

## Observations and modeling of the seasonal variation of surface ozone at Amsterdam Island: 1994 - 1996

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**Abstract.** Since January 1994, continuous surface O<sub>3</sub> measurements have been carried out at Amsterdam Island (37°S, 77°E) in the southern Indian Ocean using a UV absorption analyzer. Mean O<sub>3</sub> concentrations and standard deviations are recorded every 5 min. This paper shows and discusses the O<sub>3</sub> time series for a 3-year period (1994-1996). During this period, O<sub>3</sub> shows a seasonal variation with maxima around 30 ppbv during winter (July - September) and minima around 13 ppbv during summer (December - February). O<sub>3</sub> levels at Amsterdam Island are close to those observed at Cape Grim (Tasmania, 41°S, 145°E) for the period of 1991 to 1995. In order to improve the understanding of the mechanisms controlling the O<sub>3</sub> seasonal variation at Amsterdam Island, our observations have been analyzed by using the global three-dimensional climatological Model of the Global Universal Tracer Transport in the Atmosphere (MOGUNTIA). The model reproduces well the observed O<sub>3</sub> mixing ratios and their seasonal cycle. The seasonal variation of stratospheric origin O<sub>3</sub> calculated by MOGUNTIA shows a maximum of 18 ppbv in September and a minimum of 13 ppbv in April. The oxidation of continentally emitted O<sub>3</sub> precursors during their transport to Amsterdam Island contributes to the photochemical production of O<sub>3</sub> by up to 12 ppbv during austral summer. From this amount, 3 - 7 ppbv are directly linked to nonmethane hydrocarbon oxidation chemistry under relatively high NO<sub>x</sub> conditions. In particular, biomass burning emissions contribute up to 5.5 ppbv to the observed O<sub>3</sub> levels in September. Both photochemical production by biomass burning and stratospheric influx of O<sub>3</sub> lead to a maximum in O<sub>3</sub> mixing ratios during late winter to early spring in agreement with the observations. Minimum O<sub>3</sub> mixing ratios observed during austral summer are related to photochemical O<sub>3</sub> depletion.

### 1. Introduction

Although tropospheric ozone (O<sub>3</sub>) represents only 10% of the total O<sub>3</sub> content of the atmospheric column, its concentration and its evolution are important for the Earth's biosphere. O<sub>3</sub> is a powerful greenhouse gas, contributing 18% to the global greenhouse effect [Intergovernmental Panel on Climate Change, 1995; Megie *et al.*, 1993]. O<sub>3</sub> contributes also to the oxidizing capacity of the troposphere since it is an oxidant which, via photodissociation and the subsequent reaction of its photoproducts, leads to the formation of hydroxyl radicals (OH), the cleaning agent of the troposphere [Logan, 1985; Crutzen, 1988]. Last, but not least, the harmful effects of O<sub>3</sub> on human health and on vegetation are now well established [Megie *et al.*, 1993].

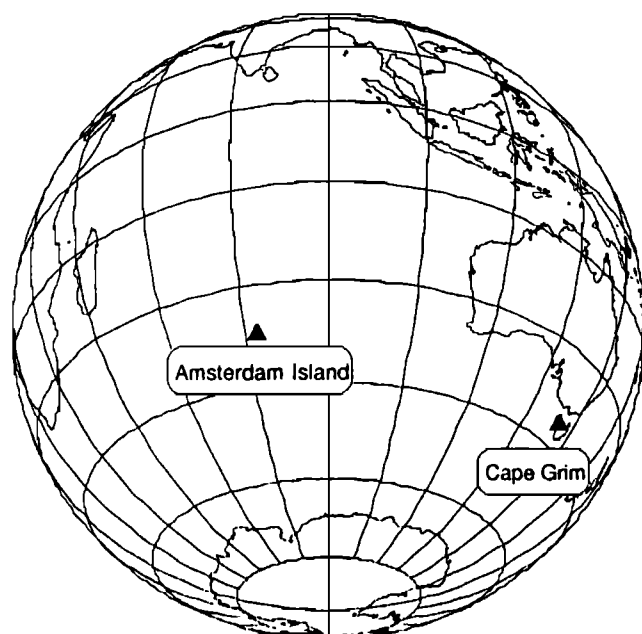
The main sources of O<sub>3</sub> in the troposphere are stratospheric intrusions and photochemical formation in the presence of nitrogen oxides (NO<sub>x</sub>=NO+NO<sub>2</sub>), whereas its main sinks are deposition on Earth's surface and photochemical destruction. In highly polluted areas, reaction with NO is also an important

removal process for O<sub>3</sub>. O<sub>3</sub> lifetime varies from 2 to 5 days in the tropical boundary layer to several months in the middle troposphere [Fishman *et al.*, 1991]. Therefore O<sub>3</sub> concentrations show a high spatial and temporal variability which needs to be taken into account in any attempt to evaluate the O<sub>3</sub> greenhouse effect.

