JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 107, NO. D11, 4109, 10.1029/2001JD000810, 2002

Missing ozone at high altitude: Comparison of in situ and satellite data

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Received 3 May 2001; revised 19 September 2001; accepted 21 September 2001; published 1 June 2002.

[1] An experiment was designed to measure ozone at a site on the Andes Mountains, near La Paz, Bolivia, at a height of 3420 m, with the objective of investigating the ozone reduction seen over the mountains and the increased UV-B radiation. A Brewer spectrophotometer was used for surface measurements of the vertical ozone column and UV-B radiation; the spatial ozone variation around the mountain site was obtained using Total Ozone Mapping Spectrometer (TOMS) data. The ozone column values show a decrease over the mountain region, which maximizes at about 20 Dobson units, in comparison to the values in the Pacific regions, to the west, and the continental values to the east, at about the same latitude. To investigate the reason for this missing ozone, the vertical ozone distribution was measured using electrochemical concentration cell ozonesondes. The ozone profiles were integrated downward to sea level. It is shown that this integral corresponds to the missing ozone over the mountain area. The strongest consequence of the reduced atmosphere at high altitude on the UV-B intensities is not the reduction of the ozone column but that of the Rayleigh- scattering effect. The absence of scattering considerably increases the UV-B radiation at high altitudes. For example, the ozone effect on the ratios of UV-B intensities between La Paz and Natal, a sea level station, is only 1.15, while for the Rayleigh-scattering reduction, the ratio between stations is 1.75, at 306.3 nm. Measured UV-B intensities at both sites show La Paz/Natal ratios of this order of magnitude. *INDEX TERMS:* 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS:* ozone, ozone column, high-altitude ozone, tropospheric ozone, ECC ozone balloon measurements, UV-B radiation

1. Introduction

[2] Since the atmospheric density decreases at an approximate exponential rate with height, a considerable portion of the overhead atmospheric column is missing at an altitude of 3.42 km. This is the height of an observation site on the Andes Mountains near the city of La Paz, Bolivia (16.54°S, 68.06°W). The low density makes Rayleigh-scattering weaker; the tropopause is closer, which probably means that there is less tropospheric ozone over the site; and these conditions indicate that the UV-B radiation is expected to be more intense, relative to sea level sites at the same latitude. The objective of this work is to investigate whether these assumptions are correct and which effect is dominant. *Zaratti et al.* [1999] showed some earlier Brewer spectrophotometer data from this site, and have hypothesized that the ozone column reduction over the mountains could not be caused only by the reduction of the troposphere, and speculated that there should also be a stratospheric effect of some kind, not specified. *Kazimirovsky and Danilov* [1997] have suggested an effect of orographic formations on total ozone. In this work, ozone data from the Total Ozone Mapping Spectrometer (TOMS) will be analyzed for spatial variations around the mountains. It has also been argued that possibly, TOMS data may have a calibration problem with the high altitude data, owing to the high albedo of the region, arising from the permanent snow cover of some of the mountain ridges [*Zaratti et al.*, 1999; see also *Kerr and McElroy*, 1995]. To investigate this hypothesis, a Brewer spectrophotometer was installed at the site, in order to have a local independent measurement of the ozone column. In addition, in order to obtain detailed ozone profiles at the site, 10 ozonesondes of the electrochemical concentration cell (ECC) type were launched. These profiles will be used to show that the missing ozone over the mountains is mostly caused by the reduced depth of the troposphere.

0148-0227/02/2001JD000810

2. Instruments and Site

[3] Total Ozone Mapping Spectrometer (TOMS) data were obtained from the National Aeronautics and Space Administration (NASA), in the form of averages obtained over a grid of 1.0° by 1.25° in latitude and longitude.

