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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 O₃ measurements have been carried out at Amsterdam Island (37°S, 77°E) in the southern Indian Ocean using a UV absorption analyzer. Mean O₃ concentrations and standard deviations are recorded every 5 min. This paper shows and discusses the O₃ time series for a 3-year period (1994-1996). During this period, O₃ shows a seasonal variation with maxima around 30 ppbv during winter (July - September) and minima around 13 ppbv during summer (December - February). O₃ 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 O₃ 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 O₃ mixing ratios and their seasonal cycle. The seasonal variation of stratospheric origin O₃ calculated by MOGUNTIA shows a maximum of 18 ppbv in September and a minimum of 13 ppbv in April. The oxidation of continentally emitted O₃ precursors during their transport to Amsterdam Island contributes to the photochemical production of O₃ 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_x conditions. In particular, biomass burning emissions contribute up to 5.5 ppbv to the observed O₃ levels in September. Both photochemical production by biomass burning and stratospheric influx of O₃ lead to a maximum in O₃ mixing ratios during late winter to early spring in agreement with the observations. Minimum O₃ mixing ratios observed during austral summer are related to photochemical O₃ depletion.

1. Introduction

Although tropospheric ozone (O₃) represents only 10% of the total O₃ content of the atmospheric column, its concentration and its evolution are important for the Earth's biosphere. O₃ is a powerful greenhouse gas, contributing 18% to the global greenhouse effect [Intergovernmental Panel on Climate Change, 1995; Megie *et al.*, 1993]. O₃ 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 O₃ on human health and on vegetation are now well established [Megie *et al.*, 1993].

The main sources of O₃ in the troposphere are stratospheric intrusions and photochemical formation in the presence of nitrogen oxides (NO_x=NO+NO₂), 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 O₃. O₃ lifetime varies from 2 to 5 days in the tropical boundary layer to several months in the middle troposphere [Fishman *et al.*, 1991]. Therefore O₃ concentrations show a high spatial and temporal variability which needs to be taken into account in any attempt to evaluate the O₃ greenhouse effect.

Since the last century, increasing industrialization in the northern hemisphere has led to an increase in tropospheric O₃ 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 O₃ in the southern hemisphere attributed the observed O₃ seasonality to penetrations of O₃ 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 O₃ in the southern hemisphere is dominated by photochemical destruction during summer. Murayama *et al.* [1992] suggest that O₃ in Antarctica is mainly affected by vertical transport from the stratosphere and by southward transport of tropospheric air with low O₃ concentrations from lower latitudes. They do not exclude a possible impact of photochemistry on O₃ levels. Ayers *et al.* [1992] suggest that surface O₃ 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 O₃ seasonal variations in the

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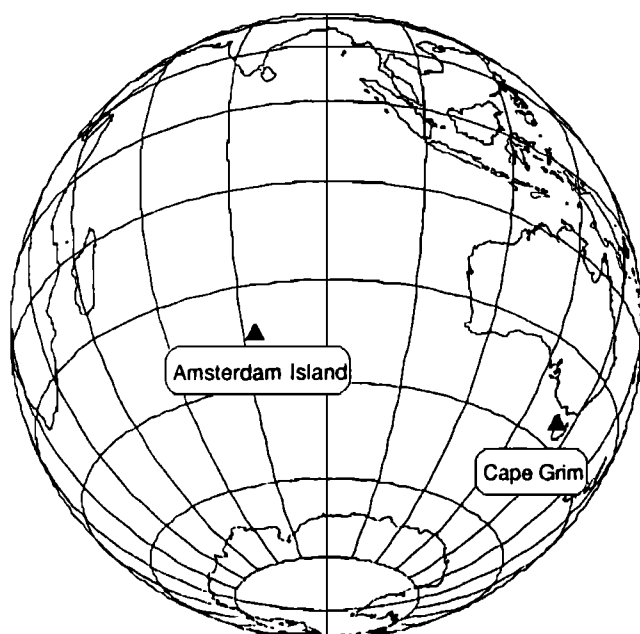


Figure 1. Amsterdam Island and Cape Grim locations in the southern hemisphere.

