

## Antarctic Tropospheric Chemistry Investigation (ANTCI) 2003 overview

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Received 19 January 2007; received in revised form 6 April 2007; accepted 9 April 2007

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### Abstract

The Antarctic Tropospheric Chemistry Investigation (ANTCI) was carried out from late November to December 2003 with both extended ground-based and tethered balloon studies at Amundsen Scott Station, South Pole. ANTCI 2003 was the first of two Antarctic field studies with the primary goal of further exploring the active photochemistry of the South Pole region that was first identified in the previous Investigation of Sulfur Chemistry in the Antarctic Troposphere (ISCAT) program. Since ISCAT was fully ground-based, ANTCI 2003 goals included expanding chemical studies both vertically upward to investigate mixing and horizontally to better understand large-scale plateau NO<sub>x</sub> production and transport. Thus, in addition to ground-based experiments at South Pole, Twin Otter aircraft sampling took place out to hundreds of kilometers in several directions from the South Pole. These were designed to specifically address the issue of how representative past South Pole chemical measurements are of the surrounding high plateau region. The Twin Otter

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was also used to make transects along the coast both north and south of McMurdo Station. The present paper summarizes the overall setting and results of this investigation and highlights the many new findings that were obtained.

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*Keywords:* Antarctic photochemistry; South Pole chemistry; Nitric oxide; Hydroxyl radical; Ozone

## 1. Introduction

The Antarctic continent is a unique landform. It covers a vast area surrounding the South Pole (SP) and average temperatures even in summertime are typically well below 0 °C except in the vicinity of the coast. As a result, it has virtually no vegetation, and apart from volcanoes, the continent has few primary emissions. In fact, the ice-covered continent acts in part like a giant cold trap for the Earth, where long-lived, low and semi-volatile atmospheric-oxidation products such as HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, methane sulfonic acid (MSA), and probably oxygenated organics, as well as trace metals are scrubbed from the atmosphere and end up being buried in the ever accumulating ice fields of this continent. Since the continent is also uninhabited, except for several isolated research stations, it is influenced very little by anthropogenic source emissions; and even these are limited to only the last half century. As a result, Antarctica provides a unique environment for making atmospheric measurements. This is particularly true when the focus of attention is the plateau region. Here, the best-known measurements as related to the atmosphere are those derived from the nearly 3000 m of ice that lies below the surface. Ice cores removed from this ice overburden have been used to decipher the content of ancient atmospheres, both for purposes of assessing changes in the climate over hundreds of thousands of years (Legrand and Saigne, 1988; Legrand et al., 1991; Wolff et al., 2006; EPICA community members, 2004) and for identifying major geophysical events such as large-scale volcanic eruptions (Legrand and Delmas, 1987; Castellano et al., 2004, 2005; Palmer et al., 2002). The successful retrieval of this kind of information, of course, requires a comprehensive understanding of the current atmosphere, both from a chemical and meteorological perspective. This is the goal of the present Antarctic Tropospheric Chemistry Investigation (ANTCI) field study as it was the recently completed Investigation of Sulfur Chemistry in the Antarctic Troposphere (ISCAT) study (Davis et al., 2004).

Although early thinking about the atmospheric chemistry on the Antarctic plateau was that very

few chemical processes were occurring; and hence, it could be viewed as a chemical graveyard, this turns out to be only partially true. If the species arriving at the plateau is in its highest oxidation state it can indeed be viewed as a graveyard. On the other hand, if the species is in a reduced oxidation state, the plateau environment is now known to be highly oxidizing and such species will, therefore, be chemically modified before their burial in snow/ice. As a result, there has been a complete re-thinking of the role played by the plateau environment in influencing the yearly chemical fingerprint that the atmosphere leaves behind for future generations to interpret.

## 2. ANTCI 2003 objectives and brief summary of past findings

The ANTCI program, of which ANTCI 2003 is the first of two field campaigns, was largely designed to verify earlier assumptions related to Antarctic nitrogen and sulfur chemistry, and, more specifically, to address many of the questions raised by the earlier NSF sponsored ISCAT and Sulfur Chemistry of the Antarctic Troposphere Experiment (SCATE) studies. The latter have been discussed in detail by Davis et al. (2004) and Berresheim and Eisele (1998), and here are presented in an overview form as a lead-in to defining the new questions being addressed by ANTCI.

The SCATE study was carried out at Palmer Station (64.7° South, 64.0° West) on Anvers Island, which is on the west side and about half way down the Antarctic Peninsula. The island itself is highly glaciated and surrounded by ocean and other local islands containing large penguin colonies. During the SCATE study it was shown that coastal areas of Antarctica could be an abundant source of sulfur in the form of dimethyl sulfide (DMS), but that this reduced sulfur was only very slowly oxidized to the stable end products methane sulfonate (MS) and non-sea salt sulfate (nss-sulfate) within the marine boundary layer (BL). That this oxidation was slow is now understandable in the context of the very low average concentrations of OH (e.g., 10<sup>5</sup> molec cm<sup>-3</sup> range) observed in the field. Among the reasons for

the low concentrations of OH was the absence of the critical species NO (i.e., typically below 5 pptv) and reduced levels of solar radiation (e.g., near continuous cloud cover). By contrast, the biogenically released sulfur compound, DMS was typically in the hundreds of pptv concentration range and the ratio of the oxidation products (i.e., MS/nss-sulfate), was found to be on the order of 0.5. High DMS and low NO concentrations have also been recorded at the coastal sites Dumont d'Urville and Neumayer, respectively (Jourdain and Legrand, 2001; Jones et al., 1999). Shifting to the SP, the ISCAT studies showed surprisingly high NO concentrations, up to two orders of magnitude greater than at Palmer Station, and 24 h average photochemical oxidation rates that were similar to that observed in tropical marine BL environments, e.g., an order of magnitude greater OH concentrations than at Palmer. By contrast, MS/nss-sulfate ratios were lower than at the coast by nearly an order of magnitude. These two completely different chemical worlds, both being measured within the atmospheric BL but separated by 3 km in altitude lead to the question: are they representative of large stretches of the Antarctic coast and the vast expanses of the Antarctic plateau? Specifically, the impact of the local environment on these observations needs to be better understood.

