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HO cycle in 1997 and 1998 over the southern Indian Ocean derived from CO, radon, and hydrocarbon measurements made at Amsterdam Island

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Abstract. A new empirical method for the derivation of average HO radical concentrations is presented. The method is based on estimation of CO lifetime through the relative variability of CO and Rn measurements, and hydrocarbon measurements are used to independently determine the relative effects of chemistry and dynamics. Data from Amsterdam Island (37°S, 77°E), a remote site in the southern Indian Ocean, are used to calculate annual and daily HO levels for 1997 and 1998. A seasonal variation in calculated daily HO, consistent with seasonally changing photolysis rates, with maxima in summer and minima in winter is also derived which is comparable but slightly lower than the most recent zonal mean HO estimates of *Spivakovsky et al.* [2000]. The calculated annual HO shows a decrease from 2.7×10^5 molecule cm^{-3} in 1997 to 0.8×10^5 molecule cm^{-3} in 1998, possibly as a result of El Niño related meteorological changes. The empirically calculated HO correlates with temperature and relative humidity measured at the island but anticorrelates strongly with CO and to a lesser extent with O_3. The limitations and improvements to this method are discussed. The method has potential for long-term monitoring of HO changes over areas upwind from remote sites.

1. Introduction

The hydroxyl radical (HO) plays a critical role in the chemistry of the atmosphere. As the main oxidant in the troposphere, it controls the lifetime of trace gases such as carbon monoxide and methane [*Graedel and Crutzen*, 1993]. An understanding of its production and sinks is therefore central to modeling and predicting the chemistry of the troposphere. Because of its high reactivity and its consequently short lifetime of less than 1 s, HO measurement is experimentally complicated, and direct measurements are limited to campaign timescales of a few weeks [e.g., *Mauldin et al.*, 1999, and references therein]. So far, no long-term direct measurements of HO exist. HO can be determined by various calculation techniques, such as via photostationary state estimates or by the atmospheric budget of long-lived species. These calculated values have already been compared with measurement data [*Carslaw et al.*, 1999; *Frost et al.*, 1999; *Grenfell et al.*, 1999]. However, these estimations are also restricted to the time span of the data (a day to weeks), or require the global budget of a species (e.g., CH_3CCl_3 or ^{14}CO) to be known [*Prinn et al.*, 1995; *Mak and Southon*, 1998]. The global HO distribution and the determination of regional long-term trends are presently derived using global models in combination with the available data [*Spivakovsky et al.*, 2000]. The interannual validation of such global models for HO is therefore complicated, as HO concentrations are extremely variable in time and space and long-term data sets are not available.

In this study we present a new empirical method for determining HO concentration changes over long time periods and over large regions, which uses measurements of carbon monoxide (CO), radon 222 (Rn), and several hydrocarbons. The instrumentation required is commercially available and more suited to long-term operation than presently available direct measurement techniques. Although the possibility of deriving HO from simultaneous Rn and hydrocarbon measurements was first suggested by [*Ehhalt et al.*, 1998], it was not developed owing to the lack of a suitable data set. We have developed and tested a method using data collected at Amsterdam Island, and here we present HO concentrations derived annually and daily for 1997 and 1998. The deduced HO are compared to the global climatological distribution of *Spivakovsky et al.* [2000] and to measurements of temperature, relative humidity, ozone (O_3), and CO made at Amsterdam Island.

2. Measurement and Site Description

All the measurements used in this study were made at Amsterdam Island (37°S, 77°E), a remote site in the southern Indian Ocean (Figure 1). Grab samples for NMHC were collected on a tower at 65 m above sea level on the windward (west) side of the island. The air inlets for continuous measurement of radon, CO, and ozone were located at the same altitude. The prevailing directional component of wind is westerly, and the wind speed remains mainly between 5 and 15 m s^{-1} throughout the year. CO was measured in situ by a gas chromatograph providing a measurement every 10 min and then averaged in hourly means, the overall uncertainty of the