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 km² and is inhabited by 25 people living at the base “Martin de Viviers.” 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 Viviers 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 ± 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 ± 1.96 ppbv) during winter (July – September) and minimum values of 14.59 ± 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

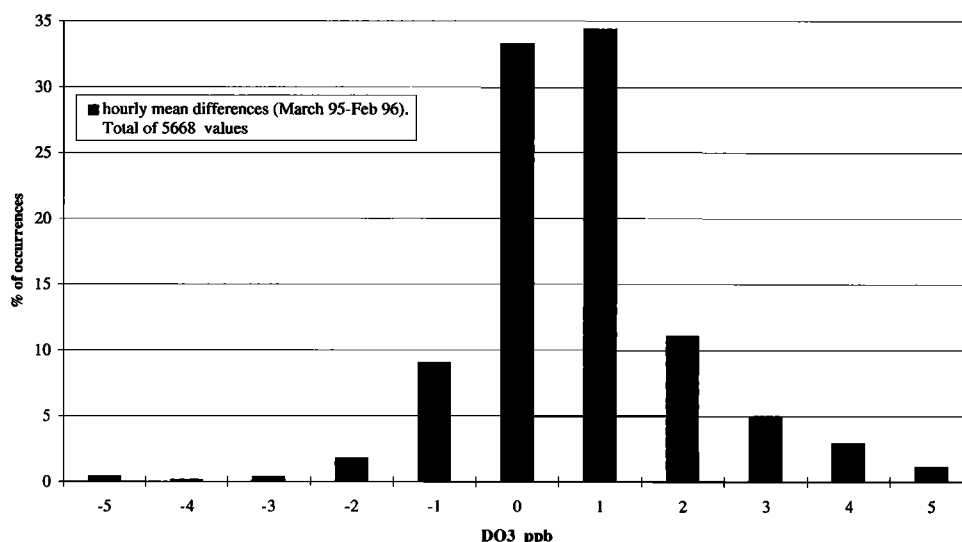


Figure 2. Hourly mean differences between the two O₃ Thermo-Electron analyzers used at Amsterdam Island (analyzer 1 - analyzer 2).

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 O₃ 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 O₃ seasonal variability at this remote oceanic station. Vertical profiles of O₃ 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 O₃ deposition and by enhanced photochemical destruction. Although

deposition of O₃ to water is a very important loss process for tropospheric O₃ [Ganzeveld and Lelieveld, 1995], the temporal variation of O₃ 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 O₃ deposition on an annual basis and its subsequent control of the O₃ seasonal cycle will not be discussed in this paper. Therefore the annual cycle of surface O₃ at Amsterdam Island could be mainly controlled by (1) stratosphere-troposphere exchange of O₃, (2) the photochemical destruction of O₃ under low NO_x conditions and (3) long-range transport of O₃ from areas rich in O₃ 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