At both the coast and the SP the available evidence indicated that near surface BL air would have quite different characteristics than the free tropospheric air column above it, thus dictating that the earlier measurements at both sites would need to be extended both vertically and horizontally. Looking still farther ahead, assuming that some degree of representativeness would be found for each measurement site, there was the obvious question related to the huge chemical gradients in species specified earlier. What is the nature of the transitional chemistry and the dynamical processes that might couple these two quite different Antarctic domains? More specifically, what impact might this transitional environment have on the speciation and distribution of nitrogen and sulfur end products at each site?

### 2.1. ANTCI objectives

Given the new ISCAT finding of extensive  $\text{NO}_x/\text{HO}_x$  chemistry at SP, the major objectives of ANTCI were (1) to evaluate in detail the dynamical and chemical processes that control spring/summer-

time levels of  $\text{NO}_x/\text{NO}_y$  and  $\text{OH}/\text{HO}_x$  at SP; (2) to assess the representativeness of SP and previous ground-based coastal measurements to the larger polar plateau and near shore areas of Antarctica; and (3) to investigate the relative importance of the oxidative processes involved in the coast-to-plateau transport of reduced sulfur and determine the principal regions of chemical transition. Secondary objectives were: (1b) to investigate snow/firn chemical species undergoing extensive exchange with the atmosphere (e.g.,  $\text{NO}_x$ ,  $\text{HNO}_3$ ,  $\text{CH}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ , and monocarboxylic acids); and (2b) to assess the different chemical forms of the trace element Hg and their relationships to the levels of  $\text{O}_3$ , OH and other oxidants. ANTCI 2003 was specifically to focus on primary objectives (1) and (2) plus secondary objectives 1b and 2b. In the case of primary objective (2), the focus was to be exploratory in nature with the measurement effort consisting primarily of observations of NO and  $\text{NO}_y$ .

### 2.2. Measurement approach

Given the nature of the ANTCI objectives, it was necessary to bring into play new measurement platforms. For the exploratory NO and  $\text{NO}_y$  measurements this involved the use of a Twin Otter aircraft, where NO served as a surrogate for enhanced photochemical activity. The flights covered a large area extending hundreds of kilometers out from the SP Station and also with coastal sampling being limited to a region along the Ross Sea. This aircraft was also equipped with a condensation nuclei counter and evacuated canisters for the collection of whole air samples that could be later analyzed for trace gases, including the important biogenic trace gas DMS. While the Twin Otter greatly extended the range of ANTCI 2003 measurements vertically and horizontally, the time it was committed to the program was limited to only 2 weeks. Thus, for purposes of obtaining routine long-term vertical-profile type chemical and meteorological information, a tethered balloon platform was established at the SP site. This allowed multiple flights per day over an extended period and offered a vertical resolution of a few meters or less. A complimentary approach used in gathering needed BL information over SP was that involving an acoustic sounder (SODAR). This system was operated over the entire measurement period at SP and was found to be extremely useful in providing estimates of the atmospheric BL depth. Finally,

there were several new chemical measurements recorded for the first time (see Table 1) that extended the ANTCI measurement array of species, to compounds including PAN and Hg species.

### 2.3. Measurement locations

The majority of chemical measurements were made from the upwind side of the Atmospheric Research Observatory (ARO) building. Most sampling ports were located at a height of ~10 m above the snow surface; however, a few compounds were also measured on the roof of ARO, at ground level, and/or at the snow surface. The SODAR and balloon borne measurements were conducted a short distance (~100–150 m) away from the ARO building to minimize interference from the building.

The approximate locations of these measurement devices are shown in Fig. 1. The SODAR was set to have a vertical range of up to 180 m above the surface while the tethered balloon was able to make NO measurements up to ~100 m and meteorological and O<sub>3</sub> measurements up to 500 m above the surface. Twin Otter science flights were concentrated in two areas, the plateau (within 400 km of SP) and the Ross Sea coast with McMurdo as the central staging point (e.g., 300–400 km north and south). There were also transit flights between McMurdo and the SP, but these tended to be at higher altitudes to maximize aircraft range and thus provided limited useful data. Most of the flights from SP were flown along the edge of the clean air sector (i.e., 340–110°) and those along the Ross Sea were within 75 km of the coast (for more detailed

Table 1  
Measurements made as part of ANTCI 2003

Compound	Investigator	Technique	Detection limit
Ground-based measurements			
HNO <sub>3</sub>	Huey	SICIMS	5 pptv
	Dibb	Mist chamber/IC	1 pptv
HO <sub>2</sub> NO <sub>2</sub>	Huey	SICIMS	5 pptv
SO <sub>2</sub>	Huey**	SICIMS	5 pptv
CH <sub>2</sub> O	Hutterli	Scrubber/Fluorescence	30 pptv
		Spectroscopy	
HONO	Tan**	LIF	1 pptv
	Dibb	Mist chamber/IC	1 pptv
H <sub>2</sub> O <sub>2</sub>	Hutterli	Scrubber/Fluorescence	40 pptv
		Spectroscopy	
OH	Eisele	SICIMS	1 × 10 <sup>5</sup> molec cm <sup>-3</sup>
H <sub>2</sub> SO <sub>4</sub>	Eisele	SICIMS	1 × 10 <sup>5</sup> molec cm <sup>-3</sup>
MSA	Eisele	SICIMS	1 × 10 <sup>5</sup> molec cm <sup>-3</sup>
Aerosol ion composition (daily measurements)	Arimoto	Cellulose filters/IC	5–10 ng cm <sup>-3</sup>
Aerosol elemental composition (daily measurements)	Arimoto	Cellulose filters/ICP-MS, AAS, Gamma Spec.	5–10 ng cm <sup>-3</sup>
NMHC and halocarbons	Blake	Grab sample/GC&GC/MS	0.1–5 pptv
DMS	Blake	Grab sample/GC/MS	1 pptv
NO	Davis/Buhr	Chemiluminescence	2 pptv
Mixing layer height	Neff	Sodar	15–180 m
Tethered balloon, vertical profiling met. O <sub>3</sub> , NO	Helmig**	Balloon/sondes, long sample line experiment	1 ppbv/10 m (ozone) 10 pptv/5 m (NO)
HCOOH and CH <sub>3</sub> COOH	Dibb	Mist chamber/IC	1 pptv
PAN	Roberts**	GC/ECD	3–5 pptv
Hg gaseous and fine particle	Brooks**	Tekran2537a/1130/1135	0.01 ng cm <sup>-3</sup>
O <sub>3</sub> , temp, DP, pressure, wind, speed/direction, col.	Polar	Multiple Techniques Irradiance-	Suitable for South Pole
O <sub>3</sub> , solar irradiance	Station	Biospherical Inst.	
Twin Otter Measurements ** (no previous aircraft measurements)			
NO and NO <sub>y</sub> /CN	Davis/Buhr	Chemiluminescence/CNN	10 and 100 pptv
NMHC and halocarbons	Blake	Grab sample/GC&GC/MS	0.1–5 pptv
DMS	Blake	Grab sample/GC/MS	1 pptv

