JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 115, D19304, doi:10.1029/2009JD013211, 2010

Summertime columnar content of atmospheric water vapor from ground-based Sun-sky radiometer measurements through a new in situ procedure

M. Campanelli,[1] A. Lupi,[2] T. Nakajima,[3] V. Malvestuto,[1] C. Tomasi,[2] and V. Estellés[4]

Received 16 September 2009; revised 28 April 2010; accepted 10 June 2010; published 7 October 2010.

[1] A new in situ technique for the retrieval of atmospheric water vapor content (i.e., precipitable water content) from Sun photometric direct solar irradiance measurements, taken at the 940 nm wavelength during clear-sky conditions, is presented. The procedure is applied to summer data recorded in 2007, 2008, and 2009 with a Sun-sky radiometer at the San Pietro Capofiume station in the Po valley, Italy. It is a preliminary development of the retrieval procedure providing the columnar water vapor content from measurements performed with PREDE Sun-sky radiometers. The technique brings improvement and innovation by retrieving the best values of constants (a and b), characterizing atmospheric water vapor transmittance while reducing simulation errors, and potentially contains information on seasonal changes in vertical profiles of temperature, air pressure, and moisture at measurement sites. Initially, the in situ procedure needs at least 1 week of independent measurements of precipitable water content taken over a range of solar zenith angles simultaneously with radiometric measurements, but it was also tested for cases in which independent measurements are not available. In the latter, the procedure was started using monthly precipitable water content estimates derived from surface observations of relative humidity, pressure, and temperature. Time patterns and absolute values of precipitable water content retrieved using the in situ procedure were in good agreement with Moderate Resolution Imaging Spectroradiometer retrievals and radiosonde measurements, with correlation coefficients of 0.8–0.9 and low percentage median differences of 7%–13%.

Citation: Campanelli, M., A. Lupi, T. Nakajima, V. Malvestuto, C. Tomasi, and V. Estellés (2010), Summertime columnar content of atmospheric water vapor from ground-based Sun-sky radiometer measurements through a new in situ procedure, *J. Geophys. Res.*, *115*, D19304, doi:10.1029/2009JD013211.

1. Introduction

[2] Routine measurements of the water vapor content within the atmospheric column (precipitable water content; W) are useful for evaluating its absorption effects on the radiation balance of the surface-atmosphere system, because they are characterized by a better accuracy than that achieved by the retrievals from satellite measurements of long-wave radiance. For this purpose, a variety of ground-based measurements are available worldwide, obtained using radiosonde (RDS) measurements, Sun photometers, Raman lidars, stratospheric balloons, microwave radiometers, instrumented aircrafts, and GPS receivers.

[3] Sun photometers are highly suitable instruments for performing continuous measurements of precipitable water content W during clear-sky conditions, since they generally are low cost and can be easily operated automatically. Several international ground-based Sun-sky photometer networks have been set up over the past years, providing aerosol characterizations on the planetary scale. Among them, AERONET [*Holben et al.*, 1998], PHOTON (http://loaphotons.univ-lille1.fr/photons/), RIMA (http://goa.uva.es/RIMA), and SKYNET [*Takamura and Nakajima*, 2004], employ Sun-sky photometers equipped with narrow-band interference filters in the visible and near-infrared windows of the solar spectrum for aerosol studies, and a filter centered at 940 nm for retrieving W from the output voltage V, which gives the direct solar irradiance measurement within the narrow spectral range of the 10 nm half-bandwidth, centered in the middle of the so-called $\rho\sigma\tau$ water vapor absorption band. The importance of simultaneous measurements of both W and columnar aerosol properties for clear-sky conditions, arises not only from the necessity of studying the water vapor trend but also

---

[1] Institute of Atmospheric Science and Climate, Consiglio Nazionale delle Ricerche, Rome, Italy.

[2] Institute of Atmospheric Science and Climate, Consiglio Nazionale delle Ricerche, Bologna, Italy.

[3] Center for Climate System Research, University of Tokyo, Chiba, Japan.

[4] Departamento Fisica de la Tierra y Termodinamica, Facultat de Fisica, Universitat de València, Burjassot, Spain.

0148-0227/10/2009JD013211

from the opportunity of investigating its influence and interaction with aerosol formation and particle growth.