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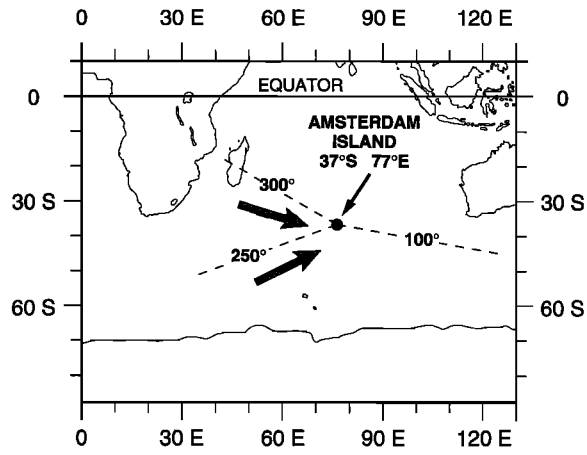

Figure 1. Amsterdam Island (37°S, 77°E) location and wind sectors (100°–250°: south; 250°–300°: northwestern).

measurement being estimated at 4% [*Gros et al.*, 1999a, 1999b]. Radon 222 (Rn) was monitored on a 2-hour basis by measuring the decrease of the alpha radioactivity of atmospheric aerosols collected on filters. The measurement has precision of 2% and has already been described by *Polian et al.* [1986]. The hydrocarbons were measured from air samples collected about once a week in 0.85 L stainless steel electropolished canisters. These samples were then analyzed in the laboratory by gas chromatography according to a technique previously described by *Bonsang et al.* [1995]. Only alkanes were considered owing to the instability of alkenes in the canisters [*Touaty*, 1999]. All the measurements used in this study, CO, Rn, ethane, propane, 2-methyl propane, and butane, are shown in Figures 2a, 2b, and 2c. The International Union of Pure and Applied Chemistry (IUPAC) approved units nmol/mol and pmol/mol are used throughout which correspond to the U.S. units ppbv and pptv, respectively. For all species used in this method, the instrumental variability in the measurements was determined to be less than the atmospheric variability. In addition, temperature, relative humidity, and ozone were recorded at the Island between 1997 and 1998. The ozone instrument is described elsewhere [*Gros et al.*, 1998]. Relative humidity (RH) and temperature data were provided by the local meteorological station (WMO 61996).

3. Variability Method

The variability in the measurements of a given species depends on its sources and sinks. It is, however, independent of the absolute concentration provided that it remains above the instrumental detection limit. We expect to observe most variability from species that are most rapidly removed from the atmosphere, whose inhomogeneous sources are nearby or whose source strengths vary strongly with time. On the basis of the pioneering work of *Junge* [1974], recent studies have used the concept of variability to derive empirical relationships between the measured variability and the HO lifetime for hydrocarbons and halocarbons for a wide range of data sets [*Jobson et al.*, 1999, 1998; *Williams et al.*, 2000]. The aforementioned works of Jobson et al. introduced the standard deviation in the natural logarithm of the mixing ratio, Sigma ln(X), as a tractable assessment of variability for short-lived gases. This relationship was given as