(\*\*) indicate new measurement or technique.

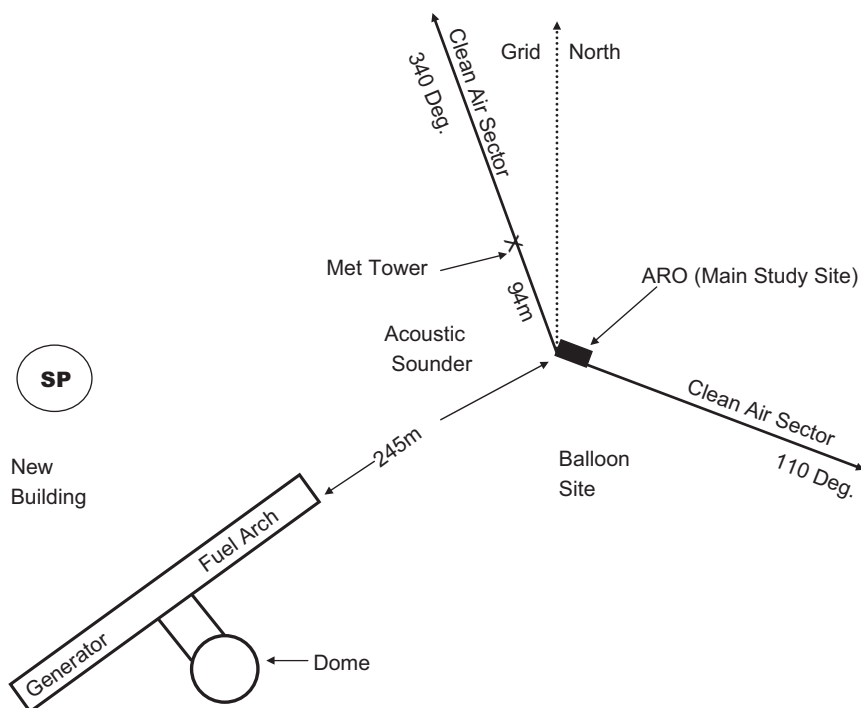


Fig. 1. Approximate location of measurement sites and potential pollution sources.

sampling flight tracks see Davis et al., 2007). The altitude range over which most aircraft sampling occurred was 15–500 m above the snow surface (above ground level, AGL).

Table 1 shows the measurements performed at the locations given in Fig. 1. In Table 1, a \*\* has been placed next to those measurements that were either new to a location/platform or made possible by the use of a new measurement technique. These new measurement capabilities contributed greatly to the success of ANTICI 2003. For further details on the aircraft study the reader is directed to Davis et al. (2007).

### 3. Results and discussion

#### 3.1. General

One of the new areas of exploration in ANTICI 2003 was that of assessing the primary source(s) of plateau nitrogen. Among the possibilities explored, was the long-range transport of the products from biomass burning/other continents. To assess this possibility both 3-D transport/chemistry models are needed as well as measurements of biomass products. PAN can be used as a long-lived tracer for air masses that have been influenced by

continental biogenic emissions such as isoprene. During ANTICI 2003, PAN was recorded for the first time at SP. The results from this study showed PAN concentrations typically falling within the 15–20 pptv range over the entire ANTICI measurement period. Given the low temperatures of Antarctica and the resulting long PAN lifetime, one can conclude that the concentration level observed was far too small to play a significant role in supplying the necessary primary nitrogen to the plateau. The correlations of PAN with  $O_3$  and  $HO_2NO_2$ , however, suggest that there is some local production of PAN on the plateau. The lack of evidence for long-range transport from other continents, suggests that the primary source of reactive nitrogen to the plateau remains poorly defined. At this time it would appear that lightning over the Southern Ocean and/or Africa/South America, denitrification processes in the stratosphere, or possibly marine sources are all still likely candidates (Davis et al., 2007). What has become much clearer from the ANTICI 2003 results is that the high concentrations of  $NO_x$  seen on the plateau during the spring/summer/fall months very much involve recycling of reactive nitrogen. The word “recycling” is being used here not in the simple context of gas phase nitrate being photochemically converted to



$\text{NO}_x$  and then  $\text{NO}_x$  being converted back to nitrate; but rather, to mean that a given nitrogen species, such as nitric acid deposited in the snow, may be photochemically converted into  $\text{NO}_x$  more than once in a given season. In this context, a “recycling factor” has been initially explored by Davis et al. (2007). A full understanding of the mechanism responsible for this recycling factor and how it varies with location or altitude is still lacking.

There is also growing evidence from the ANTCI results that the high concentrations of NO as well as the spring/summer time photochemical enhancements in  $\text{O}_3$  are more pronounced on the high Antarctic plateau, as opposed to the lower regions. The latter conclusion is in concert with the 3-D modeling activity (Wang et al., 2007) as well as with ozone level comparisons at several Antarctic sites ranging from the coast to the high plateau. The latter suggests that observed enhancements in ozone are associated with plateau regions above ~2400 m in altitude (Oltmans et al., 2007; Helmig et al., 2007a; Frey et al., 2005). Generally, low-coastal NO concentrations observed during the ANTCI Twin Otter flights have provided additional evidence for this trend (Davis et al., 2007). However, the reasons for differences in reactive nitrogen levels, and probably recycling rates as well, between the plateau and lower elevations are not yet fully understood. At least part of the explanation may involve differences in the freeze/thaw cycles or related temperature-dependent trapping mechanisms at high and low altitudes that control differences in reemission of reactive nitrogen. Initially, nitrate is likely deposited on the outside of snow particles or on the snow surface where its photochemical products can be easily released back into the atmosphere. If even very brief periods of warming occur on the lower plateau, deposited nitrate can become entrapped in an ice matrix that would impede its release back into the atmosphere. This possibility was originally proposed for study in the second half of ANTCI and still remains a plausible explanation for the large observed gradients in NO concentrations. The broader coverage of ANTCI 2005 should provide a far greater opportunity to address this question.