Since the last century, increasing industrialization in the northern hemisphere has led to an increase in tropospheric O<sub>3</sub> in this hemisphere which is now quite well documented [Logan, 1985; Chameides *et al.*, 1992; Logan, 1994]. In contrast, in the southern hemisphere, mainly covered by oceans, the trend is not yet well established because it is based on too few measurements (see Scheel *et al.* [1990] and review data by Galbally *et al.* [1996]). The first studies of surface O<sub>3</sub> in the southern hemisphere attributed the observed O<sub>3</sub> seasonality to penetrations of O<sub>3</sub> from the stratosphere in the middle latitudes and subsequent transport toward higher and lower latitudes [Oltmans and Komhyr, 1986; Levy *et al.*, 1985]. More recent studies by Schnell *et al.* [1991] suggest that surface O<sub>3</sub> in the southern hemisphere is dominated by photochemical destruction during summer. Murayama *et al.* [1992] suggest that O<sub>3</sub> in Antarctica is mainly affected by vertical transport from the stratosphere and by southward transport of tropospheric air with low O<sub>3</sub> concentrations from lower latitudes. They do not exclude a possible impact of photochemistry on O<sub>3</sub> levels. Ayers *et al.* [1992] suggest that surface O<sub>3</sub> at Cape Grim in the southern hemisphere is dominated by photochemistry. Recently, Roelofs and Lelieveld [1997] conclude from their study with a general circulation model that surface O<sub>3</sub> seasonal variations in the

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**Figure 1.** Amsterdam Island and Cape Grim locations in the southern hemisphere.

southern hemisphere are dominated by the seasonality of  $O_3$  transported from the stratosphere. Thus the importance of the stratospheric component of  $O_3$  relative to its photochemical production and destruction in the southern troposphere remains an open question.

To observe and understand the seasonality and the long-term trends of  $O_3$  in the remote marine atmosphere of the southern hemisphere, continuous monitoring of surface  $O_3$  has been performed at Amsterdam Island ( $37^{\circ}47'S$ ,  $77^{\circ}31'E$ ) in the southern Indian Ocean since January 1994. Although a long series of  $O_3$  measurements is required to deduce trends, the seasonal variations of surface  $O_3$  can be analyzed to identify and quantify the atmospheric processes that control the  $O_3$  budget and thus can be used to understand its interannual variability.

In this paper, the  $O_3$  measurements from the first 3 years (1994-1996) of observations are presented, and the observed seasonal variability of  $O_3$  is determined. Amsterdam observations are also compared with other measurements of the southern hemisphere, especially those of Cape Grim. They are then analyzed and discussed using a global three-dimensional model of the troposphere.

## 2. Experiment

Amsterdam Island (Territoire des Terres Australes et Antarctiques Françaises) is located 5000 km from Africa and 4000 km from Australia. The island has a surface of 55 km<sup>2</sup> and is inhabited by 25 people living at the base "Martin de Viviès." The sampling site at Amsterdam Island is part of the World Meteorological Organization network for  $CO_2$  which has been measured since 1980 [Lambert *et al.*, 1995]. This site is under pure marine influence during most times of the year and under continental influence from Africa during only some periods of winter months [Miller *et al.*, 1993; Ramonet and Monfray, 1996]. Figure 1 presents the location of Amsterdam Island and Cape Grim, another important  $O_3$  monitoring station in the southern hemisphere.

$O_3$  measurements are performed halfway up on a 20-m high tower located at "Pointe Benedicte," 2.5 km windward of the base Martin de Viviès and 65 m above the sea level. Air is sampled through a 15-m Teflon line which has negligible  $O_3$  loss. Indeed, tests performed at Amsterdam Island showed that the loss of  $O_3$ , resulting from the use of the 15-m Teflon sample line was less than 1 ppbv for levels of  $O_3$  below 30 ppbv typical of those observed at Amsterdam Island. Thus, in Amsterdam Island conditions, the underestimation in the  $O_3$  data due to the sampling device of about 3% was lower than the instrument accuracy. Particular attention has been paid to the calibration and intercomparison of the instruments used for  $O_3$  measurements at the island to guarantee consistency of the results and allow interpretation of possible  $O_3$  trends that might be detected in the future.

Measurements started in January 1994 when the first  $O_3$  analyzer (analyzer 1, Thermo-Electron) was installed after being calibrated and zeroed by the manufacturer. Between March and December 1995, the zero of the analyzer was checked each month with synthetic zero air. A second Thermo-Electron analyzer (analyzer 2) was installed in March 1995 after being calibrated by the manufacturer. Both analyzers were intercompared during 9 months (March 1995 to February 1996, except from August to October 1995). This intercomparison showed the analyzer 1, which had not been calibrated for a year, did not present any significant drift. We see on Figure 2 that in 99% of occasions the hourly mean concentrations differed by less than 5 ppbv and in 75% of occasions differed by 1 ppbv or less. On average, the difference  $DO_3 = (\text{analyzer 1} - \text{analyzer 2})$  was  $0.32 \pm 1.76$  ppbv.

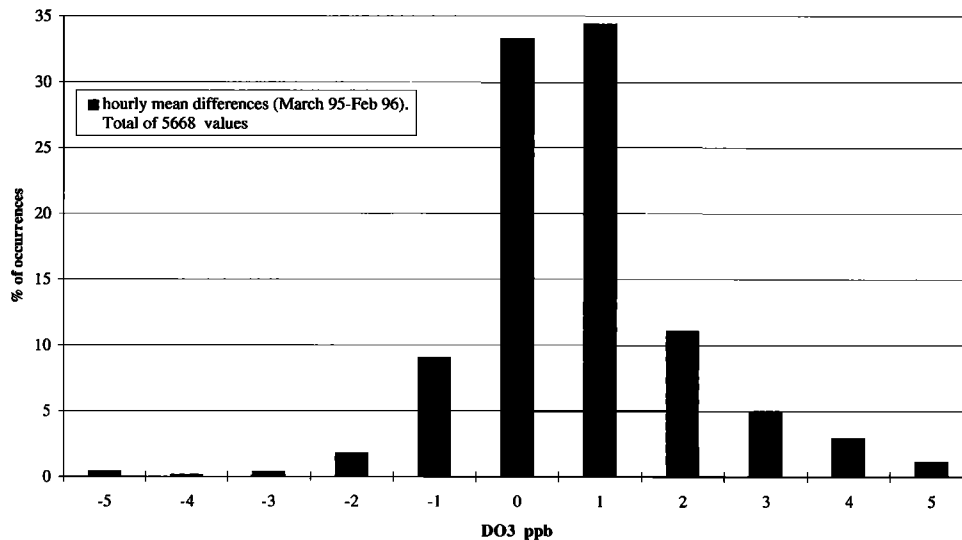
In 1996, the zero and calibration were checked monthly using an  $O_3$  generator (Thermo-Electron, model 165) allowing us to control that there was no significant drift. The  $O_3$  generator was previously calibrated in the laboratory at Gif sur Yvette.