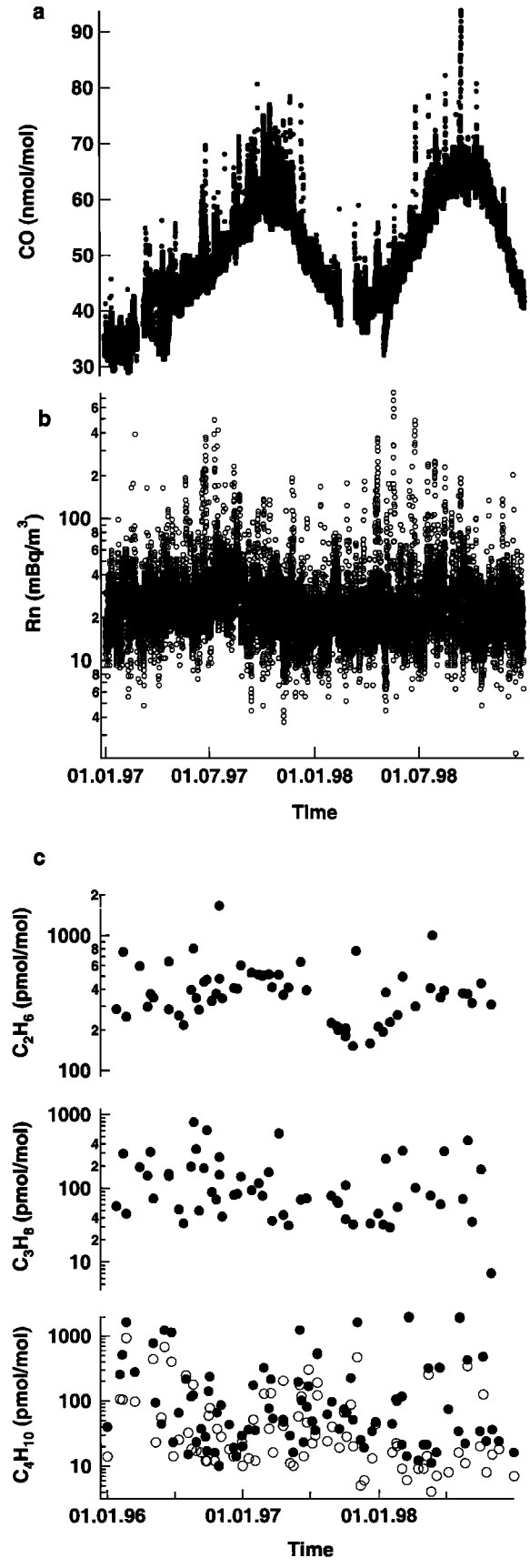

Figure 2. (a) CO data, (b) Rn data, and (c) hydrocarbon data, ethane, propane, 2-methyl propane (open circles), and butane (solid circles), used in this study are shown from 1997 to 1998.

$$\text{Sigma_ln(X)} = A\tau^{-b}, \quad (1)$$

where τ is the lifetime and A is a fitting parameter. The exponent b has a value between 0 and 1, and is an indicator of the relative strength of chemical sink and turbulent mixing terms, upwind of the measurement location. Values of b close to 1 would indicate dominance of the chemical sink which would be expected only in regions remote from sources. It has been shown that proximity to continental sources produced a weaker dependence ($b \approx 0$) than remote oceanic environments [*Ehhalt et al.*, 1998; *Jobson et al.*, 1998, 1999]. Examination of derived trends for variability-lifetime relationships provides insights into the hydrocarbon data set quality, the remoteness of the location from sources, and into the general atmospheric processing.

In this study we consider the variability of two species CO and Rn which are assumed to predominantly originate from the same continental sources, at long distances from the sampling site. Measurements of lead 212 (thoron), a short-lived daughter product of radon (half-life equal to 10.6 hours), were used to eliminate local influence from Amsterdam Island on the data set: all data coincident with lead 212 values greater than 3.7 mBq m^{-3} were excluded [*Polian et al.*, 1986]. The occurrence of local influence was less than 1%. Owing to the remoteness of the site from sources, we expect the variability of the CO, Rn, and hydrocarbons measured at the island to show a strong dependence on species lifetime, and therefore b in (1) to be significantly greater than zero. If we take the ratio of the variabilities of two species, then we can eliminate the A coefficient to determine the relationship in (2), which can be further transformed to (3).

$$\frac{\text{Sigma ln(CO)}}{\text{Sigma ln(Rn)}} = \left(\frac{\tau_{\text{CO}}}{\tau_{\text{Rn}}}\right)^{-b} \quad (2)$$

$$\ln(\tau\text{CO}) = \ln(\tau\text{Rn}) - \left\{\ln\left(\frac{\text{Sigma ln(CO)}}{\text{Sigma ln(Rn}}\right)\right)\frac{1}{b}\right\}. \quad (3)$$