[4] Retrieval of aerosol characteristics from the spectral series of output voltages V provided by a Sun-sky radiometer at the various visible and near-infrared wavelengths requires the use of correct Langley plot methodologies for calibrating these instruments, that is, for estimating the incident solar irradiance at the top of the atmosphere V_0 [*Campanelli et al.*, 2007; *Cachorro et al.*, 2008]. Similarly, the accuracy of the estimate of W depends closely on the quality of Sun-sky radiometer calibration within the channel centered at 940 nm. In fact, the output voltage V giving the direct solar irradiance measurement taken by the Sun photometer at the 940 nm wavelength can be related to the extra-terrestrial voltage V_0 of the instrument at the same wavelength through the expression

$$V = V_0 \cdot e^{-m\cdot(\tau_a + \tau_R)\cdot} \cdot e^{-a\cdot(m_w\cdot W)^b}, \quad (1)$$

where m is the relative optical air mass [*Kasten and Young*, 1989] and m_w is the optical air mass for water vapor [*Kasten*, 1966], both functions of the apparent solar zenith angle; τ_a and τ_R are the optical thicknesses due to aerosol extinction and molecular Rayleigh scattering at 940 nm, respectively; and term $T = e^{-a\cdot(mw\cdot W)b}$ is the partial atmospheric transmittance at 940 nm, relative to atmospheric water vapor, expressed as a function of m_w and W, with a and b as constants. Once a and b have been determined, V_0 can be estimated, and W can be calculated.

[5] Parameters a and b can be determined by means of a curve-fitting procedure of partial atmospheric transmittance T, whose behavior as a function of W is computed using a radiative transfer model over a wide range of slant path water vapor amounts (equal to the products of m_w W for several pairs of m_w and W). The procedure takes into account the spectral shape of the interference filter transmission curve, the water vapor molecular absorption effects (as described by an appropriate absorption model), and the vertical profiles of pressure, temperature, absolute humidity, and the aerosol extinction coefficient. This method is commonly used by the main ground-based networks (such as AERONET [*Smirnov et al.*, 2004; *Alexandrov et al.*, 2009]), where one pair of parameters (a, b) is used for each kind of 940 nm interference filter, by neglecting the dependence features of atmospheric transmittance T on the vertical profiles of air pressure and moisture at the various sites. This assumption is convenient for a network consisting of several instruments, avoiding the use of more than one pair of constants (a, b) for each instrument, but its suitability needs to be more deeply investigated. Another problem related to the use of this methodology is that the real response function of the system of measurement (i.e., the product of the filter response function times the detector response function) is not known unless the effect of spectral dependence of the detector in the shortwave IR region is measured. However, this measure is difficult to perform and requires expensive instrumentations. An error in the modeled response function can produce a wrong modeling of transmittance and lead to a serious problem in the determination of the (a, b) pair.

[6] In this study, a new in situ technique is developed, capable of retrieving the pair of constants (a, b) by the direct use of field measurements of V. The improvement and innovation of the technique is that the values of (a, b) are no longer affected by transmittance simulation errors and can potentially contain information on seasonal changes in the vertical profiles of temperature, air pressure and moisture occurring at each site, as will be explained in the next section. To start the procedure at least 1 week of independent measurements of precipitable water content (such as those by radiosondes, microwave radiometers or GPS) taken over a large range of solar zenith angle simultaneously with radiometric measurements is needed, but it was also tested for cases where these independent measurements are not available. Other past studies used correlative standard measurements of precipitable water content from microwave radiometers or GPS [*Schmid et al.*, 2001] for training Sun photometric retrieval algorithms, or calibrating instruments by comparison. In the present work, these measurements have been used only for starting the procedure, and so far, there is no proposal of similar methods for retrieving columnar water content from Sun-sky radiometer measurements.

[7] The proposed method is a preliminary development of the retrieval procedure providing the precipitable water content from the measurements performed with PREDE Sun-sky radiometers, employed as standard instruments in the SKYNET network, where inversion of the output voltage at the 940 nm wavelength is not yet officially used, in contrast to the analysis procedure adopted in the AERONET network.