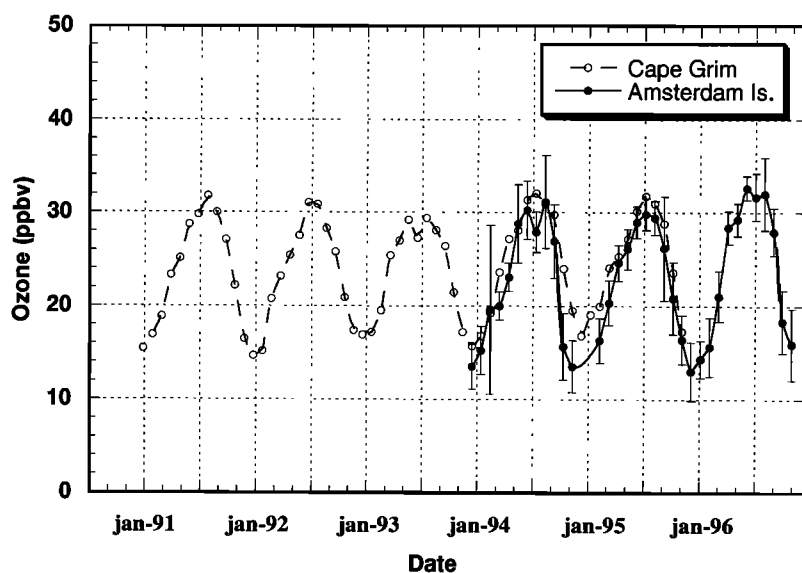


Figure 3. Variations of surface ozone in the southern hemisphere at Cape Grim from 1991 to 1995 (all sectors, after Galbally *et al.* [1996]) and at Amsterdam Island from 1994 to 1996. The lines attached to the means are the within-month variabilities (± 1 standard deviation).

simulate the spatial and temporal variation of the tropospheric chemical compounds with a 10° latitude \times 10° 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/CH₄/NO_x/HO_x/O₃ 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 O₃ seasonality: stratospheric influx of O₃, NMHC chemistry, and biomass burning emissions of O₃ precursors (long-range transport).

3.2. Impact of Stratospheric Influx of O₃ 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 O₃. In particular, they demonstrated that the contribution of O₃ from the stratosphere to the surface O₃ is maximum in winter and spring when the photochemical lifetime of O₃ is relatively long. According to their estimates, the contributions of stratospheric O₃ to the tropospheric content of O₃ in the southern hemisphere are 35% and 50% during summer and winter, respectively. By distinguishing the stratospheric-originating O₃ from the photochemical tropospheric O₃, these authors show that the

seasonal cycle of O₃ 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 O₃ influx from the stratosphere in the model is quite poor [Gallardo-Kleenner, 1996], we used it to evaluate the impact of the stratospheric source of O₃ on calculated surface mixing ratios at Amsterdam Island. For this purpose, all photochemical processes have been turned off in the MOGUNTIA model. O₃ was treated as an inert tracer, having only a stratospheric source and a tropospheric sink by dry deposition. The O₃ calculated concentrations for Amsterdam Island when neglecting photochemistry (model-stratosphere) and when taking into account the CO/CH₄/NMHC oxidation in the troposphere (model-NMHC) are depicted in Figure 4. For comparison purposes, the observed O₃ concentrations are also shown in Figure 4. According to our calculations, O₃ of stratospheric origin could contribute more than 50% to wintertime surface O₃ 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 O₃ values, since for the "model-stratosphere" simulation the chemical destruction of O₃ in the troposphere has been neglected. The calculated impact of the stratospheric influx of O₃ appears to be maximum in late winter and in early spring, in phase with the observed surface O₃ seasonality, although the calculated amplitude is much smaller than observed. It is worth noting that when neglecting photochemistry, the computed O₃ levels for January (summer) are higher than the observations. This is due to the omission of photochemical destruction of O₃ by photolysis and by the CO/CH₄/NMHC chemistry in the marine environment during the austral summer (December - February).