The ratio of the CO and Rn variabilities can be calculated from the measurements directly, on a daily basis from the 12 coincident measurements of CO and Rn every 24 hours. The lifetime of radon is accurately known (half-life equal to 3.825 days), and so only the b coefficient and τ_{CO} remain unknown in (3). The b coefficient can be derived independently from C_2–C_4 hydrocarbon measurements which were taken approximately four times a month. The lifetimes of the hydrocarbons used here are similar to the lifetime of CO and Rn supporting the applicability to this data. The NMHC species, ethane, propane, 2-methyl propane, and butane, are assumed to be predominantly emitted from the same continental source regions as CO and Rn. The measurements were also filtered to remove clear influences from local sources, and samples were not considered if all of the species were not quantified: 10% of the samples were disregarded. By assuming a nominal HO concentration we determined the variability lifetime dependence of the hydrocarbon measurements based on the rate coefficient data in Table 1. Figure 3 shows the relationship for 1997 and 1998 and the resulting A and b coefficients are given in Table 2. It should be noted that the b coefficient derived from these hydrocarbons is not affected by the nominal choice of HO radical concentration. If a different HO concentration were selected, the points would shift to the same extent along the x axis, but the gradient b remains the same. The derived b coefficients, around 0.5, indicate a strong dependence of variability and lifetime consistent with the site being remote and the data unaffected by local sources. When the b value is known, then the lifetime of CO, τ_{CO}, can be calculated. Assuming that the CO is only lost through the reaction with HO radicals, then the concentration of HO radicals may be calculated by using the reaction coefficient of HO + CO (2.4×10^{-13} cm^3 $molecule^{-1}$ s^{-1} [*DeMore et al.*, 1997]).

Table 1. Rate of Reaction of HO With Hydrocarbons Used in This Study[a]

Hydrocarbon	HO Rate Coefficient, cm^3 molecule s^{-1}	Reference
Ethane C_2H_6	2.21×10^{-13}	*Atkinson et al.* [1997]
Propane C_3H_6	1.03×10^{-12}	*Atkinson et al.* [1997]
2 Methyl propane C_4H_{10}	2.05×10^{-12}	*Donahue et al.* [1998]
Butane C_4H_{10}	2.25×10^{-12}	*Donahue et al.* [1998]

[a]T = 288 K; pressure equal to 1000 hPa.

As the HO concentrations derived are clearly dependent on the b coefficient, and to apply this technique to intra-annual HO calculation, we must first determine how the b coefficient varies as a function of season. The seasonal dependence of the b coefficient on the hydrocarbon data from 1997 and 1998 was examined by grouping the data into two categories, according to the seasonal extremes October to March and April to September. The b and A coefficients are given in Table 2. The b coefficients derived show no significant difference between winter and summer. Similar results were also found by *Jobson et al.* [1999] for a site in Harvard forest, where similar b coefficients were generated for winter and summer data sets. The transport patterns of air to the Harvard forest site were found to be the same for both seasons, and the absence of a seasonal change in the b coefficient was attributed to the invariance in air mass origin distribution with season. As stated previously, we interpret the b coefficient as the degree of chemical versus dynamical control on the variability. If the source geometry remains the same throughout the year, then the same sources affect the variability measured at the island throughout the year, only the HO concentration changes. Changes in HO do not affect the b coefficient as the lifetimes of all hydrocarbons are affected to the same extent; see Figure 3. In the case of Amsterdam island, although the wind is westerly throughout the year, a seasonal change in the proportion of winds from the SW and NW has been reported by [*Miller et al.*, 1993]. An additional factor in this case is that the hydrocarbon samples were not taken randomly, at regular intervals, or indeed at high frequency. Instead, the canisters were predominantly filled when strong onshore winds from the NNW prevailed, and hence the effect of the same source geometry can be expected in the data. It is therefore not possible from the limited hydrocarbon data set available to determine whether the calculated absence of a seasonal dependence on the b coefficient is due to the persistence of the prevailing westerly winds or due to an artifact of the hydrocarbon sampling method.

The HO calculated in this way is not an in situ measurement but instead the average HO concentration along the back trajectory since contact with an emissions source. The distance over which a measurement variability is sensitive to a source depends on the instrument precision, the wind velocity, and the lifetime of the species concerned, and has been discussed in detail elsewhere [*Williams et al.*, 2000]. In this case, taking radon half-life of 3.825 days, an instrument precision of 2%,