[8] The present in situ procedure was applied to regular measurements performed at San Pietro Capofiume (SPC; 44°23′N, 11°22′E, 11 m above sea level) in the Po valley (northern Italy; Figure 1) with the PREDE model POM-02L Sun-sky radiometer, during the period from May 2007 to August 2009, within the frame of the AEROCLOUDS national program and the cooperative activity of the SKYNET network. The PREDE POM-02L is also one of the standard instruments in the European SkyRad users network (ESR) [*Estellés et al.*, 2009], developed to furnish Sun photometer users with a complete package of free open source programs and control script (ESR.pack) for the independent calibration and processing of radiometric raw data. The present in situ procedure for retrieving precipitable water content from solar direct irradiance measurements at 940 nm will be included in the ESR package.

2. Methodology

[9] The proposed in situ technique employs sets of ground-based measurements of direct solar irradiance V, which is attenuated on passing through the atmosphere and, hence, is affected by the various radiative transfer effects occurring along the atmospheric slant path, and influenced by the seasonal changes in the vertical profiles of absolute humidity, pressure and temperature that occur at each measurement site. In fact, because the measured value V is proportional to the whole atmospheric transmittance, it contains information on the atmospheric thermodynamic structure, associated with water vapor absorption, Rayleigh-scattering optical thickness (mainly depending on pressure and temperature along the vertical path), and aerosol optical thickness. Moreover, it also contains information on the real response function of the system of measurements. There-

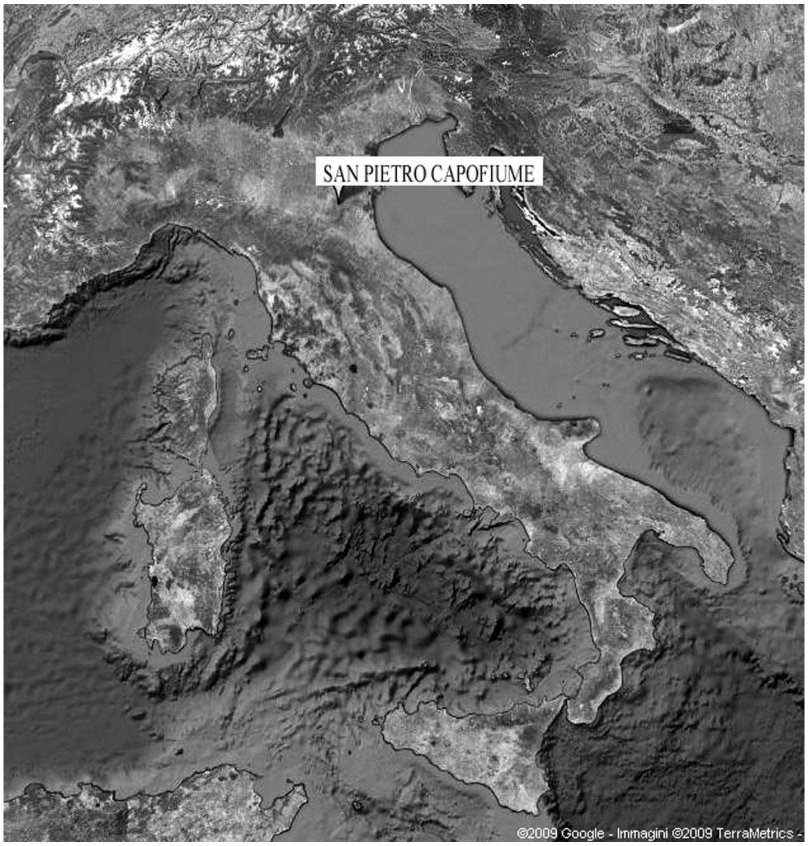

Figure 1. Geographical position of the San Pietro Capofiume station in the Po valley (Italy).

fore, the retrieved parameters *a* and *b* also take into account the above matters and can be treated as “equivalent structural parameters” that are unaffected by simulation errors, while their variability with season or geographical position is most likely due to changes in the average mass content of water vapor along the slant path, arising from day-to-day and month-to-month variations in the thermodynamic characteristics of the atmosphere.

[10] It must be borne in mind that parameter *a* is the absorption coefficient of the $\rho\sigma\tau$ water vapor band within the 930–950 nm wavelength range, properly weighted by both spectral curves of interference filter transmission and sensor responsivity, while exponent *b* depends on the intensity of the $\rho\sigma\tau$ water vapor band within the spectral interval covered by the interference narrow-band filter. With regard to exponent *b*, it is also worth noting that a variety of water vapor absorption bands is distributed throughout the solar spectrum from ~0.54 μm to >3 μm. Thus, considering the largely different absorption intensity features of these bands, parameter *b* is expected to assume values varying between 0.5 and 1.0 over this spectral range. The lower limit is pertinent to the asymptotic case of the strongest absorption band, and the upper one to the asymptotic case of the weakest absorption band, as predicted by the Matheson diagram defined for arrays of unequal but independent lines giving form to an absorption band [*Goody*, 1964]. The concept of the Matheson diagram applies fully to water vapor and implies that an increase in the mass concentration of this atmospheric constituent (i.e., in absolute humidity) causes the gradual increase in the intensity of each absorption band, and of the $\rho\sigma\tau$ band in turn.