[4] The Brewer spectrophotometer is a commercial instrument in wide use globally, originally designed to measure the total

Table 1. Nominal Brewer UV-B Wavelengths Used for Ozone Measurements

Channel	Wavelength, nm
1	306.3
2	310.1
3	313.5
4	316.8
5	320.1

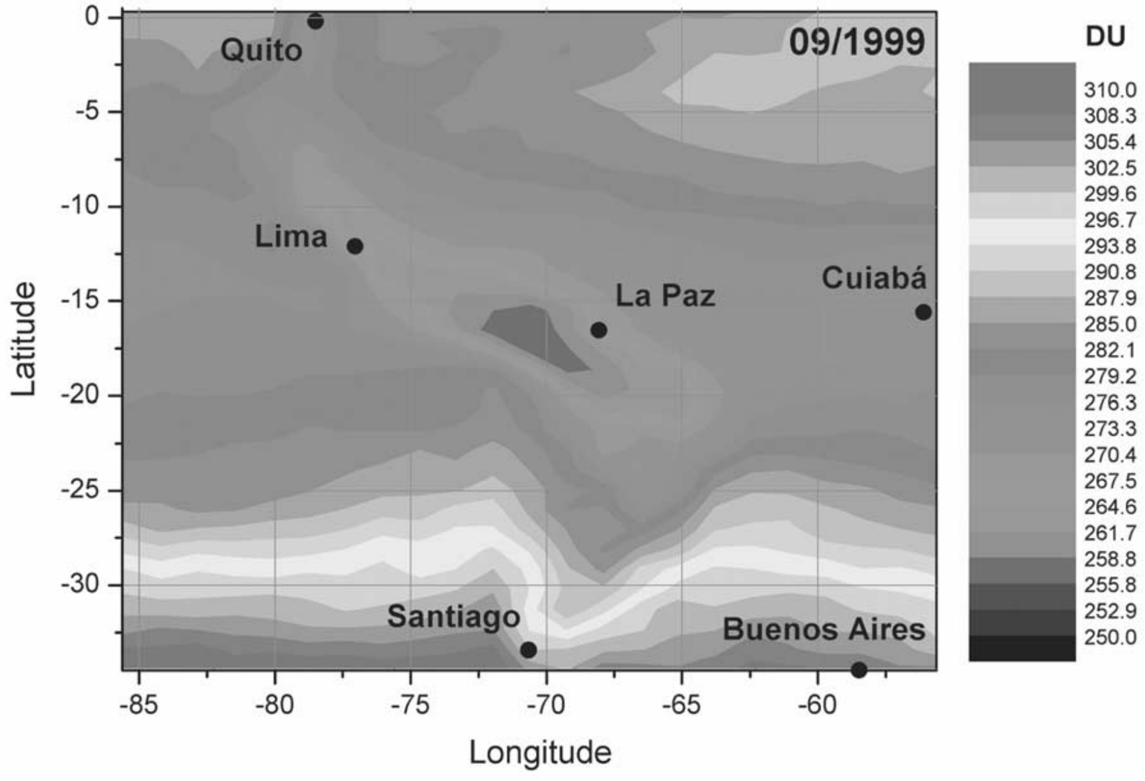

Figure 1. Total ozone spatial distribution over the Andes Mountains, obtained from TOMS data, showing an ozone minimum near La Paz. See color version of this figure at back of this issue.

column of ozone in the atmosphere [*Brewer*, 1973]. For the spectral separation of the solar radiation it uses an Ebert-type spectrometer, with an effective F6 optical aperture and a diffraction grating of 1200 lines/mm. The UV-B wavelengths in the Brewer ozone mode are separated into five channels, shown in Table 1. In addition to ozone the more recent instruments allow also the observation of NO_2, SO_2, and global UV-B radiation. The Canadian-built Brewer spectrophotometer is totally automatic and can be programmed to perform the observations as necessary for each special interest. In Brazil this instrument has been used to observe stratospheric ozone and UV-B variations [*Kirchhoff et al.*, 1997a] and atmospheric SO_2 of volcanic origin [*Sahai et al.*, 1997]; and at high latitude, measurements of the ozone hole in the Antarctic region [*Kirchhoff et al.*, 1997b, 1997c] have been obtained. For the present experiment, the instrument was programmed to perform direct Sun observations at regular intervals of the solar zenith angle.

