MBL is important for the global ozone budget.

[23] It may be added that on account of decrease in the concentration of sea salt after 13 July there was effective reduction in ozone destruction. Also, it is seen that during the period after 13 July 2002, prevailing wind was nearly westerly to northwesterly which might have advected ozone-rich air from continental region located to the west, i.e., from eastern part of Africa. Both these factors could have caused some increase in the level of ozone after 13 July. It may further be noted that data on the concentration of TSP during the period prior to 1–13 July is very limited and hence any concrete conclusion regarding influence of sea salt on the mixing ratio of ozone during that period cannot be drawn.

5. Conclusions

[24] Thus we summarize the study as follows.

[25] Ozone is significantly low over the Arabian Sea during monsoon. It is proposed that destruction of ozone by reactive halogens provides a sink mechanism which plays crucial role for occurrence of such low ozone mixing ratio. Theoretical calculation based on proposed hypothesis has shown that, on average, ozone loss due to catalytic action of halogens amounts to 2.15 nmol mol^{-1} d^{-1} which constitutes about 31.5% of the total loss of ozone by various sink mechanisms. Enhanced dry deposition of ozone, facilitated by increased marine surface reactivity due to more surface content of active halogens, also contributes partially (~0.12 nmol mol^{-1} d^{-1}) to the reduction of boundary layer ozone mixing ratio. The result indicates that the mechanism of ozone loss by reactive halogens may be considered in the model studies of ozone only when considering particular regions and seasons. Also, halogen chemistry in the MBL is important for the global ozone budget.

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