Another set of measurements new to ANTCI, that provided additional insight into both  $\text{NO}_x$  and  $\text{HO}_x$  photochemistry, were laser-induced fluorescence (LIF) measurements of HONO. These measurements suggest much lower concentrations of HONO than observed by mist chamber/ion chro-

matography (MC/IC) in either ISCAT 2000 or ANTCI 2003 (Liao et al., 2006; Dibb et al., 2004). However, even these lower values when used to constrain models, are still inconsistent with observations of both NO and OH. These new results, therefore, continue to point toward concerns about potential interferences in the measurement of HONO or a major omission of sinks in the model.

In addition to these more general findings, ANTCI 2003 produced many unique results in specific areas of research related to the primary and secondary objectives outlined above. These are briefly outlined/discussed in the text below. The reader should also examine Tables 2–4 for a quick overview of ANTCI 2003 results and their comparison with previous years. For those readers searching for more detailed information concerning the findings, they are encouraged to go to the specific paper referenced in this “highlight section” which appears in this special issue.

### 3.2. Specific highlights

#### 3.2.1. Eclipse

Since both the ANTCI and earlier ISCAT field studies have taken place at SP around the time of the summer Austral solstice, there has typically been relatively little variability in solar irradiance throughout the study periods. Thus, the 24 h of continuous sunlight has been only altered by changes in weather patterns, particularly those involving changing cloud cover. The occurrence of a solar eclipse (sun occluded by ~85%) early in the ANTCI 2003 study provided a unique opportunity to investigate photochemical processes driven solely by smoothly varying incident radiation over the course of the ~2 h over which the eclipse took place. As discussed in Mauldin et al. (2007), the photochemical model predictions tracked very closely the observed changes in the photochemical equilibrium of the  $\text{NO}/\text{NO}_2/\text{O}_3$  system with the final change in NO concentration being a decrease of about a factor of three. For OH the changes were much larger, as expected, but the modeling uncertainties in these calculations were higher (Mauldin et al., 2007). For example, since  $\text{CH}_2\text{O}$  was not measured, it was necessary to estimate a  $\text{CH}_2\text{O}$  concentration as a model constraining input parameter. A value of 40 pptv (the average  $\text{CH}_2\text{O}$  concentration observed in the first and last half of December were 67 and 73 pptv, respectively) provided the best fit just before and after the eclipse and resulted in model

Table 2  
Median and mean MET parameters for ISCAT 1998 and 2000 and ANTCI 2003

Parameters	1998		2000		2003	
	Average	Median	Average	Median	Average	Median
<i>Nov. 15–30</i>						
WS ( $\text{m s}^{-1}$ )	$6.4 \pm 2.4$	5.9	$6.1 \pm 1.7$	6.17	$4.1 \pm 1.0$	4.0
P (mb)	$681 \pm 4$	680	$690 \pm 5$	690	$679 \pm 5$	678
T(2) ( $^{\circ}\text{C}$ )	$-33.3 \pm 3.6$	-33.8	$-29.6 \pm 2.8$	-29.1	$-38.6 \pm 1.8$	-38.7
T(22) ( $^{\circ}\text{C}$ )	$-32.9 \pm 3.4$	-33.5	$-29.2 \pm 2.7$	-28.5	$-38.1 \pm 1.7$	-38.2
$\Delta T$ ( $^{\circ}\text{C}$ )	$0.4 \pm 0.4$	0.3	$0.4 \pm 0.5$	0.2	$0.5 \pm 0.6$	0.4
Td ( $^{\circ}\text{C}$ )	$-36.4 \pm 4.0$	-37.2	$-33.1 \pm 2.9$	-32.6	$-42.1 \pm 1.9$	-42.4
<i>Dec. 1–15</i>						
WS ( $\text{m s}^{-1}$ )	$4.7 \pm 1.8$	4.3	$4.6 \pm 1.6$	4.9	$6.1 \pm 1.6$	6.1
P (mb)	$680 \pm 7$	679	$692 \pm 2$	692	$695 \pm 6$	695
T(2) ( $^{\circ}\text{C}$ )	$-28.2 \pm 2.4$	-29.0	$-27.0 \pm 1.1$	-27.1	$-26.5 \pm 2.8$	-27.1
T(22) ( $^{\circ}\text{C}$ )	$-28.1 \pm 2.4$	-29.0	$-26.7 \pm 1.1$	-26.6	$-26.5 \pm 2.8$	-26.9
$\Delta T$ ( $^{\circ}\text{C}$ )	$0.1 \pm 0.2$	0.1	$0.3 \pm 0.3$	0.3	$0.0 \pm 0.2$	0.0
Td ( $^{\circ}\text{C}$ )	$-31.3 \pm 2.4$	-32.0	$-30.4 \pm 1.0$	-30.4	$-29.6 \pm 3.2$	-30.5
<i>Dec. 16–31</i>						
WS ( $\text{m s}^{-1}$ )	$3.2 \pm 1.3$	3.2	$3.7 \pm 1.5$	3.74	$4.7 \pm 1.9$	4.9
P (mb)	$686 \pm 4$	688	$691 \pm 5$	692	$695 \pm 3$	695
T(2) ( $^{\circ}\text{C}$ )	$-28.8 \pm 2.4$	-29.1	$-27.7 \pm 1.7$	-27.6	$-23.6 \pm 1.8$	-23.9
T(22) ( $^{\circ}\text{C}$ )	$-28.5 \pm 2.2$	-28.8	$-27.7 \pm 1.4$	-27.6	$-23.4 \pm 1.5$	-23.8
$\Delta T$ ( $^{\circ}\text{C}$ )	$0.3 \pm 0.5$	0.2	$0.0 \pm 0.5$	-0.1	$0.2 \pm 0.5$	0.0
Td ( $^{\circ}\text{C}$ )	$-31.4 \pm 2.4$	-31.8	$-31.2 \pm 1.8$	-31.0	$-26.2 \pm 1.9$	-26.5