[5] The ozonesondes are electrochemical concentration cells (ECCs), with a cell size of 2.5 ml. They were developed by *Komhyr* [1969] and *Komhyr and Harris* [1971] and tested and

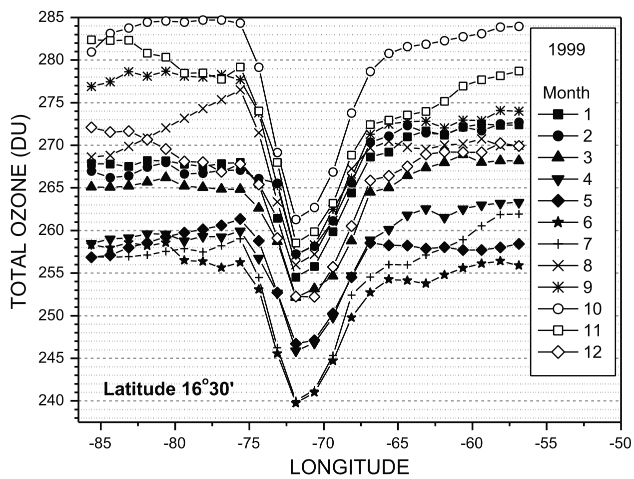

Figure 2. Average monthly means of longitudinal variations of total ozone east and west of La Paz, Bolivia, as obtained from TOMS data.

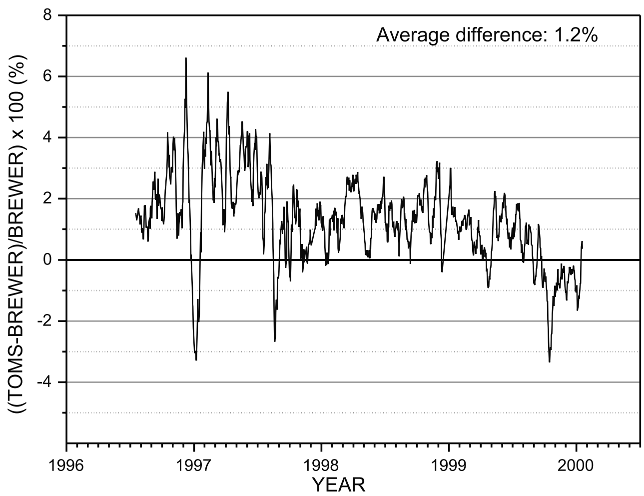

Figure 3. Comparison of TOMS and Brewer spectrophotometer total ozone data at the latitude of La Paz, Bolivia, showing a difference of only about 1%.

Table 2. Basic Parameters for 10 Ozone Soundings

Date	Local Launch Time	Surface Pressure, hPa	Burst Pressure, hPa	Surface Ozone, μhPa
June 07	1209	676.05	11.15	21.41
June 08	1557	677.89	13.08	24.91
June 09	1537	675.95	6.42	29.82
June 10	1027	676.63	8.28	26.33
June 11	1127	677.00	11.96	25.71
June 12	1100	676.41	11.43	20.65
June 13	1030	673.73	7.80	28.99
June 15	1618	674.42	8.15	20.24
June 16	1140	676.22	7.81	24.81
June 17	1723	676.18	6.91	22.85

validated by *Torres and Bandy* [1978], *Barnes et al.* [1985], and *Hilsenrath et al.* [1986]. *Kirchhoff et al.* [1991] describe previous low-latitude results.

[6] The site of observations is located near the capital city of La Paz, Bolivia, at 16.54°S, 68.06°W, at an altitude of 3420 m.

3. Results

3.1. Geographic Variations of Total Ozone Column Near La Paz

[7] The latitude-longitude structure of total ozone, for September 1999, over the Andes mountain complex is shown in Figure 1. This false color image representation shows that there is very clearly a minimum ozone column region over the Andes Mountains, near La Paz, Bolivia, and Lima (12°S, 77°W), Peru. Similar images were produced for the whole TOMS (version 7) data period, from July 1996 to June 2000; they all show the same characteristics, namely, a considerable reduction of ozone over the mountains during all seasons of the year, and during different years. Thus the missing ozone characteristic shown in the TOMS data is a robust feature. While TOMS data can quantify that column ozone has low values over the mountains, it contains no information about the height at which this occurs. Ozone soundings will be used to obtain this.