[11] For initiation, the in situ procedure requires at least 1 week of independent measurements of precipitable water content, such as those derived from radiosondes, microwave radiometers, or GPS receivers, taken over a large range of solar zenith angle, simultaneously with radiometric measurements. If these measurements are not available, the present procedure may be started using monthly estimates of precipitable water content derived from surface observations of relative humidity, pressure, and temperature, the so-called “surface humidity method.”

2.1. The In Situ Procedure

[12] The in situ procedure uses the following five steps: (1) calculation of *a* and *b* for two case types: when independent measurements of precipitable water content are available and when the surface humidity method is used; (2) analysis of possible discrepancies between the values of *a* and *b* retrieved when the surface humidity method is used; (3) calibration of the Sun-sky radiometer (i.e., calculation of constant V_0 at 940 nm); (4) calculation of the time patterns of precipitable water content from the Sun-sky radiometer measurements (W_P); and (5) comparison of W_P with the values obtained from radiosonde measurements performed at San Pietro Capofiume (W_{RDS}), and with estimates from the Terra satellite Moderate Resolution Imaging Spectroradiometer (MODIS; W_{TERRA}) and the Aqua satellite MODIS (W_{AQUA}) radiance observations.

Table 1. Available Data Set of Radiosonde Measurements at the San Pietro Capofiume Site

Year	Months	RDS Time (UT)	Days
2007	May–Dec	1200	46
2008	Jan–Jul	1200	70
2009	Jul	0600, 1200, 1800	6

[13] Step 2 is needed to validate the in situ procedure started with the surface humidity method, but is not necessary in an operative phase. Equation (1) can be also written as

$$y = \ln V_0 - a \cdot x, \tag{2a}$$

$$\text{with} \begin{cases} y = \ln V + m \cdot (\tau_a + \tau_R) \\ x = (m_w \cdot W)^b \end{cases}. \tag{2b}$$

Aerosol optical thickness τ_a was calculated at wavelength $\lambda = 940$ nm, according to the well-known Ångström formula,

$$\tau_a(\lambda) = \beta \cdot \lambda^{-\alpha}, \tag{3}$$

where wavelength λ is measured in μm, α is the so-called Ångström exponent, and β is the atmospheric turbidity parameter giving the best-fit value of aerosol optical thickness at wavelength $\lambda = 1$ μm. Parameters α and β were determined for each spectral series of τ_a, obtained through the inversion of PREDE Sun-sky radiometer measurements taken at the other visible and near IR wavelengths equal to 400, 500, 675, 870, and 1020 nm, by drawing the regression line in terms of equation (3).

[14] In equation (2), the Rayleigh-scattering optical thickness τ_R was calculated at the 940 nm wavelength using the value of this quantity determined by *Tomasi et al.* [2005] for the mid-latitude summer atmosphere standard model of *Anderson et al.* [1986]. The value, calculated for a surface pressure of 1013 hPa, was normalized to the daily values of surface-level pressure measured at the SPC meteorological station.

[15] Calibration constant V_0 tends to vary over long time-periods because of filter and/or detector deteriorations. However, it is reasonable to assume that no appreciable variations in V_0 normally occur within a time window of 1 month or so, as found by *Campanelli et al.* [2007]. On this assumption, the following time average over y during a 1 month interval can be performed as

$$\langle y \rangle = \ln V_0 - a \cdot \langle x \rangle, \tag{4}$$

where $\ln V_0 = \langle \ln V_0 \rangle$, and the operation $\langle\ \rangle$ stands for the period average over the time window. Thus, calculating the difference between (2a) and (4), the number of unknown variables can be reduced in the problem, which assumes the following analytical form,

$$y' = -a \cdot x', \tag{5a}$$

$$\text{with} \begin{cases} y' = y - \langle y \rangle \\ x' = x - \langle x \rangle \end{cases}. \tag{5b}$$