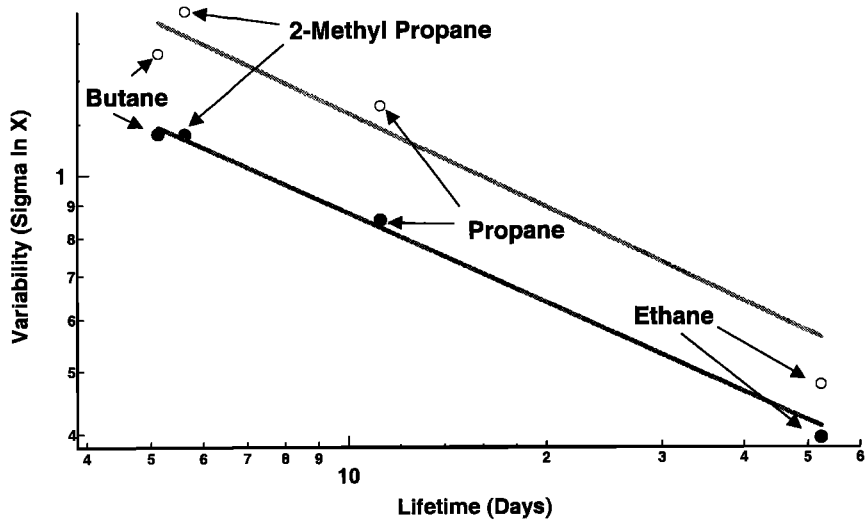

Figure 3. A plot of Sigma ln(X) against lifetime in days for the entire hydrocarbon data set in 1997 (solid circles) and 1998 (open circles). Lifetimes were calculated using HO = 1×10^6 molecules cm^{-3} and with rate coefficients corresponding to 288 K and 1000 hPa.

and assuming a constant wind speed of 5 m s^{-1}, we estimate the range to be approximately 6000 km. This is equivalent to the distance from Amsterdam Island to the Atlantic coast of South Africa (see Figure 1) but represents an upper limit as the wind is unlikely to be unidirectional.

4. Results and Discussion

4.1. Intra-Annual Variation in Derived HO

Assuming the b coefficients generated for each year to be applicable to the whole year, we have extended the method to calculate HO concentrations for each day of 1997 and 1998 from the daily CO and radon measurements with the annual b coefficient. As the HO derived is the average HO that has been present in the air parcel since contact with a source, we can expect a dependence on the air mass trajectory, that is, different calculated HO concentrations in air masses coming from the north than from the south. The HO concentrations were therefore segregated according to the noontime wind direction into two sectors named south (100°–250°) and northwest (250°–300°); see Figure 1. These wind sectors were first used in categorizing a 10-year climatology of 850 hPa back trajectories for Amsterdam island [*Miller et al.*, 1993]. It has been previously shown that air from the northwest exhibits the strongest effects from continental Africa, whereas air from the south is more representative of the background atmosphere as it originates from the remote southern Indian Ocean [*Miller et al.*, 1993; *Gros et al.*, 1999a]. The data were smoothed using a 31-point box method and compared with the monthly zonal mean values at 1000 hPa of *Spivakovsky et al.* [2000] (hereinafter referred to as S2000) (Figure 4). These authors have computed a global climatological distribution of tropospheric HO, and their work constitutes the most complete and up-to-date HO distribution.

Table 2. Coefficients for the Fit of Function Sigma (lnX) = $A\ \tau^{-b}$, Where X Is a Hydrocarbon Species and τ Is the Corresponding Lifetime, Assuming HO = 1×10^6 molecules cm^{-3}

Year	A Coefficient	b Coefficient
1997	2.5 ± 0.2	0.46 ± 0.03
1998	3.8 ± 1.0	0.48 ± 0.13
April–September 1997 and 1998	3.2 ± 0.5	0.48 ± 0.1
October–March 1997 and 1998	2.8 ± 0.6	0.42 ± 0.1