Measurements are performed with a time step of 10 s and mean  $O_3$  mixing ratios and standard deviations are recorded every 5 min. Because of some power failures which induced uncorrected and scattered data during a few minutes, a filter was applied to suppress these data. Therefore 5-min  $O_3$  data associated with a standard deviation greater than 1.25 ppbv, representing 3 times the mean of the standard deviation calculated over the 1994 year, were discarded. These outliers were always less than 10% of the total data on a monthly basis (except for August 1996 when 16.3% of the data were discarded because of some technical problems due to contamination of the line by seawater). The remaining data were then aggregated into hourly and monthly averages.

## 3. Results and Discussion

### 3.1. $O_3$ Observations at Amsterdam Island

Figure 3 presents the monthly mean mixing ratios of  $O_3$  at Amsterdam Island from 1994 to 1996. No statistically significant trend is observed over this short period of 3 years ( $+0.63 \pm 1.64$  ppbv/yr).  $O_3$  mixing ratios show maximum values around 30 ppbv ( $29.51 \pm 1.96$  ppbv) during winter (July - September) and minimum values of  $14.59 \pm 1.30$  ppbv during summer (December - February) with the lowest monthly mean value of 13 ppbv in January. The seasonal variation of the surface  $O_3$  measured at Amsterdam Island is in phase with the observations performed at Cape Grim from 1991 to 1995 [Galbally *et al.*, 1996] as depicted in Figure 3. However, Amsterdam Island  $O_3$  levels seem to be slightly lower than those



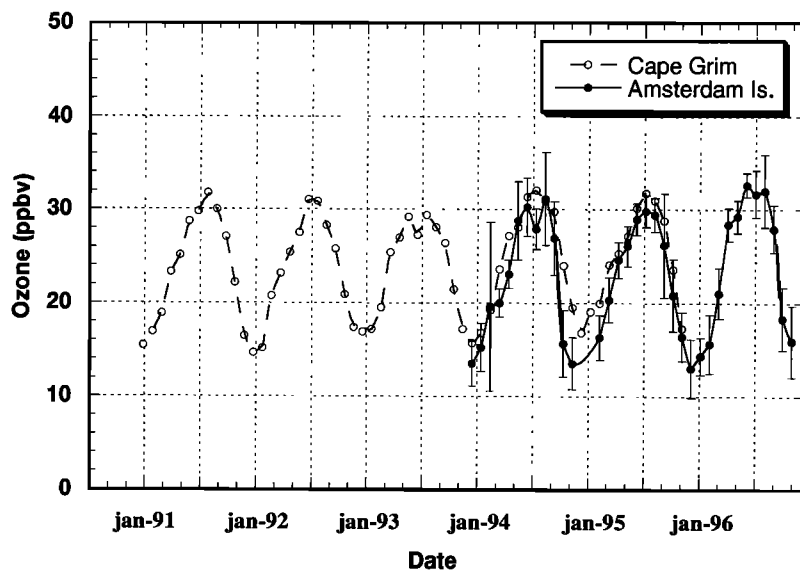
**Figure 2.** Hourly mean differences between the two O<sub>3</sub> Thermo-Electron analyzers used at Amsterdam Island (analyzer 1 - analyzer 2).

at Cape Grim, especially during summer when this difference reaches 3 ppbv. This small difference could be explained by a very clean marine atmosphere at Amsterdam Island, which is more than 3000 km far from any continent, whereas Cape Grim measurements, which include all observations, could be partly influenced by Australia. Nevertheless, intercomparison of O<sub>3</sub> analyzers operating at Cape Grim and at Amsterdam is necessary to evaluate any possible instrumental offset.

To proceed in the analysis of our observations at Amsterdam Island, one must consider the processes that might affect O<sub>3</sub> seasonal variability at this remote oceanic station. Vertical profiles of O<sub>3</sub> in the marine atmosphere typically exhibit the lowest values in the boundary layer [Murayama *et al.*, 1992; Kley *et al.*, 1996]. This vertical gradient is mainly controlled by O<sub>3</sub> deposition and by enhanced photochemical destruction. Although

deposition of O<sub>3</sub> to water is a very important loss process for tropospheric O<sub>3</sub> [Ganzeveld and Lelieveld, 1995], the temporal variation of O<sub>3</sub> due to deposition over remote oceanic stations is estimated to be at most a few percent [Ganzeveld and Lelieveld, 1995; and Roelofs and Lelieveld, 1995]. Therefore variation of O<sub>3</sub> deposition on an annual basis and its subsequent control of the O<sub>3</sub> seasonal cycle will not be discussed in this paper. Therefore the annual cycle of surface O<sub>3</sub> at Amsterdam Island could be mainly controlled by (1) stratosphere-troposphere exchange of O<sub>3</sub>, (2) the photochemical destruction of O<sub>3</sub> under low NO<sub>x</sub> conditions and (3) long-range transport of O<sub>3</sub> from areas rich in O<sub>3</sub> precursors.