[16] The present in situ procedure consists of definition of the most appropriate pair of values (a, b), which maximizes the (x', y') correlation. In particular, the maximization of the (x', y') correlation is used to determine the best exponent b. After this, the optimal x' can be computed and coefficient a can be found from (5a) After the determination of pair (a, b), the value of V_0 can be calculated from (2a). *Halthore et al.* [1997] and *Schmid et al.* [2001] used a modified Langley plot method (type 1 modified Langley) to determine V_0 as the intercept of the straight line obtained by fitting y versus the power term m_w^b. In the present paper a different method is proposed (a type 2 modified Langley) where V_0 is retrieved by plotting y versus the product $a \cdot x$. Whereas the type 1 modified Langley has strong limitations [*Halthore et al.*, 1997; *Schmid et al.*, 2001] because it requires that the columnar water vapor amount is low and stable, the type 2 modified Langley largely improves its application to cases where the time patterns of precipitable water content are not stable. Improvements arise mainly from the fact that the former method neglects the dependence of y on W (it assumes that y only depends on air mass m_w and that all points have the same W) causing a scatter of the points that depends on the real, but neglected, variability of W and introducing calibration errors and large day-to-day changes in the retrieved calibration constants. The type-2 modified Langley, conversely, gives evidence to the dependence of y on ($m_w \cdot W$) and the variability of y is explained by the real variability of the product ($m_w \cdot W$). This point provides a better retrieval of the intercept ($\ln V_0$) when the time pattern of precipitable water content is not stable.

[17] Once parameters V_0, a and b have been determined, the values of precipitable water content W_P, can be calculated by

$$W_P = \frac{1}{m_w} \cdot \left[\frac{1}{a} \cdot (\ln V_0 - y)\right]^{\frac{1}{b}}. \tag{6}$$

Parameter V_0 can be monitored month-by-month in order to diagnose the Sun-sky radiometer performances and responsivity conditions, since the value of V_0 can vary considerably due to instrumental drift effects [*Campanelli et al.*, 2004].

2.2. Criteria for the Application of the In Situ Procedure to Field Data

[18] To start the application of the proposed in situ procedure requires W measurements taken over a large range of solar zenith angle, i.e., a wide range of (m_w W) performed simultaneously with radiometric measurements. In fact, a wide range of (m_w W)can be obtained in all cases where a data set of W measurements taken over a large range of solar zenith angle is examined, thus obtaining a wide range of m_w.

[19] In the present case, the available data set of independent measurements of (m_w W)taken at SPC is shown in Table 1. During 2007 and 2008, measurements of W were determined from the regular radiosonde measurements performed by Agenzia Regionale Protezione Ambientale (ARPA) Emilia-Romagna, whereas the values of W in 2009 were collected during the Budget of the Atmosphere-Soil Exchange: A Long-term Fluxes Analysis (BASE-ALFA) campaign (http://base-alfa.wikispaces.com/) performed by ARPA Servizio IdroMeteoClima of Bologna.

[20] Unfortunately, the criterion of using a "wide range" of $m_w\ W$ was respected only in July 2009, when three launches a day were performed. Precipitable water content measured in this period is hereinafter labeled with symbol W_{RDS3}. On the contrary, the time series of W_{RDS} determined in 2007 and 2008 were found to be unsatisfactory for use, because the radiosondes were launched only at 1200 UT each day and such data were unsuitable for use in the procedure. In fact, these values of W were found to show appreciable variations throughout the year, but they did not provide large monthly intervals of $m_w \cdot W$ due to the strong limitations in the range of m_w, associated with the high solar elevation angles observed at the central diurnal hours during the whole year. Therefore, they cannot be used in the present analysis.

[21] Over the past decades, the scientific community has made a concerted effort to overcome the intermittence of the information provided by radiosonde data and their sparse coverage, developing alternative methodologies for determining precipitable water content. A great number of models have been developed for estimating precipitable water content from surface level observations of moisture parameters (water vapor partial pressure, dew point temperature, absolute humidity, and mixing ratio). Although relationships between precipitable water content and the above surface humidity parameters have been defined corresponding to favorable conditions of atmospheric vertical mixing [*Reitan*, 1963; *Smith*, 1966], decoupling of the atmospheric layers under inversion conditions can significantly alter such relationships [*Liu et al.*, 1992; *Schwarz*, 1968; *Glahn*, 1973; *Tomasi*, 1977]. Thus, success in predicting precipitable water content from surface moisture data is expected to depend on the characteristics of the vertical profiles of thermodynamic parameters and, in particular, of absolute humidity. This is because the most favorable conditions for the use of the average relationships between W and surface measurements of moisture parameters appear to be those associated with marked convectivity features, when the vertical profile of absolute humidity describes an exponentially decreasing curve with a prescribed height scale.