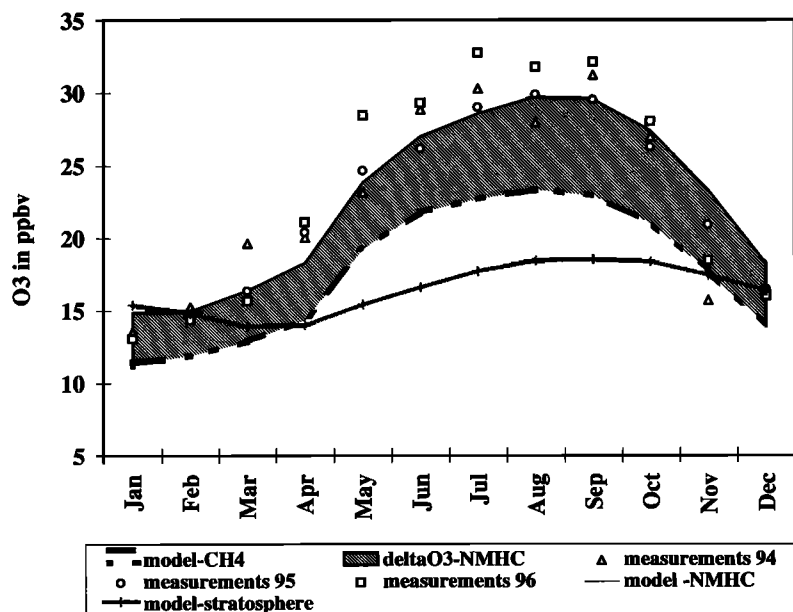


Figure 4. Yearly seasonal surface ozone mixing ratios at Amsterdam Island : comparison between observations and model calculations. Triangles correspond to O₃ measurements in 1994, circles represent 1995 measurements, and open squares show 1996 measurements. Shaded area stands for the difference in ozone levels due to the consideration of nonmethane hydrocarbons (NMHC) chemistry in the Model of the Global Universal Tracer Transport in the Atmosphere (MOGUNTIA). Model-CH₄ curve shows simulations considering only CH₄, 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 O₃ Concentrations at Amsterdam Island

The observed low O₃ concentrations in austral summer associated with the high level of solar UV radiation are consistent with photochemical destruction of O₃ by photolysis and CO, CH₄, and NMHC oxidation chemistry under low NO_x conditions [Ayers *et al.*, 1992]. When only CH₄, CO, NO_x, and HO_x chemistry is taken into account in the MOGUNTIA model (model-CH₄), the model reproduces well the observed seasonal trend of O₃ as depicted in Figure 4. However, the calculated O₃ 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 O₃ concentrations are significantly higher than in the CH₄ simulation and in good agreement with both the seasonal variation and the levels of O₃ observed at Amsterdam Island. The difference in the calculated O₃ 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 O₃ surface levels results from (1) the local NMHC photochemistry which in this low-NO_x environment is expected to lead to a net chemical destruction of O₃ and (2) the oxidation of NMHC emitted over continental area rich in NO_x (Africa) and transport of the subsequently produced O₃ to Amsterdam Island. This transport process affecting the O₃ 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 O₃ from continentally emitted NMHC and NO_x and subsequent transport over the oceans could dominate over the local photochemical destruction of O₃ by hydrocarbon oxidation under low-NO_x conditions. According to our model calculations, NMHC chemistry contributes 22% to the calculated annual mean O₃.