Our observations are compared to the results of the climatological 3-D global model of the troposphere, Model of the Global Universal Tracer Transport in the atmosphere (MOGUNTIA) [Zimmermann, 1988]. This Eulerian model can



**Figure 3.** Variations of surface ozone in the southern hemisphere at Cape Grim from 1991 to 1995 (all sectors, after Galbally *et al.* [1996]) and at Amsterdam Island from 1994 to 1996. The lines attached to the means are the within-month variabilities ( $\pm 1$  standard deviation).

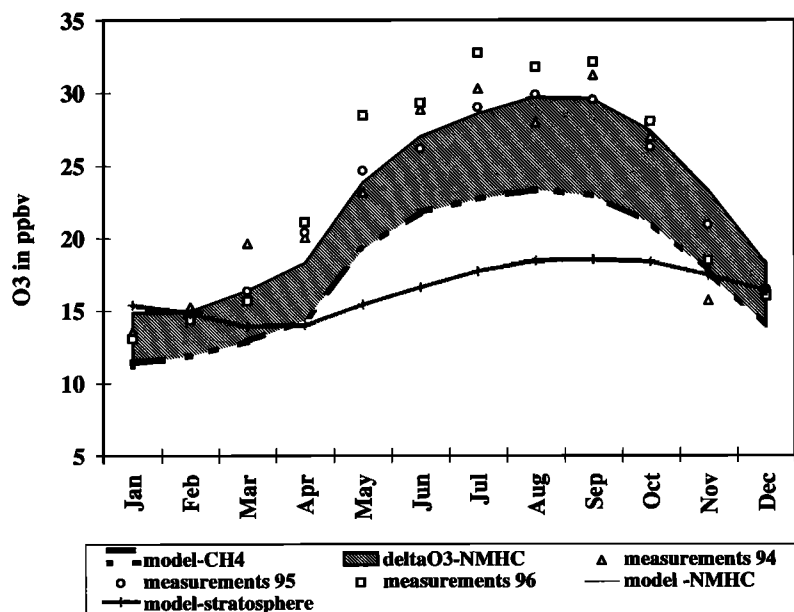
simulate the spatial and temporal variation of the tropospheric chemical compounds with a  $10^\circ$  latitude  $\times$   $10^\circ$  longitude horizontal resolution and 10 vertical layers between the surface and 100 hPa, spaced every 100 hPa. MOGUNTIA is able to simulate the background CO/CH<sub>4</sub>/NO<sub>x</sub>/HO<sub>x</sub>/O<sub>3</sub> chemistry [Crutzen and Zimmermann, 1991] and that of natural and anthropogenic nonmethane hydrocarbons (NMHC) [Kanakidou and Crutzen, 1993; Poisson and Kanakidou, 1996; Poisson, 1997; and N.Poisson et al., Impact of nonmethane hydrocarbons in tropospheric chemistry and the oxidizing power of the global troposphere: Three-dimensional modeling results, submitted to *Journal of Atmospheric Chemistry*, 1998 (hereafter referred to as Poisson et al., submitted manuscript, 1998)]. MOGUNTIA will be used to identify and quantify the impact of different factors on the O<sub>3</sub> seasonality: stratospheric influx of O<sub>3</sub>, NMHC chemistry, and biomass burning emissions of O<sub>3</sub> precursors (long-range transport).

### 3.2. Impact of Stratospheric Influx of O<sub>3</sub> on the Observed Surface Concentrations

A recent modeling study by Roelofs and Lelieveld [1997] using the general circulation European Center Hambourg Model (ECHAM) shows that intrusion of stratospheric air might be a significant source of surface tropospheric O<sub>3</sub>. In particular, they demonstrated that the contribution of O<sub>3</sub> from the stratosphere to the surface O<sub>3</sub> is maximum in winter and spring when the photochemical lifetime of O<sub>3</sub> is relatively long. According to their estimates, the contributions of stratospheric O<sub>3</sub> to the tropospheric content of O<sub>3</sub> in the southern hemisphere are 35% and 50% during summer and winter, respectively. By distinguishing the stratospheric-originating O<sub>3</sub> from the photochemical tropospheric O<sub>3</sub>, these authors show that the

seasonal cycle of O<sub>3</sub> at Cape Grim might be governed by the stratospheric contribution. They did not report results concerning Amsterdam Island.

Although MOGUNTIA is a climatological model and therefore the parametrization of the O<sub>3</sub> influx from the stratosphere in the model is quite poor [Gallardo-Kleener, 1996], we used it to evaluate the impact of the stratospheric source of O<sub>3</sub> on calculated surface mixing ratios at Amsterdam Island. For this purpose, all photochemical processes have been turned off in the MOGUNTIA model. O<sub>3</sub> was treated as an inert tracer, having only a stratospheric source and a tropospheric sink by dry deposition. The O<sub>3</sub> calculated concentrations for Amsterdam Island when neglecting photochemistry (model-stratosphere) and when taking into account the CO/CH<sub>4</sub>/NMHC oxidation in the troposphere (model-NMHC) are depicted in Figure 4. For comparison purposes, the observed O<sub>3</sub> concentrations are also shown in Figure 4. According to our calculations, O<sub>3</sub> of stratospheric origin could contribute more than 50% to wintertime surface O<sub>3</sub> at Amsterdam Island, which is consistent with the results of Roelofs and Lelieveld [1997]. Note that these calculations represent an upper limit for the stratospheric impact on O<sub>3</sub> values, since for the "model-stratosphere" simulation the chemical destruction of O<sub>3</sub> in the troposphere has been neglected. The calculated impact of the stratospheric influx of O<sub>3</sub> appears to be maximum in late winter and in early spring, in phase with the observed surface O<sub>3</sub> seasonality, although the calculated amplitude is much smaller than observed. It is worth noting that when neglecting photochemistry, the computed O<sub>3</sub> levels for January (summer) are higher than the observations. This is due to the omission of photochemical destruction of O<sub>3</sub> by photolysis and by the CO/CH<sub>4</sub>/NMHC chemistry in the marine environment during the austral summer (December - February).