For HO calculated in the southern sector we calculate a maximum between February and April (6×10^5 molecule cm^{-3} in 1997 and 2×10^5 molecule cm^{-3} in 1998) and a winter minimum in July (6×10^4 molecule cm^{-3} in 1997 and 3×10^4 molecule cm^{-3} in 1998). Comparing our estimations with calculations from S2000, we observe a general good agreement for both seasonal cycle and absolute value of HO. We note that the agreement is better when considering the S2000 value for latitude 44°S confirming that our estimations are representative of a latitude band south of Amsterdam Island (36°S). However, we note that our estimations, especially in 1998, are in the lowest range of the predicted HO values by S2000. It should be noted that the modeled HO concentrations of S2000 shown are for 1000 hPa and that the HO values at 900 hPa are approximately 25% higher. The HO predicted by this empirical variability method is therefore lower than predicted by S2000 for an air parcel confined to the boundary layer. This is consistent with the suggestion made by S2000 that the global model HO estimations may be overestimated in the Southern Hemisphere. HO calculated in the northwestern sector (NW) shows the same main features as for the southern sector, although a difference occurs in the spring season (September–November). Indeed, when the air masses originate from the NW sector during this time, we calculate higher values of HO. As this period corresponds to the time of intense biomass burning activity in southern Africa and America [*Goldammer*, 1990], we attribute this increase of HO to high concentrations of NO_x (NO and NO_2) and hydrocarbons in the burning affected air. The increase in deduced HO could also arise from increased variability in the CO concentration caused by intermittant transport from burning areas. However, the trend is consistent with the estimations of S2000 which also shows a

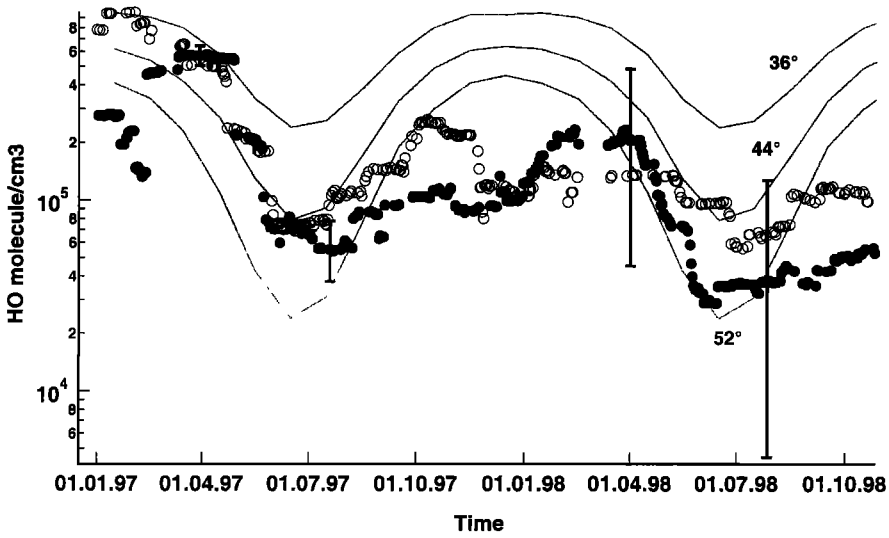

Figure 4. HO calculated from south (solid circles, 100°–250°) and NW (open circles, 250°–300°) wind sectors. The HO data error bars are calculated by the fit parameter of the *b* coefficient given in Table 2. Presented are also the monthly zonal mean HO estimations by *Spivakovsky et al.* [2000] for 36°S, 44°S, and 52° latitude.

sharper increase in HO during October than in April for latitudes between 28°S and 52°S; see Figure 4. As Amsterdam Island is situated at 37°S, we expect HO concentrations north of the island to be on average greater than those from the south. However, calculated values of HO from the NW and southern wind sectors differ only slightly. This we ascribe to the predominance of the westerly wind in the data set, for although the data are divided into NW and southern wind sectors, the average wind angle for each sector is WNW and SW, respectively. We would expect a greater difference if the average wind angle for each sector were north and south, as HO fields vary strongly with latitude but weakly with longitude.