Table 3  
Median and mean values for gas phase species and photochemical parameters for ISCAT 1998 and 2000 and ANTCI 2003

Parameters	1998		2000		2003	
	Average	Median	Average	Median	Average	Median
<i>Nov. 15–30</i>						
J(O <sup>1</sup> D) ( $10^{-6} \text{ S}^{-1}$ )			$5.9 \pm 1.8$	5.3	$8.0 \pm 1.2$	7.7
J(NO <sub>2</sub> ) ( $10^{-2} \text{ S}^{-1}$ )			$0.88 \pm 0.15$	0.91	$0.7 \pm 0.0$	0.7
NO (pptv)			$102 \pm 69$	93.379	$538 \pm 219$	529
O <sub>3</sub> (ppbv)	$34.4 \pm 5.3$	35.1	$32.2 \pm 3.4$	32.3	$34 \pm 2$	34
CO (ppbv)	45.1	44.2	$40.1 \pm 1.6$	40.0	$47 \pm 1$	47
C <sub>2</sub> H <sub>6</sub> (pptv)			$215 \pm 12$	214	$206 \pm 8$	207
CH <sub>2</sub> O (pptv)						
H <sub>2</sub> O <sub>2</sub> (pptv)						
OH ( $10^6 \text{ molec cm}^{-3}$ )			$2.5 \pm 0.6$	2.4	$2.2 \pm 29.0$	0.8
HO <sub>2</sub> + RO <sub>2</sub> ( $10^7 \text{ molec cm}^{-3}$ )						
<i>Dec. 1–15</i>						
J(O <sup>1</sup> D) ( $10^{-6} \text{ S}^{-1}$ )	$8.2 \pm 0.5$	8.16	$6.7 \pm 0.7$	6.8	$7.1 \pm 1.8$	6.2
J(NO <sub>2</sub> ) ( $10^{-2} \text{ S}^{-1}$ )	$1.1 \pm 0.1$	1.0	$1.0 \pm 0.1$	1.1	$0.8 \pm 0.1$	0.8
NO (pptv)	$214 \pm 84$	209	$95 \pm 103$	82.	$201 \pm 138$	164
O <sub>3</sub> (ppbv)	$32.6 \pm 5.9$	32.6	$35.6 \pm 3.1$	35.2	$31 \pm 4$	32
CO (ppbv)	37.7		$37.4 \pm 2.0$	37	$47 \pm 5$	46
C <sub>2</sub> H <sub>6</sub> (pptv)	$439 \pm 186$	417	$181 \pm 26$	180	$188 \pm 13$	188
CH <sub>2</sub> O (pptv)			$109 \pm 36$	122	$67 \pm 26$	65
H <sub>2</sub> O <sub>2</sub> (pptv)			$288 \pm 129$	294	$277 \pm 65$	291
OH ( $10^6 \text{ molec cm}^{-3}$ )	$1.6 \pm 0.4$	1.4	$2.6 \pm 1.0$	2.9	$1.1 \pm 0.4$	1.1
HO <sub>2</sub> + RO <sub>2</sub> ( $10^7 \text{ molec cm}^{-3}$ )						

Table 3 (continued)

Parameters	1998		2000		2003	
	Average	Median	Average	Median	Average	Median
<i>Dec. 16–31</i>						
J(O <sup>1</sup> D) (10 <sup>-6</sup> S <sup>-1</sup> )	8.6±1.3	8.9	8.5±0.8	8.5	8.4±0.7	8.5
J(NO <sub>2</sub> ) (10 <sup>-2</sup> S <sup>-1</sup> )	0.95±0.11	1.0	1.0±0.1	1.1	0.8±0.1	0.8
NO (pptv)	244±120	237	113±102	88	158±155	76
O <sub>3</sub> (ppbv)	27.7±7.0	26.1	29.3±5.8	30.0	34±7	32
CO (ppbv)	34.5		34.3±2.7	34.35	49±5	48
C <sub>2</sub> H <sub>6</sub> (pptv)	383±153	376	144±13.6	145	156±11	159
CH <sub>2</sub> O (pptv)			100±29	105	73±23	74
H <sub>2</sub> O <sub>2</sub> (pptv)			231±74	229	278±69	286
OH (10 <sup>6</sup> molec cm <sup>-3</sup> )	1.9±1.1	1.7	2.1±0.8	2.3	1.2±0.6	1.2
HO <sub>2</sub> +RO <sub>2</sub> (10 <sup>7</sup> molec cm <sup>-3</sup> )			8.3±2.4	8.1		
<i>Nov. 15–30</i>						
HCO <sub>2</sub> H (pptv)						
CH <sub>3</sub> CO <sub>2</sub> H (pptv)						
HONO <sup>a</sup> (pptv)					82±20	76
HONO <sup>b</sup> (pptv)					6.9±3.8	7.1
HNO <sub>3</sub> <sup>a</sup> (pptv)					61±9	68
HNO <sub>3</sub> <sup>b</sup> (pptv)					190±19	194
HO <sub>2</sub> NO <sub>2</sub> (pptv)					63±2	63
DMS (pptv)					4±2	3.0
SO <sub>2</sub> (pptv)			7.8±4.6	6.5		
PAN (pptv)					18.4±2.3	15.0
H <sub>2</sub> SO <sub>4</sub> (10 <sup>5</sup> molec cm <sup>-3</sup> )			2.9±1.2	2.9	1.5±0.8	1.4
MSA (10 <sup>4</sup> molec cm <sup>-3</sup> )			5.3±3.2	4.81	13.6±10.9	11.9
<i>Dec. 1–15</i>						
HCO <sub>2</sub> H (pptv)			70±42	58		
CH <sub>3</sub> CO <sub>2</sub> H (pptv)			231±126	215		
HONO <sup>a</sup> (pptv)			8.0±3.7	7	52±25	51
HONO <sup>b</sup> (pptv)					7.3±4.2	7.3
HNO <sub>3</sub> <sup>a</sup> (pptv)			35.3±8.4	33.8	32±13	29
HNO <sub>3</sub> <sup>b</sup> (pptv)					67±49	63
HO <sub>2</sub> NO <sub>2</sub> (pptv)					40±11	42
DMS (pptv)	<2	<2	6.6±5.3	3.3	< 2	1.0
SO <sub>2</sub> (pptv)			9.9±11.4	4.5	11±9	10
PAN (pptv)					14.1±3.6	16.1
H <sub>2</sub> SO <sub>4</sub> (10 <sup>5</sup> molec cm <sup>-3</sup> )	2.5±0.3	2.5	3.0±1.3	3.0	1.7±1.3	1.6
MSA (10 <sup>4</sup> molec cm <sup>-3</sup> )	5.9±2.8	5.6	5.9±6.3	4.4	4.7±7.1	4.3
<i>Dec. 16–31</i>						
HCO <sub>2</sub> H (pptv)			124±83	85		
CH <sub>3</sub> CO <sub>2</sub> H (pptv)			275±119	264		
HONO <sup>a</sup> (pptv)			27.0±7.4	28		
HONO <sup>b</sup> (pptv)					5.1±3.8	4.9
HNO <sub>3</sub> <sup>a</sup> (pptv)			23.5±11.4	19.9		
HNO <sub>3</sub> <sup>b</sup> (pptv)			19.3±11.4	18.2	106±86	84
HO <sub>2</sub> NO <sub>2</sub> (pptv)			23.3±10.9	23.5	39±18	39
DMS (pptv)	1.7±3.9	0.7	1.9±1.0	1.4	4.8±6.6	2.0
SO <sub>2</sub> (pptv)			5.7±4.3	2.8	10±2	10
PAN (pptv)					15.6±4.9	18.6
H <sub>2</sub> SO <sub>4</sub> (10 <sup>5</sup> molec cm <sup>-3</sup> )	2.5±1.5	2.4	2.4±1.4	2.3	1.1±0.9	1.0
MSA (10 <sup>4</sup> molec cm <sup>-3</sup> )	7.5±12	4.6	6.9±8.2	3.8	2.8±5.7	2.5