**Figure 4.** Yearly seasonal surface ozone mixing ratios at Amsterdam Island : comparison between observations and model calculations. Triangles correspond to O<sub>3</sub> measurements in 1994, circles represent 1995 measurements, and open squares show 1996 measurements. Shaded area stands for the difference in ozone levels due to the consideration of nonmethane hydrocarbons (NMHC) chemistry in the Model of the Global Universal Tracer Transport in the Atmosphere (MOGUNTIA). Model-CH<sub>4</sub> curve shows simulations considering only CH<sub>4</sub>, CO chemistry; model-NMHC curve shows simulations taking into account NMHC oxidation; model-stratosphere curve shows simulations neglecting all photochemical processes (see text).

### 3.3. Impact of NMHC Chemistry on Surface O<sub>3</sub> Concentrations at Amsterdam Island

The observed low O<sub>3</sub> concentrations in austral summer associated with the high level of solar UV radiation are consistent with photochemical destruction of O<sub>3</sub> by photolysis and CO, CH<sub>4</sub>, and NMHC oxidation chemistry under low NO<sub>x</sub> conditions [Ayers *et al.*, 1992]. When only CH<sub>4</sub>, CO, NO<sub>x</sub>, and HO<sub>x</sub> chemistry is taken into account in the MOGUNTIA model (model-CH<sub>4</sub>), the model reproduces well the observed seasonal trend of O<sub>3</sub> as depicted in Figure 4. However, the calculated O<sub>3</sub> mixing ratios are lower by 2 - 7 ppbv than the observations, depending on the season (the highest difference is calculated for winter).

Then, ethane, propane, ethene, propene, n-butane, and isoprene chemistry has been taken into account in the model as described by Poisson *et al.* (submitted manuscript, 1998). N-butane has been used as a generic species to account for the hydrocarbons with more than four carbon atoms (other than isoprene) having both anthropogenic and natural emissions. Nonmethane hydrocarbon total emissions in the model are 567 Tg- C/yr from which 464.4 Tg- C/yr are of natural origin.

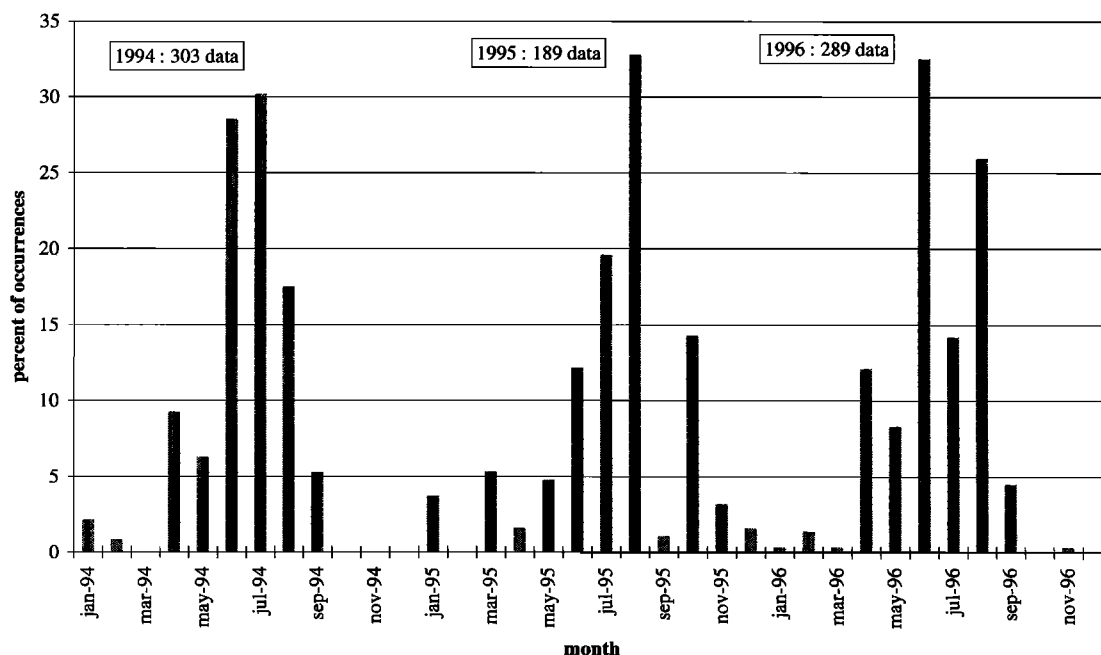
When the chemistry of natural and anthropogenic NMHC is taken into account in the model (model-NMHC), calculated O<sub>3</sub> concentrations are significantly higher than in the CH<sub>4</sub> simulation and in good agreement with both the seasonal variation and the levels of O<sub>3</sub> observed at Amsterdam Island. The difference in the calculated O<sub>3</sub> in these two simulations,  $\Delta O_3 = O_3(\text{model-NMHC}) - O_3(\text{model-CH}_4)$ , becomes maximum during winter. This impact of NMHC on O<sub>3</sub> surface levels results from (1) the local NMHC photochemistry which in this low-NO<sub>x</sub> environment is expected to lead to a net chemical destruction of O<sub>3</sub> and (2) the oxidation of NMHC emitted over continental area rich in NO<sub>x</sub> (Africa) and transport of the subsequently produced O<sub>3</sub> to Amsterdam Island. This transport process affecting the O<sub>3</sub> budget at Amsterdam Island is enhanced during winter months since most of the air masses coming from the African continent sector