[22] Convective conditions are often observed in the atmosphere above the Po valley during the summer months. *Tomasi and Paccagnella* [1988] found that the vertical profile of absolute humidity for summer conditions generally decreases as a function of height, in a nearly exponential fashion through the lower part of the troposphere, up to 3–4 km altitude. In such cases, the ratio between W and surface-level absolute humidity approximates more closely the mixing layer height than in the other seasonal periods, determining summer values of the water vapor scale height mainly ranging between 1 and 3 km, with a median seasonal value of 1.7 km. Moreover, considering the thermodynamic characteristics of the atmosphere, it is evident that the summer months are in general characterized by higher values of W and more extended intervals of air mass m_w. These conditions are generally associated with larger intervals of $m_w W$ than in other months of the year.

[23] As results of the above considerations, it was decided to estimate precipitable water content from surface level observations of moisture parameters (surface humidity method), using the data sets of summer 2007 and summer 2008, and to examine in a further work the data sets relating to the other seasons.

[24] The linear formula of *Hay* [1970] was used to recover the required independent data set of W. It establishes the following relationship between precipitable water content W and water vapor partial pressure e_0 (in hPa) at the surface:

$$W_C = c_1 \cdot e_0 + c_2, \tag{7}$$

where quantity e_0 is calculated as the product of surface relative humidity f_0 by the saturation water vapor pressure ($E(T_0)$; in hPa), calculated as a function of surface temperature T_0 (in K) using the formula of *Bolton* [1980].

[25] Coefficients c_1 and c_2 have been estimated in the literature, using different daily or monthly data sets from varying numbers of measurements and sites [*Hay*, 1970; *Tuller*, 1977; *Choudhury*, 1996]. It was first attempted in the present analysis to estimate specifically both coefficients c_1 and c_2 at the SPC site, using the values of W determined from the RDS measurements and hourly or monthly mean values of e_0 calculated for the ground level measurements of T_0 and f_0 measured at the SPC meteorological station. Unfortunately, the above data sets collected to perform the linear fits in terms of equation (7) were found to be very poor and unlikely to provide reliable results. Therefore, it was decided to use the values of coefficients c_1 and c_2 retrieved by *Choudhury* [1996], examining a data set consisting of monthly mean values of W and e_0 taken at 45 stations distributed over the entire planet, to obtain the average global values $c_1 = 1.70$ and $c_2 = -0.1$.

[26] This choice was based on the following points: (1) All the stations considered by *Choudhury* [1996] were far from water surfaces, with negligible influences due to evaporation and transport of humid air from marine regions, and the SPC site is located in the middle of the Po valley, about 50 km from the Adriatic Sea coast; (2) the altitudes of the stations were all lower than 1 km above sea level (asl), to minimize possible altitude effects on the relationship between W and the surface moisture conditions, and SPC altitude is 11 m asl; and (3) the values of W used by *Choudhury* [1996] were all obtained from RDS measurements performed at 1200 UT at each site, meaning that the linear relation in equation (7) was validated for largely different radiometric observation local times and, hence, over a wide range of solar zenith angles, while all W_{RDS} values measured at SPC refer to 1300 LT.

[27] On the basis of the above choice, the hourly values of precipitable water content W_C were determined in terms of the *Hay* [1970] linear relationship in equation (7), for the average values of coefficients c_1 and c_2 established by *Choudhury* [1996].