Table 4  
Median and mean aerosol species for ISCAT 1998 and 2000 and ANTCI 2003

Parameters	1998		2000		2003	
	Average	Median	Average	Median	Average	Median
<i>Nov. 15–30</i>						
Na <sup>+</sup> (μg m <sup>-3</sup> )					0.06±0.03	0.04
NO <sub>3</sub> <sup>-</sup> (μg m <sup>-3</sup> )			0.13±0.06	0.14	0.40±0.18	0.39
SO <sub>4</sub> <sup>=</sup> (μg m <sup>-3</sup> )			0.11±0.02	0.104	0.17±0.03	0.16
MS (μg m <sup>-3</sup> )			0.01±0.00	0.01	0.02±0.01	0.01
Be <sup>7</sup> (fCi m <sup>-3</sup> )			LOD	LOD	127±27	131
Pb <sup>210</sup> (fCi m <sup>-3</sup> )			LOD	LOD	4.6±1.5	4.6
Hg (ng m <sup>-3</sup> )			0.19±0.11	0.18	0.27±0.11	0.25
<i>Dec. 1–15</i>						
Na <sup>+</sup> (μg m <sup>-3</sup> )	0.05±0.02	0.04			0.05±0.02	0.06
NO <sub>3</sub> <sup>-</sup> (μg m <sup>-3</sup> )	0.04±0.02	0.045	0.16±0.06	0.154	0.26±0.15	0.22
SO <sub>4</sub> <sup>=</sup> (μg m <sup>-3</sup> )	0.21±0.05	0.20	0.09±0.02	0.09	0.15±0.04	0.15
MS (μg m <sup>-3</sup> )	0.01±0.00	0.01	0.00±0.00	0.00	0.01±0.00	0.01
Be <sup>7</sup> (fCi m <sup>-3</sup> )	205±90	174	LOD	LOD	156±31	153
Pb <sup>210</sup> (fCi m <sup>-3</sup> )	LOD	LOD	LOD	LOD	4.9±2.2	4.5
Hg (ng m <sup>-3</sup> )			0.20±0.16	0.22	0.20±0.09	0.21
<i>Dec. 16–31</i>						
Na <sup>+</sup> (μg m <sup>-3</sup> )	0.04±0.02	0.03			0.04±0.02	0.05
NO <sub>3</sub> <sup>-</sup> (μg m <sup>-3</sup> )	0.04±0.02	0.032	0.15±0.04	0.14	0.22±0.19	0.15
SO <sub>4</sub> <sup>=</sup> (μg m <sup>-3</sup> )	0.22±0.05	0.21	0.10±0.02	0.10	0.11±0.04	0.13
MS (μg m <sup>-3</sup> )	0.01±0.00	0.01	0.00±0.00	0.00	0.00±0.00	0.00
Be <sup>7</sup> (fCi m <sup>-3</sup> )	157±28	148.5	LOD	LOD	195±35	182
Pb <sup>210</sup> (fCi m <sup>-3</sup> )	LOD	LOD	LOD	LOD	4.9±1.2	4.6
Hg (ng m <sup>-3</sup> )			0.09±0.04	0.08	0.13±0.07	0.11

calculated OH values tracking the observations reasonably well; however, the predicted OH level was found to decrease more slowly than the observed OH. Equally significant, the predicted OH level was slower to return to the non-eclipse value, suggesting that there may be missing chemical processes in the model.