are reaching the island from June through August (see section 3.4). The transport/chemistry model results show that photochemical production of O<sub>3</sub> from continentally emitted NMHC and NO<sub>x</sub> and subsequent transport over the oceans could dominate over the local photochemical destruction of O<sub>3</sub> by hydrocarbon oxidation under low-NO<sub>x</sub> conditions. According to our model calculations, NMHC chemistry contributes 22% to the calculated annual mean O<sub>3</sub>.

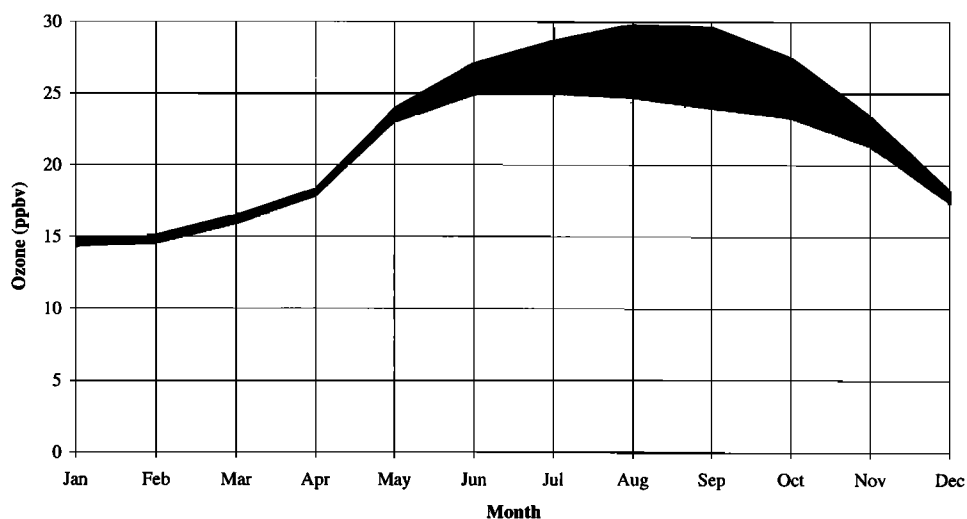
### 3.4. Impact of Long-Range Transport

Typical air mass back trajectories and radon 222 measurements have been studied to determine the origin of the continental influence that can be seen at Amsterdam Island. The air mass back trajectory analysis by Miller *et al.* [1993] showed that 74% of the air masses arriving at Amsterdam Island originated from the west sector, whereas only a few percent (<10%) came from the east sector. Hence Africa is the predominant continental source area for trace material that could be transported to Amsterdam Island. Miller *et al.* also showed that air masses coming from South Africa, representing 19% of the cases year-round, were the most frequent in winter and early spring (June-October). A recent study by Cooke *et al.* [1996] based on satellite observations of fires showed that the burning season in southeastern Africa occurred between June and November with space and time dependent maxima between July and October.

The enhancement of transport of polluted air to Amsterdam Island during winter is confirmed by the radon 222 observations. Radon 222 is a continental tracer, measured on a 2-hours basis since 1960 at Amsterdam Island [Polian *et al.*, 1986]. It is emitted mainly over continents and has a lifetime due to radioactive decay of 3.8 days. The Rn 220 ("thoron") half-life is only 54 s, but its daughter, Pb 212, has a 10.6 hour half-life and therefore can be measured. Thoron measurements allow us to determine the local origin of an air mass. Figure 5 presents (in percent) the monthly distribution of the radon 222 observations



**Figure 5.** Histogram showing monthly distribution of the frequency of simultaneous appearance of Rn 222 > 2 pCi/m<sup>3</sup> and Rn 220 < 0.1 pCi/m<sup>3</sup> at Amsterdam Island for 1994 - 1996.



**Figure 6.** Biomass burning contribution on surface ozone at Amsterdam Island calculated by the MOGUNTIA model. Shaded area stands for the difference in ozone levels due to the consideration of biomass burning in the model. Lower bound of the curve represents the  $O_3$  MOGUNTIA calculations without biomass burning emissions.

that were greater than  $2 \text{ pCi/m}^3$  and were associated with Rn 220 activities below  $0.1 \text{ pCi/m}^3$  for the years 1994 through 1996 (G. Polian, personal communication, 1997). Air with radon 222 activity higher than  $2 \text{ pCi/m}^3$  in conjunction with absence of Rn 220 activity is considered to be significantly influenced by the continent. Note that Rn 222 values greater than  $2 \text{ pCi/m}^3$  represented only 8, 4 and 7% of all the data for the years 1994, 1995, and 1996, respectively. According to these observations, most of the air masses coming from the continent were reaching Amsterdam Island between June and August, depending on the year, in agreement with the analysis of air mass back trajectories by Miller *et al.* [1993] and Ramonet and Monfray [1996]. Therefore, during winter,  $O_3$  levels at Amsterdam Island may be affected by transport of  $O_3$  from southern Africa. This hypothesis is confirmed by Fishman *et al.* [1991], who detected the influence of biomass burning from southern Africa on  $O_3$  levels over the Indian Ocean by satellite observations. Moreover, Thompson *et al.* [1996] have also presented the impact of biomass burning on  $O_3$  measured levels in southern Africa and the surrounding oceans during the Southern African Fire-Atmosphere Research Initiative 1992 (SAFARI-92) experiment.