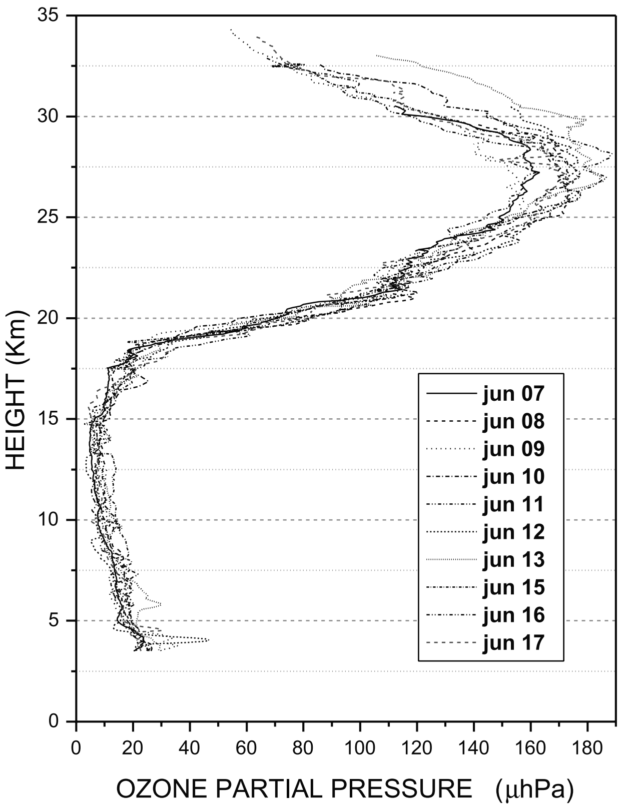

Figure 4. Vertical ozonesonde profiles for La Paz, Bolivia, obtained from 10 ECC ozone soundings launched in June 1998, listed in Table 2.

Table 3. Average Ozone Profile at La Paz From 10 Soundings

Pressure, hPa	Ozone Partial Pressure, μhPa	Standard Deviation, μhPa
681.3	25.8	6.0
584.3	19.9	4.4
501.2	17.5	4.0
429.9	15.7	3.0
368.7	13.0	3.3
316.2	11.0	2.8
271.2	9.7	2.3
232.6	8.9	2.2
199.5	8.5	2.8
171.1	6.2	6.9
146.8	7.2	1.8
125.9	9.0	2.5
108.0	12.8	2.6
92.61	17.1	3.7
79.43	21.6	5.7
68.13	38.0	12.3
58.43	67.9	10.9
50.12	96.0	11.6
42.99	111.5	10.1
36.87	122.8	9.2
31.62	137.5	9.2
27.12	151.7	9.1
23.26	164.0	9.2
19.95	169.6	9.4
17.11	168.0	11.0
14.68	160.4	12.7
12.59	140.9	16.3
10.80	118.4	17.9
9.261	96.9	18.2
7.943	76.6	12.7

[8] Figure 2 shows the monthly mean total ozone variations, at latitude 16.5°S, as a function of longitude, showing that ozone is missing in each month of the year. The ozone difference between the Pacific side and the minimum measured in Dobson units (DU) is about 25 DU in October and 16 DU in June. It is interesting to note that along 16.5°S, ozone is slightly larger on the Pacific side (to the west, 285 DU for October) than over the continent side (to the east, about 282–283 DU), which is thought to be partly an altitude effect, since over the continent to the east of La Paz, the altitude is around 600–700 m or 930 hPa, which at a partial pressure of ozone of about 2.6 mPa sums up from sea level to this height, to about 1.5–2.0 DU.

[9] Figures 1 and 2 show the missing ozone over the high altitudes of the Andes Mountains. To identify from what height this ozone is missing is one of the objectives of this study. Note that the minimum ozone is found, approximately, at longitude 72°W, which corresponds to high ridges of nearly 6 km altitude (maximum height = minimum ozone). The city of Cuiabá (16°S, 56°W) is approximately located at the same latitude of La Paz and can be used as a comparison site. For the TOMS yearly averages, the total ozone difference Cuiabá-La Paz was 7.7 DU, and the difference Cuiabá-minimum was 16.5 DU, as will be discussed shortly. Can this amount of missing ozone be explained by the reduced troposphere at the mountains? This question will be addressed shortly with the ozonesonde data.