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

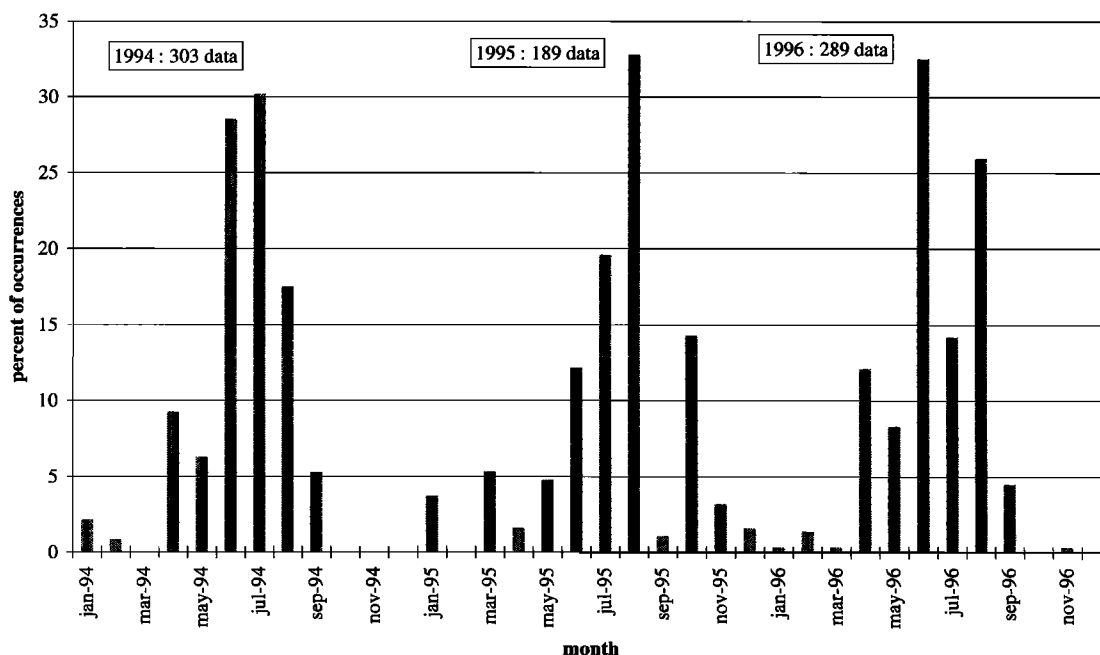


Figure 5. Histogram showing monthly distribution of the frequency of simultaneous appearance of Rn 222 > 2 pCi/m³ and Rn 220 < 0.1 pCi/m³ at Amsterdam Island for 1994 - 1996.

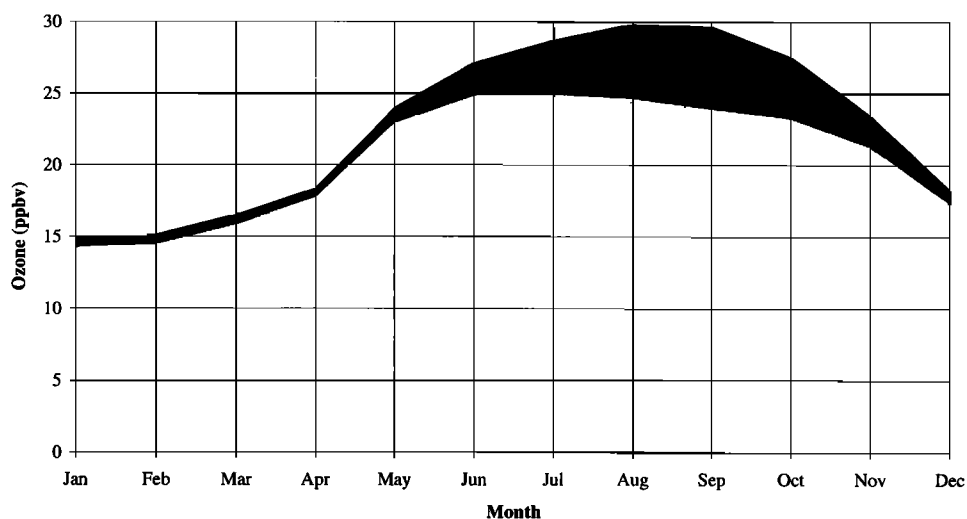


Figure 6. Biomass burning contribution on surface ozone at Amsterdam Island calculated by the MOGUNTIA model. Shaded area stands for the difference in ozone levels due to the consideration of biomass burning in the model. Lower bound of the curve represents the O_3 MOGUNTIA calculations without biomass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

that were greater than 2 pCi/m^3 and were associated with Rn 220 activities below 0.1 pCi/m^3 for the years 1994 through 1996 (G. Polian, personal communication, 1997). Air with radon 222 activity higher than 2 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 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_x areas contributes to the background O₃ level. A longer record of O₃ at Amsterdam Island may allow us to detect any possible interannual variability and any trends in background O₃ due to anthropogenic activities like deforestation, agriculture, and biomass burning.

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