In Figure 6, the impact of biomass burning in terms of phase and amplitude on the surface  $O_3$  observed at Amsterdam Island is demonstrated by comparison of two different model calculations: one considering all sources and one neglecting the emissions of all  $O_3$  precursors by biomass burning. As depicted in Figure 6, the impact of biomass burning is negligible between January and May (<4%) and varies from 4 to 19% between June and December, with the maximum value of 19% occurring in September. According to these MOGUNTIA model results, the removal of the emissions by biomass burning leads to a maximum of  $O_3$  in June, that is 1-3 months earlier than effectively observed at Amsterdam Island (from July to September, depending on the year). Therefore the model calculations suggest that the biomass burning emissions, mostly occurring in the tropics and in the subtropical southern Africa, affect the seasonal pattern of surface  $O_3$  observed at Amsterdam Island during winter and spring. The key factor for  $O_3$  enhancement in the midlatitudes of the southern

hemisphere is emissions of  $O_3$  precursors in the intertropical belt. Subsequent photochemical production of  $O_3$  and long-range transport propagates  $O_3$  enhancement to oceanic midlatitude areas.

#### 4. Summary and Conclusions

During the first 3 years of  $O_3$  monitoring at Amsterdam Island, surface  $O_3$  mixing ratios show a minimum in January (around 13 ppbv) and a maximum during winter (around 30 ppbv) with no significant interannual variation. This seasonal pattern is in agreement with the observations made at other remote sites in the southern hemisphere, indicating possible similar contributions of the different sources/sinks of  $O_3$  in these sites. It has been shown that the annual cycle of surface  $O_3$  observed at Amsterdam Island from 1994 to 1996 is consistent (1) with predominant photochemical destruction of  $O_3$ , mainly of stratospheric origin during summer, (2) with long range transported  $O_3$ , (mainly due to biomass burning in southern Africa and Madagascar) and enhanced  $O_3$  levels of stratospheric origin during winter.

The observed and calculated surface  $O_3$  seasonal cycles at Amsterdam Island are in very good agreement. Therefore the model can be used to quantify some of the main factors contributing to the observed seasonal cycle of  $O_3$  in this region. Thus, on an annual average, impact of stratospheric  $O_3$  has been shown to contribute less than 75% to the calculated  $O_3$ . This impact maximizes in summer when all calculated  $O_3$  could originate from the stratosphere, whereas in winter, stratospheric  $O_3$  could explain up to 60% of the calculated  $O_3$ . Model calculations also point out the key role of continentally emitted NMHC in the occurrence of tropospheric  $O_3$  over this oceanic remote location in the southern hemisphere. On an annual average, the NMHC chemistry contributes 22% to the calculated  $O_3$  level. According to model calculations, biomass burning over southern Africa and Madagascar shifts the  $O_3$  maximum from June to July-September and enhances the annual mean surface  $O_3$  mixing ratios by 8% with its maximum impact of 19% occurring in September. Thus our results show that even at a remote station

in the Indian Ocean, more than 3000 km from any continent, the long-range transport of pollutants from continental high-NO<sub>x</sub> areas contributes to the background O<sub>3</sub> level. A longer record of O<sub>3</sub> at Amsterdam Island may allow us to detect any possible interannual variability and any trends in background O<sub>3</sub> due to anthropogenic activities like deforestation, agriculture, and biomass burning.