3.2. Comparison With Brewer Spectrophotometer Data

[10] A Brewer spectrophotometer was installed at the La Paz site in 1996. The spectrophotometer obtains ozone data by looking

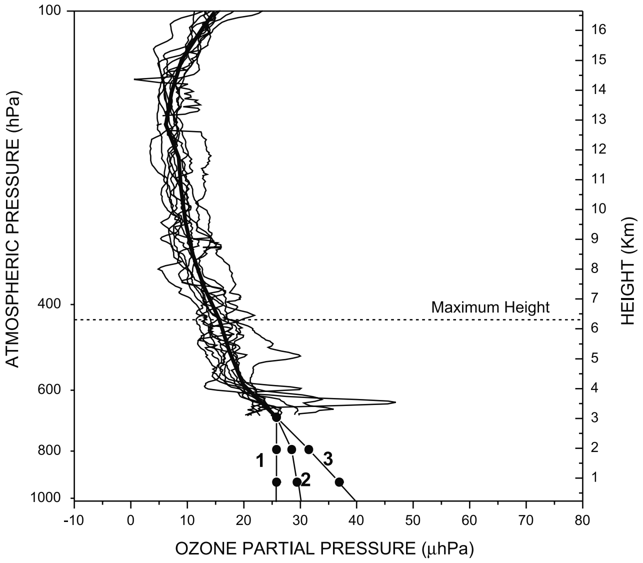

Figure 5. Integration of the average La Paz ozone profile down to sea level, using three choices of profile shapes: (1) constant partial pressure, (2) as observed for Cuiabá, and (3) extrapolating downward from the measured average profile.

directly at the Sun, whereas TOMS looks down to the Earth's surface; so in principle, TOMS might be more susceptible to an algorithm error due to albedo than the spectrophotometer. The comparison of the data is shown in Figure 3. The data points shown are 10-point running means of the ratio (TOMS-Brewer)/Brewer in percentage. The average difference between the two data sets, for the period shown, is 1.2%, which is considered an acceptable difference. This means that whatever the albedo effect might be, it does not affect TOMS data beyond acceptable limits, a concern expressed by *Zaratti et al.* [1999].

3.3. The Ozone Profile From Sonde Data

[11] A field campaign to measure the vertical distribution of ozone was made at the La Paz site in June 1998. A total of 10 ozone profiles were obtained, as shown in Table 2. The ozone profiles were integrated to 15 hPa, and the residual ozone above balloon burst altitude was obtained for each profile using the climatology of *McPeters et al.* [1997]. The total ozone integrals from the 10 sondes are slightly larger than TOMS values, the average difference (sonde-TOMS)/TOMS being 7.6%. This value is close to the climatological Natal average of 5.2%. The observed ozone vertical profiles are shown in Figure 4, and Table 3 shows the ozone partial pressures, at given heights for the average of the 10 profiles.

[12] It is possible now to "extend" the average La Paz profile down to sea level and calculate the corresponding ozone integral. To do this, the average ozone profile shape in this region of the lower troposphere, at the La Paz latitude, can be estimated by using the profile shape observed at Cuiabá (profile 2 in Figure 5), located at about the same latitude. In addition, one could investigate the effect of using additional known profile shapes, such as the constant partial pressure shape (profile 1 in Figure 5), and an extrapolation from the average obtained at La Paz (profile 3 in Figure 5). These three possible conditions are summarized in Figure 5. The ozone integral results in this small portion of the tropospheric profile for each of the three assumptions are shown in Table 4 and are 8.06, 8.9, and 10.4 DU, respectively, for La Paz, and for the maximum height region (minimum ozone), the values are 15.1, 15.9, and 17.4 DU, with typical standard deviations of about 1–1.5 DU. These values show that the comparison of the ozone differences using TOMS and using the integrals from the sonde data are very close (see Table 4), which seems to indicate that most of the ozone differences are the result of the reduced troposphere.

3.4. Impacts on UV-B Radiation at High Altitude

[13] Figure 6 compares the UV-B radiation at 306.3 nm measured at La Paz and Natal, at the fixed solar zenith angle of 50.6°. The La Paz value is much larger, during the time period from Julian days 209 to 236 of 1999. This is, of course, the combined effect of the missing ozone and the reduced atmosphere. However, what is the effect of each term separately?