### 3.2.2. Abnormally high NO concentrations

While previous studies have resulted in several observations of NO concentrations exceeding 500 pptv for periods of several hours (typically less than a day), the ANTCI 2003 study resulted in nearly twice these levels being observed and high levels persisting for several days. In the latter case a peak concentration of 1.0 ppbv was reached in late November. There are several possible reasons for these particularly high measurements. First, ISCAT results from a limited sampling period provided a NO<sub>x</sub> flux estimate of  $3.9 \times 10^8$  molec cm<sup>-2</sup> s<sup>-1</sup> (Onclay et al., 2004). However, the 1-D modeling results of Wang et al. (2007) for the high concentration period suggested flux values that were factors of 2–3 times

higher. A second factor may lie in the fact that the winds during this period were predominantly out of the east. Twin Otter NO measurements clearly indicated that when flying out of SP the highest NO values were observed when sampling into the eastern sector (i.e., 45–120°). This finding is also consistent earlier ground-based data sets, which have shown that some of the highest NO levels measured have tended to be associated with air parcels whose winds have been out of the east. One could hypothesize that there was enhanced accumulation over the high plateau in thin BLs subject to non-linear NO<sub>x</sub> chemistry (e.g., Davis et al., 2004) that then grew in depth as air parcels moved downslope toward the pole. A third factor may also lie in the pattern of snow accumulation and loss at the SP. As noted by Neff et al. (2007), significant accumulation of snow occurred in September (~0.11 m) followed by ablation of the snow in October (-0.049 cm) and November (-0.01 m). One must then question whether high nitrate snow was exposed in the ablation process leading to the high NO flux values inferred in the modeling results of

Wang et al. (2007). These results suggest that much more needs to be learned about the distribution and recycling of snow nitrate over the high plateau.

### 3.2.3. Confirmation that SP results are characteristic of the plateau

Despite much effort during ISCAT, there was no convincing way to demonstrate that the ARO NO measurements were totally free of local interferences either from the building itself or from the larger area defined by the outer most perimeter of the SP research facility. Thus, there was a credibility issue if SP results were to be extended to the plateau at large. The ANTCI 2003 airborne results clearly demonstrate that the unexpected high levels of NO seen at SP in 1998 and 2000 are, in fact, characteristic of a plateau area extending out from the pole to 400 km or more (Davis et al., 2007). Although the size of the plateau far exceeds this distance, there is no reason to believe that this phenomenon is not common to the entire high plateau region. Indeed, an empirical snow NO<sub>x</sub> emission parameterization is constructed using only the measurements at SP and it is then applied in a regional chemical transport model (Wang et al., 2007). The model simulations were able to capture the spatial distribution patterns observed by Twin Otter, implying a common snow NO production mechanism in plateau regions.

### 3.2.4. Confirmation and new understanding of coastal NO

Aircraft flights along the coast helped to confirm that, in general, coastal NO concentrations are typically one or more orders of magnitude lower than those over the plateau. Previously, these coastal observations had been limited to the USA's Palmer Station, and the German base of Neumayer. Twin Otter sampling covered approximately 400 km along the Ross Sea to the north of McMurdo and an equal distance to the south, again along the Ross Sea. With one major exception the levels of NO observed confirmed the earlier ground-based observation. This major exception came on November 27, 2006 at ~17:35 h at which time the Twin Otter was crossing Byrd Glacier at a very low altitude. At this time and for the next ~9 min highly elevated levels of NO<sub>y</sub> and NO were observed. The maximum seen in NO was 550 pptv and that for NO<sub>y</sub> ~900 pptv. As discussed by Davis et al. (2007), this unusual event demonstrates for the first time two important things: (1) there are certain coastal

areas of Antarctica that can, at certain times, experience highly elevated NO; and (2) when this glacial valley drainage occurs, the plateau is losing net reactive nitrogen. The latter is of particular interest since whatever the magnitude of this nitrogen loss, the primary nitrogen source strength to the plateau will have to be correspondingly increased since current estimates of this strength assume that the only nitrogen loss from the plateau is that due to its burial in deep ice. For further details see Davis et al. (2007).

### 3.2.5. Plateau oxidizing canopy

Among the several new findings emerging from the airborne sampling program was a vertical distribution for NO and NO<sub>y</sub>. These first of their kind data made possible two quite significant hypotheses about the chemical nature of the Antarctic plateau, especially as related to the role of reactive nitrogen. The first of these is related to the question of what fraction of the reactive nitrogen on the plateau undergoes photochemical recycling each year. As already noted, the new vertical profiles for NO have been used to estimate this factor. The results suggest a value as small as one time per year with the average value being slightly larger than two (Davis et al., 2007). How this number might vary with location/altitude has a major impact on the interpretation of nitrogen as a proxy species in ice core records.

The second hypothesis follows from the fact that typically as NO increases the chemically coupled oxidizing species OH also increases along with the net production of photochemical O<sub>3</sub> (at least for NO concentrations up to several hundred pptv). In this case, modeling calculations based on the airborne NO distributions have shown that the plateau should behave in a similar chemical fashion. Thus, a simple extension of these results would lead one to the conclusion that the entire high plateau should be enshrouded in an oxidizing canopy of OH as well as enhanced O<sub>3</sub> (i.e., see Davis et al., 2007; Wang et al., 2007). Centrally important here is the recognition that the presence of an OH oxidizing canopy potentially changes the role of the plateau in terms of its influence on ice core chemical proxy species. Instead of it being just a graveyard for burial, the plateau atmosphere also can potentially modify any species entering it that might be in a reduced chemical state. This it appears is what happens to sulfur compounds like DMS, thus leading to MS/nss-sulfate ratios being quite unlike

those found along the coast. For further details on sulfur see [Arimoto et al. \(2007\)](#).

### 3.2.6. Ozone studies

The results of previous ISCAT studies suggested that ozone was being produced at the SP, but the magnitude and spatial extent of this production remained unclear. While absolute surface layer production rates are highly variable, values of up to 4–5 ppbv day<sup>-1</sup> have been estimated from the earlier ISCAT studies. The vertical ozone distributions seen from the tethered balloon profiles provide further evidence for the significant ozone production rates occurring near the SP ([Helmig et al., 2007b](#) this issue). This production is seen to result in gradients as large as 25 ppbv between the surface and 200 m. Evidence has also been found for spring/summer time production of ozone, not just at the SP, but over much of the polar plateau above about 2400 m ([Oltmans et al., 2007](#)). The regions of ozone production clearly appear to be related to high NO<sub>x</sub> and HO<sub>x</sub> levels, and are thus expected to follow many of the same trends discussed above for NO. These new results are also in agreement with the oxidizing canopy hypothesis suggested by [Davis et al. \(2007\)](#) and discussed by [Wang et al. \(2007\)](#). Highly elevated O<sub>3</sub> levels were observed to reach up to 300 m above the plateau surface ([Helmig et al., 2007b](#), this issue) but because of the long lifetime of O<sub>3</sub> under Antarctic conditions and the relative thin layer in which it is formed, the upward mixing of ozone, produced near the surface, will not dramatically enhance free tropospheric ozone concentrations over the Antarctic plateau.