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## References

- Ayers, G.P., S.A. Penkett, R.W. Gillett, B. Band, I.E. Galbally, C.P. Meyer, C.M. Elsworth, S.T. Bentley and B.W. Forgan, Evidence for photochemical control of ozone concentrations in unpolluted air, *Nature*, **360**, 446-449, 1992.
- Chameides, W.L. et al., Ozone precursor relationships in the ambient atmosphere, *J. Geophys. Res.*, **97**, 6037-6055, 1992.
- Cooke, W.F., B. Koffi, and J.M. Gregoire, Seasonality of vegetation fires in Africa from remote sensing data and application to a global chemistry model, *J. Geophys. Res.*, **101**, 21,051-21,065, 1996.
- Crutzen, P.J., Tropospheric ozone: An overview, in *Tropospheric Ozone*, edited by Isaksen, pp. 3-31, D. Reidel, Norwell, Mass., 1988.
- Crutzen, P.J., and P.H. Zimmermann, The changing photochemistry of the troposphere, *Tellus, Ser. B*, **43**, 136-151, 1991.
- Fishman, J., K. Fuhkrzjasman, B. Cros, and D. Nganga, Identification of widespread pollution in the southern hemisphere deduced from satellites analyses, *Science*, **252**, 1693-1696, 1991.
- Galbally, I.E., C.P. Meyer, Y. Ye, S.T. Bentley, L.J. Carpenter, and P.S. Monks, Ozone, nitrogen oxides (NO<sub>x</sub>) and volatile organic compounds in near surface air at Cape Grim, in *Baseline Atmospheric Program Australia 1994-95*, edited by R.J. Francey, A.L. Dick and N. Derek, pp. 81-88, Bur. of Meteorol. and Commonw. Sci. and Ind. Res. Organ. Atmos. Res., Melbourne, 1996.
- Gallardo-Kleenner, L., Oxidized nitrogen in the troposphere: the role of lightning, Ph.D. thesis, 160 pp, Univ. of Stockholm, Stockholm, 1996.
- Ganzeveld, L., and J. Lelieveld, Dry deposition parametrization in a chemistry general circulation model and its influence on the distribution of reactive trace gases, *J. Geophys. Res.*, **100**, 20,999-21,012, 1995.
- Intergovernmental Panel on Climate Change (IPCC), *Climate Change 1994: Radiative Forcing of Climate Change and an Evaluation of the IPCC IS 92 Emissions Scenarios*, edited by Houghton J.T. et al., 339 pp., Cambridge Univ. Press, New York, 1995.
- Kanakidou, M., and P. J. Crutzen, Scale problems in global tropospheric chemistry modeling: Comparison of results obtained with a three-dimensional model, adopting longitudinally uniform and varying emissions of NO<sub>x</sub> and NMHC, *Chemosphere*, **26**, 1-4, 787-802, 1993.
- Kley, D., P.J. Crutzen, H.G.J. Smit, H. Vömel, S.J. Oltmans, H. Grassl, V. Ramanathan, Observations of Near-Zero Ozone concentrations Over the Convective Pacific: Effects on Air Chemistry, *Science*, **274**, 230-233, 1996.
- Lambert, G., P. Monfray, B. Ardouin, G. Bonsang, A. Gaudry, V. Kazan, and G. Polian, Year-to-year changes in atmospheric CO<sub>2</sub>, *Tellus, Ser. B*, **47**, 53-55, 1995.
- Levy, H., II, J.D. Mahlman, W.J. Moxim, and S.C. Liu, Tropospheric ozone: the Role of transport, *J. Geophys. Res.*, **90**, 3753-3772, 1985.
- Logan, J.A., Tropospheric ozone: Seasonal behavior, trends, and anthropogenic influence, *J. Geophys. Res.*, **90**, 10,463-10,482, 1985.
- Logan, J.A., Trends in the vertical distribution of ozone: An analysis of ozonesonde data, *J. Geophys. Res.*, **99**, 25,553-25,585, 1994.
- Megie, G. et al., Ozone et propriétés oxydantes de la troposphère, *Rapp. de l'Acad. des Sci.*, **30**, 262 pp., Technique et documentation, Lavoisier, Paris, 1993.
- Miller J.M., J.L. Moody, J.M. Harris, and A. Gaudry, A 10-year trajectory flow climatology for Amsterdam Island, 1980-1989, *Atmos. Environ.*, **27**(12), 1909-1916, 1993.
- Murayama, S., T. Nakasawa, M. Tanaka, S. Aoki, and S. Kawaguchi, Variations of tropospheric ozone concentration over Syowa Station, Antarctica, *Tellus, Ser. B*, **44**, 262-272, 1992.
- Oltmans, S.J., and W.D. Komhyr, Surface ozone distributions and variations from 1973-1984 measurements at the NOAA Geophysical Monitoring for Climatic Change baseline observatories, *J. Geophys. Res.*, **91**, 5229-5236, 1986.
- Poisson, N., Impact des hydrocarbures non méthaniques sur la chimie troposphérique, Ph.D. thesis, 253 pp., Univ. Paris VII, Paris, 1997.
- Poisson, N., and M. Kanakidou, A global 3-dimensional study of the impact of NMHC on tropospheric chemistry, in *Proceedings of EUROTRAC Symposium 1996*, pp. 601-605, edited by P.M. Borrell et al., Computational Mechanics Publications, Southampton, 1996.
- Polian, G., G. Lambert, B. Ardouin, and A. Jegou, Long range transport of continental radon in subantarctic and antarctic areas, *Tellus, Ser. B*, **38**, 178-189, 1986.
- Ramonet, M., and P. Monfray, CO<sub>2</sub> baseline concept in 3-D atmospheric transport models, *Tellus, Ser. B*, **48**, 502-520, 1996.
- Roelofs, G.J., and J. Lelieveld, Distribution and budget of O<sub>3</sub> in the troposphere calculated with a chemistry general circulation model, *J. Geophys. Res.*, **100**, 20,983-20,998, 1995.
- Roelofs, G.J., and J. Lelieveld, Model study of the influence of cross-tropopause O<sub>3</sub> transports on tropospheric O<sub>3</sub> levels, *Ser. B, Tellus*, **49**, 38-55, 1997.
- Scheel, H.E., E.G. Brunke, and W. Seiler, Trace gas measurements at the monitoring station Cape-Point, South Africa, between 1978 and 1988, *J. Atmos. Chem.*, **11**, 197-210, 1990.
- Schnell, R.C., et al., Decrease of summer tropospheric ozone concentrations in Antarctica, *Nature*, **351**, 726-729, 1991.
- Thompson, A.M., K.E. Pickering, D.P. McNamara, M.R. Schoeberl, R.D. Hudson, J.H. Kim, E.V. Browell, V.W.J.H. Kirchhoff, and D. Nganga, Where did tropospheric ozone over southern Africa and the tropical Atlantic come from in October 1992? Insights from TOMS, GTE TRACE A, and SAFARI 1992, *J. Geophys. Res.*, **101**, 24,251-24,278, 1996.
- Zimmermann, P.H., MOGUNTIA: A handy global tracer model, in *Air Pollution Modelling and its Application VI*, edited by H. van Dop, pp. 593-608, Plenum, New York, 1988.

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