[14] The calculation of the effect of the missing ozone alone, over La Paz, can be made as follows: Write the intensities at each site using Beer's law.

$$I = I_o \exp(-\tau\mu),$$

where I is the intensity of radiation (W/m^2/nm) at the site, I_o is the intensity above the atmosphere, τ is the optical extinction coefficient, and μ is the optical air mass. The ratio R of intensities at both sites, La Paz and Natal, for the same optical air mass of μ = 1.567 (for the fixed solar zenith angle used) and for two wavelengths λ = 306.3 and 320.1 nm will be calculated. Using ozone absorption and Rayleigh scattering as the main extinction factors, $\tau_{ozone} = \sigma LX$, and $\tau_{Rayleigh}$ [from *Froelich and Shaw*, 1980] is equal to $\sigma_{Rayleigh} LHp/p_o$, where σ is the absorption cross section ($\sigma = 3.62 \times 10^{-19}$ cm^2), $L = 2.69 \times 10^{19}$ cm^{-3} is the Loschmidt number, and X is the ozone integral along the path. Expressed in atm cm, using average total ozone contents from TOMS for the corresponding periods, values are 0.2788 for Natal and 0.2570 for La Paz; $\sigma_{Rayleigh}$ is the Rayleigh-scattering cross section, H is the atmospheric scale height, p is atmospheric pressure, and p_o is the atmospheric pressure at sea level. The radiation ratio then becomes

$$R_{306.3} = I_{(\text{La Paz})}/I_{(\text{Natal})} = 2.03,$$
$$R_{320.1} = I_{(\text{La Paz})}/I_{(\text{Natal})} = 1.63.$$

The comparison between the ozone and the Rayleigh effects gives the following result: (1) ratio at 306.3 nm, 2.03; for ozone only, 1.15; for Rayleigh only, 1.75; and (2) ratio at 320.1 nm, 1.63; for ozone only, 1.02; for Rayleigh only, 1.59. From these calculations it is clear that possibly, against expectations, the Rayleigh scattering effect is much larger than the ozone absorption effect, at La Paz, for both the 306.3 and the 320.1 nm wavelengths. The comparison between the calculated radiation ratio La Paz/Natal

Table 4. Comparison of Missing Ozone Column Amounts Using Different Techniques or Methods of Measurement for La Paz and the Minimum

	Downward Ozone Integral (DU) From Sondes			
	Profile 1	Profile 2	Profile 3	Ozone Differences (DU) From TOMS
La Paz	8.06	8.90	10.36	Cuiabá-La Paz 7.7 (SD = 2.9)
Minimum	15.09	15.93	17.39	Cuiabá-minimum 16.5 (SD = 3.5)

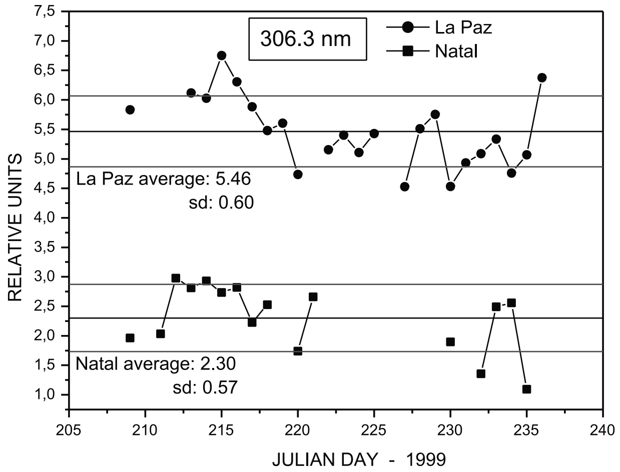

Figure 6. Comparison of the UV-B radiation at La Paz and Natal, as measured by a Brewer spectrophotometer, for 1999.

(2.03 and 1.63) and the measured values (2.37 ± 0.64 and 1.94 ± 0.51) is very close, within the statistical error of the measurement variability.

4. Conclusions

[15] The total ozone column reduction over high altitudes has been examined for the Andes mountain complex. Latitude-longitude variations have been obtained using TOMS data to show the spatial distribution of ozone.

1. These data have been compared at one station, La Paz, with surface Brewer spectrophotometer data. This comparison shows that the ratio (TOMS-Brewer)/Brewer is 1.2%, and therefore TOMS algorithm errors or deviations owing to a possible albedo effect from the persistent snow cover over some of the Andes Mountains (a concern mentioned by *Zaratti et al.* [1999]) is not observed for the La Paz station.