The ozone measurements required for this study were derived from several different surface and balloon-borne instruments. The most pronounced ozone gradients were typically only a factor of two and important trends might be as small as a few percent change in ozone concentration. Thus, to increase confidence in observed ozone gradients and trends an intercomparison and evaluation of ozone measurements was conducted. The results of measurement comparisons, under conditions where no gradients were thought to exist between instruments, are discussed in [Johnson et al. \(2007\)](#).

### 3.2.7. Hg studies

First ever mercury speciation and surface exchange measurements at the SP ([Brooks et al., 2007a](#)) showed very high levels (both relative to

gaseous elemental mercury, and in absolute magnitude) of oxidized mercury species (in gaseous and particulate-bound species) in the near-surface air with concentrations two orders of magnitude higher than typical oxidized mercury concentrations in central North America or Europe. High filterable mercury levels (presumably oxidized species) had been measured during ISCAT 2000 ([Arimoto et al., 2004](#)) and were repeated in 2003.

Rapid deposition of these oxidized mercury species was evidenced by the high total mercury concentrations in the surface snow which averaged 198 ng(Hg)/l (two orders of magnitude higher than typical surface snow in central North America or the Alps). Measurements of the surface exchange showed significant emission fluxes of the gaseous elemental mercury via photoreduction within the first few centimeters of the snow pack.

A smaller fraction of mercury in the snow pack escapes photoreduction to become buried in the firn and ultimately in the glacial ice, elucidating a previously unknown role of the vast polar plateau in the global mercury budget (for further detail see [Brooks et al., 2007 a, b](#)).

### 3.2.8. Aerosol studies

The ratio of MS to nss (MS/nss-sulfate) generally varies greatly from coast to plateau with a much larger ratio typically observed at the coast. While average values of this ratio observed during ANTCI were fairly similar to those measured in the two previous ISCAT campaigns, the SP measurements from 29 November to 3 December resulted in a particularly high MS/nss-sulfate ratio along with high sodium concentrations, suggesting an oceanic influence. This supposition was supported by calculated back-trajectories that showed the origin of the air masses for these days to be from the Weddel Sea ([Arimoto et al., 2004](#)). This provided some of the clearest evidence yet that marine air can be rapidly transported to the SP.

Filterable nitrate was also quite high during the ANTCI campaign with an average value nearly twice as high as during ISCAT 2000 and more than 6 times higher than ISCAT 1998 results ([Arimoto et al., 2004](#)). More importantly, the correlations between these measurements and those for NO, HNO<sub>3</sub>, and HNO<sub>4</sub> have again pointed to local photochemistry as the most important source of atmospheric nitrogen during the spring/summer/fall months on the plateau (see [Arimoto et al., 2007](#); [Davis et al., 2007](#), for details).

#### 4. Summary of meteorological and chemical parameter variability

While not a specific goal of the ISCAT and ANTCI studies, the ensemble of data emerging from these studies shown in Tables 2–4 is starting to paint a rather interesting picture of plateau meteorology and chemistry. Among the most interesting aspects is the high degree of variability particularly in wind-driven mixing and transport, and the associated changes in reactive nitrogen concentrations that in turn play a large role in controlling the photochemistry of the region. Large variations are observed from year to year but in some cases even from month to month. While some similarities in chemical composition do exist, such as elevated NO, OH, enhanced oxidation rates, and the production of ozone, the timing, magnitude, and to some extent even the causes of these events can be quite different. High NO can be strongly influenced by local dynamics working in conjunction with non-linear NO<sub>x</sub> chemistry in some cases and by regional dynamics in other cases as demonstrated by the late November versus late December results. However, as noted earlier in our discussions of nitrogen, the role of the recycling factor may yet be found to play a major role also. Tables 2–4 allow for a comparison of these meteorological factors as well as variations in trace gases and aerosol species for all three programs.

#### 5. Summary

The high plateau is very photochemically active in the spring and summer months. The driving force for enhanced OH and ozone production on the plateau appears to be photodissociation of nitrate compounds in the snow, but presently the geographical distribution of both the reactive oxidation products and the NO precursor remains sketchy. Also still unclear is whether nitrate in the snow is less efficient in producing NO in the atmosphere at lower altitude/coastal sites than on the high plateau. Both of the latter concerns will be investigated in ANTCI 2005. The importance of high OH concentrations enshrouding the entire Antarctic plateau lies in its ability to reduce the atmospheric lifetime of tracer compounds used in the study of ice cores, pollutant transport, and marine air transport. However, while these enhanced OH and ozone levels over the Antarctica plateau can provide a

major impact locally, their global effect is probably quite small.

Beyond the practical matter of understanding Antarctic photochemistry in order to better understand ice cores/paleoclimate and its influence on regional and global chemistry, the Antarctic continent also provides nearly pristine laboratory-like conditions that extend for hundreds, and even thousands of kilometers. Under these conditions tropospheric photochemical oxidation processes can be isolated and studied independent of biogenic and/or anthropogenic emissions. For example, ANTCI 2003 measurements showed the consistent near absence of compounds such as PAN which should have a lifetime of month or more in Antarctica. In most places in the world this compound is typically quite abundant because of anthropogenic or combustion plumes. Thus, the isolation of the Antarctic continent combined with the lack of primary local emissions allows NO<sub>y</sub>/HO<sub>x</sub> chemistry to be studied in the absence of other complex chemical reactions while still providing a large dynamic range of nearly two orders of magnitude in NO concentration.

#### Acknowledgments

We would like to acknowledge the NSF Office of Polar Programs for their support of this research (NSF Grant nos. OPP 0229633, 0230246, and 0230051). We would also like to thank NOAA's Global Monitoring Division and Kenn Borek Air Ltd.'s personnel for their support of the ANTCI research effort at the South Pole ARO facility and the Twin Otter research aircraft, respectively.

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