4.2. Correlation of Derived HO With Other Parameters

In the troposphere, HO is predominantly formed through the reaction of water with O^1D radical which is formed through the photolysis of ozone, shown below.

$$\text{(R1)} \qquad O_3 \rightarrow O_2 + O^1D$$

$$\text{(R2)} \qquad O^1D + H_2O \rightarrow 2HO.$$

We can therefore expect a correlation between HO and temperature, which is a proxy for the seasonally changing photolysis rate, the higher temperatures in summer (January) corresponding to higher photolysis rates. Similarly, a positive correlation with relative humidity is expected as water vapor reacts directly with O^1D in (R2) to form HO. The correlations of derived HO with measured temperature and relative humidity show indeed positive values (Figure 5 and Table 3), although the correlation coefficients are not high as linear dependences are not expected. It must be noted that while the HO values represent average upwind levels, the other parameters are in situ measurements. In the remote atmosphere, HO reacts predominantly with CO (≈70%), the reaction of CO with HO being the primary sink for both species. This is manifested in the anticorrelation of HO from the south wind sector with CO for all data; see Table 3. Finally, the derived HO is anticorrelated with O_3 measured at Amsterdam Island for the whole year data set, which presents a maximum in winter and a minimum in summer [*Gros et al.*, 1998]. This reflects that, in a NO_x-poor environment like Amsterdam Island, the same photochemical processes which lead to HO formation also lead to O_3 destruction.

4.3. Interannual Variations

We may also calculate an annual HO concentration using this variability method in two ways. First, by averaging the calculated daily HO levels we obtain a value of 2.7×10^5 molecules cm^{-3} in 1997 and 0.8×10^5 molecules cm^{-3} in 1998. A second approach is to consider the variability of the whole year data set rather than on a daily basis. By this method we derive larger HO concentrations, 8.8×10^5 molecules cm^{-3} in 1997, and 5.3×10^5 molecules cm^{-3} in 1998. In the later case the variability in the CO signal is greater as it inherrently includes the seasonal variation of the CO source strength which occurs throughout the hemisphere in the course of the year. When HO is calculated from the daily data, the source strength and distribution affecting the air masses sampled will probably remain relatively constant. The method of daily HO calculation and yearly averaging is therefore preferred. These values are comparable but slightly lower than the annual zonal mean values given by S2000 which for 1000 hPa are 6.5×10^5 molecules cm^{-3} at 36°S and 3.7×10^5 molecules cm^{-3} at 44°S.

The results of both methods described above show a decrease in HO levels from 1997 to 1998. By the preferred method of daily HO calculation the annual calculated HO decrease by a factor of 3 from 1997 to 1998. This HO decrease, if real, could have likely three origins, that is, a change in the air mass origins, a change of the intensity of HO sink or production; a combination of these causes is possible. The interannual variation of the air mass origins has been investigated by studying the wind distribution for the 2 years. The proportion of air masses coming from the southern sector were 40% in 1997 and 36% in 1998, while the corresponding proportion of air masses coming from the northwest sector were 39% and 42%. As there is only small difference in the wind

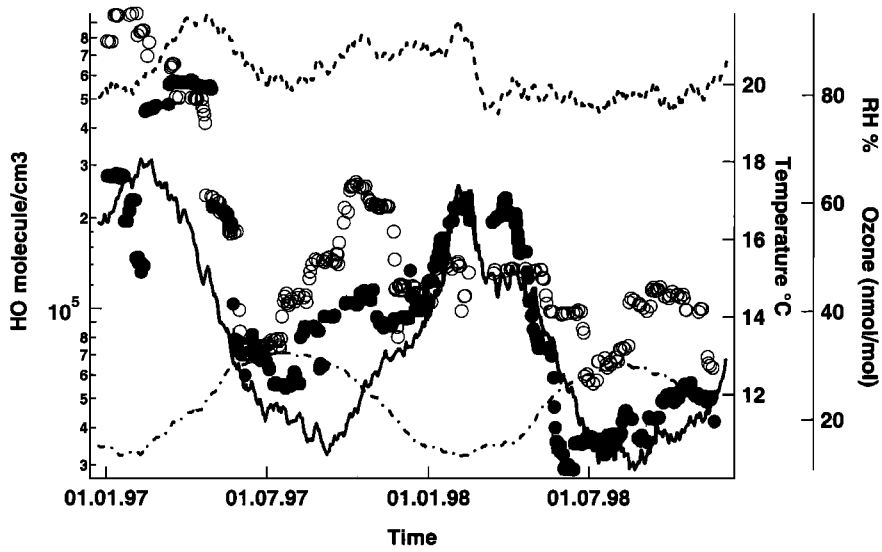

Figure 5. HO calculated from south (solid circles, 100°–180°) and NW (open circles, 250°–300°) wind sectors plotted with temperature (solid line), ozone (dash-dotted line), and relative humidity (dashed line) between 1997 and 1998.

distribution between both years, we suggest this is not the main reason to explain the HO decrease.