2. Using ozone variations with height obtained from ozone soundings in the area, and integrating the profile downward to sea level, it is found that the ozone column reduction observed over the mountain region is mostly a result of the reduced troposphere, an effect of about 8.9 DU, assuming profile 2 in Figure 5. An additional stratospheric effect, as suggested by *Zaratti et al.* [1999], if it exists, must be very small, since the difference between TOMS observations at Cuiabá and La Paz is 7.7 DU (Table 4).

3. Measurements of the UV-B radiation at high altitude show results at La Paz which are higher than Natal values by a factor of 2.37. This is compatible with the theoretical expectations. However, in the UV-B comparison between La Paz and Natal the major factor of causing these differences is not the ozone reduction, responsible for only a factor of 1.15, but to the decreased Rayleigh-scattering effect, which produces a factor of 1.75, at a wavelength of 306.3 nm.

[16] **Acknowledgments.** This work was started when a Brewer spectrophotometer was installed at La Paz, in 1996, as a collaboration between the Brazilian Institute for Space Research (INPE) and the Universidad Mayor de San Andres. The authors are grateful for the collaboration and help of the whole Bolivian team, especially Francesco Zaratti. Special thanks are directed to Marcelo Araujo and Luiz Mangueira for the launching of the ozonesondes at the site.

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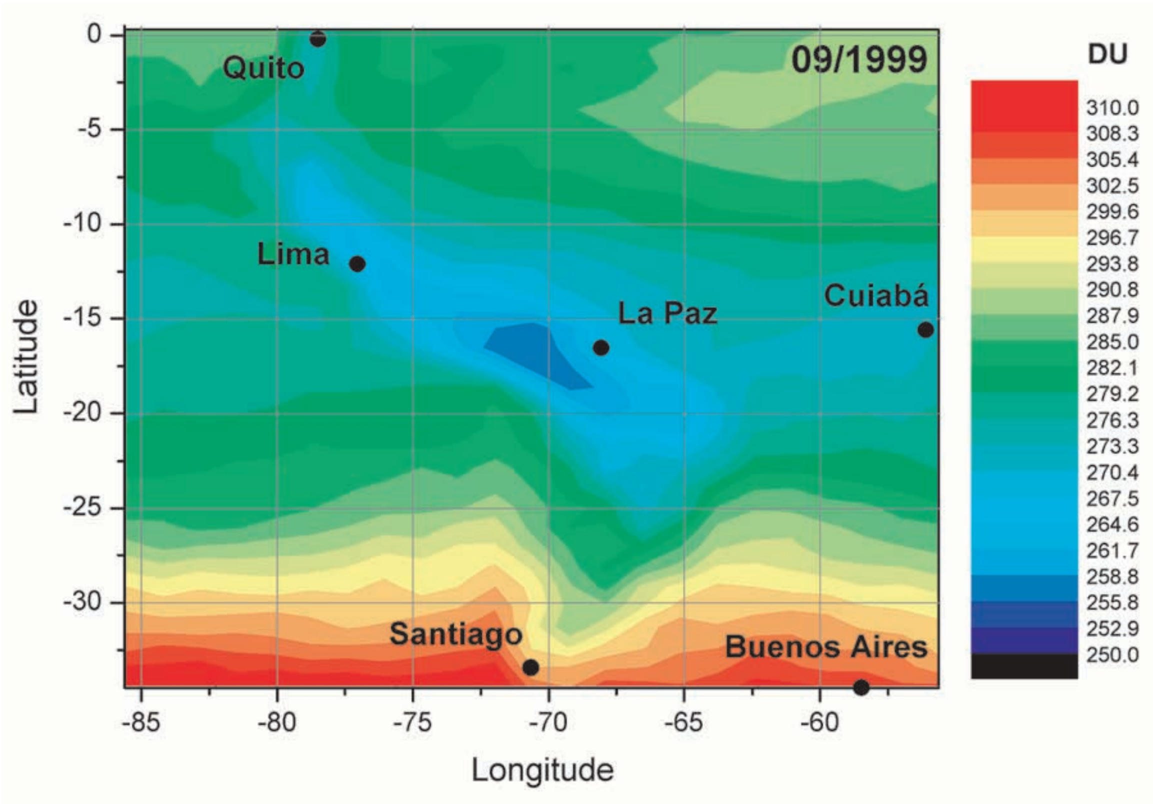

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