Studying the interannual variability of HO main sink, that is, CO, we observe that CO background values were significantly higher in summer 1998 than summer 1997, whereas comparable values were observed for both years for the winter–spring period. Such interannual variations were also observed at Cape Point, South Africa (H. E. Scheel, personal communication, 2001), indicating this was a large-scale feature. This change in CO concentrations could be linked to the strong El Niño conditions which were observed from mid 1997 until early 1998 over the Pacific Ocean which resulted in altered weather patterns across the globe. Typically, South Africa, Madagascar, and the surrounding Indian Ocean area become unusually dry during such events [*Bell et al.*, 1999], which could lead to unusual CO emissions by higher biomass burning at that time. The declining relative humidity values in Figure 5 suggest that this effect was indeed observed in the Amsterdam Island data. Moreover, a lower relative humidity could also explain, at least partly, a lower production of HO. Therefore we tentatively postulate that the decrease in calculated HO from both wind sectors is associated with the El Niño event and caused by a combination of moisture decreases in the area to the west of the island and of CO increase emission. A much longer data set should be analyzed in order to establish the HO seasonal cycle in more "normal" years and to determine whether these effects in HO levels are reproducible in El Niño times.

4.4. Uncertainties

The main uncertainty in this analysis stems from the derivation and use of the *b* coefficient which is based on the measurements of C_2–C_4 alkanes. The hydrocarbon measurements used in this study were taken much less frequently than CO and Rn. Although similar *b* coefficients are generated for 1997 and 1998, the fit quality differs markedly (see Table 2), leading to smaller error bars in estimations for 1997 than for 1998; see Figure 4. It should be noted that the measurements of CO, Rn, and hydrocarbons shown here were not planned to investigate the method presented here. Increasing the hydrocarbon measurement frequency to one every 2 hours would be a considerable improvement to this method, as a "*b*" coefficient could then be determined each day and hence separate *b* coefficients could be employed for the northwest and south wind sectors. Commercially available automatic gas chromatographs for the purpose of quasi-continuous monitoring have been developed and characterized [*Konrad and Volz-Thomas*, 2000]. This would be a valuable addition to the measurement capability at Amsterdam island.

5. Conclusions

The method described here allows for calculation of HO values from measurements of the variability of CO, Rn, and several hydrocarbons. The main provisos are that the measurement should remain above the detection limit of the instru-

Table 3. Correlation Coefficients (r) and Number of Points (n) for the HO Values Calculated Within the South and Northwest Wind Sectors With Temperature, Relative Humidity, O_3, and CO

	HO (Wind 100°–250°S) South	HO (Wind 250°–300°S) Northwest
Temperature	$r = 0.57$, $n = 293$	$r = 0.37$, $n = 266$
CO	$r = -0.61$, $n = 277$	$r = -0.56$, $n = 253$
Ozone (O_3)	$r = -0.44$, $n = 282$	$r = -0.53$, $n = 254$
Relative humidity	$r = 0.42$, $n = 293$	$r = 0.25$, $n = 266$

ment and the source strengths should not vary rapidly temporally or spatially, which is the case for remote stations. By this method we are able to determine daily HO concentrations and thereby study interannual and intra-annual variations of HO. The main limitation of the present calculation is the uncertainty associated with the *b* coefficient calculation which could be considerably improved if hydrocarbon measurements were taken at higher frequency allowing the determination of daily *b* coefficients. The absolute value, seasonal variation, and correlation of the derived HO concentrations with O_3, CO, relative humidity, and temperature are consistent with our present understanding of HO chemistry. A general decrease in HO levels was calculated over the Indian Ocean regions WNW and SW of Amsterdam Island between 1997 and 1998, possibly as a result of El Niño related climate changes. We conclude that this method has great potential for monitoring HO changes on long timescales over wide areas from remote sites but must be tested for longer periods and on further data sets.

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