3. Analysis of Field Data and Results

[28] Simultaneous measurements of Sun photometric output voltages V and W_{RDS3} or W_C were selected for the application of equations (2a) and (2b). All measurements of signal V taken within 15 min before and after the estimation time of W_{RDS3}, or W_C, and all estimates of τ_A and τ_R within the same intervals were selected and averaged over 30 min intervals. The overall data set was then subdivided into monthly data sets. Separately for each month, the present

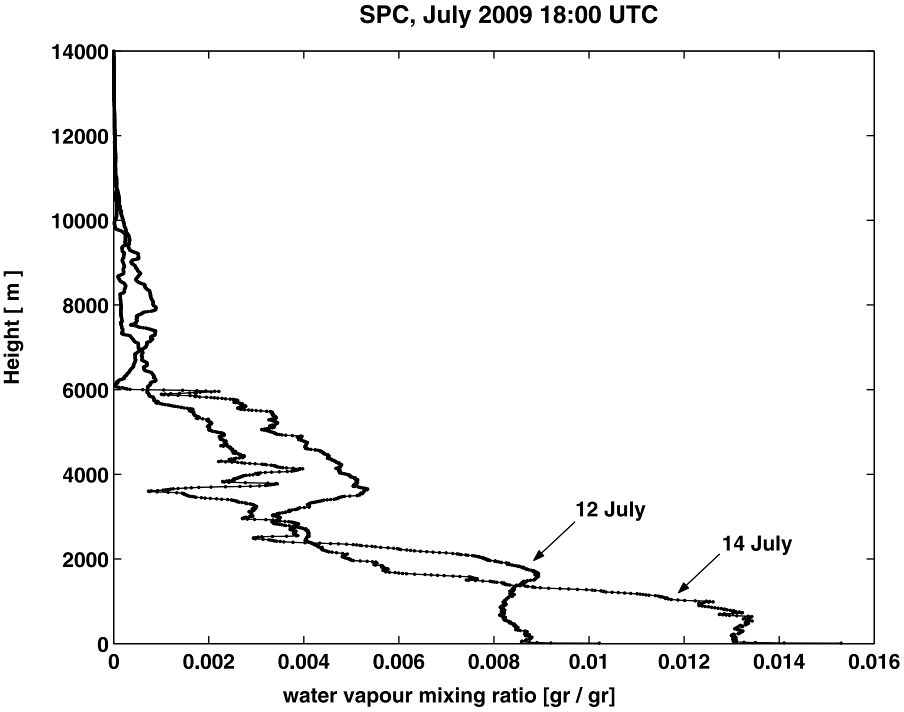

Figure 2. Vertical profile of water vapor mixing ratio for the two rejected days in the 2009 data set.

method was applied in the range of solar elevation angle yielding $m_w < 8$.

3.1. Retrieval of the Best (*a*, *b*) Pair Using W_{RDS3} Measurements

[29] The in situ procedure was initially applied using the precipitable water content measured three times every day by RDS measurements (W_{RDS3}) performed in July 2009. The (x', y') data set was calculated using equations (2b) and (5b). A preliminary check on the quality of the (x', y') scatterplot was performed, based mainly on a statistical method, but also on a heuristic discarding of outliers. The statistical method consists of assuming an average indicative value of $b = 0.6$, taken from *Halthore et al.* [1997], and performing the linear fit of the (x', y') scatter diagram. All the values of y' found to be distant by more than twofold the standard deviation σ from the best-fit line, were discarded, quantity σ being calculated over the entire data set. It is very interesting to note that the preliminary quality check rejected two points, one by the statistical method and one by the heuristic method. They both correspond to situations in which the decrease of water vapor with height does not follow a nearly exponentially decreasing trend (Figure 2), but exhibits some multi-layered features, easily recognizable in the RDS data. Thus, it was concluded that equation (1) was not suitable for realistically representing such situations.

[30] Using the selected data set, the most appropriate pairs of *a* and *b* were determined by: i. Assuming a series of prescribed values of *b*, taken in steps of 0.01 from 0.4 to 1.0; ii. computing x' for each of the *b* values; iii. retrieving the corresponding best-fit values of *a* from equation (5a) for each of the (x', y') lines; iv. computing the (x', y') correlation coefficient R^2 calculated for each (*a*, *b*) pair; and v. finally choosing the best pair (*a*, *b*) as the pair corresponding to the highest R^2 value.

[31] The best pair (*a*, *b*) retrieved in July 2009 is $a = 0.1886 \pm 0.0024$; $b = 0.57 \pm 0.005$ (Table 2) with Δa as the absolute error made in the best-fit and Δb the half-step of the *b* series used as described in point i above. Table 2 also shows the correlation coefficient, R^2, the numbers of data after (N_{good}) and before (N_{tot}) the preliminary quality check of the (x', y') data set. Figure 3 shows the scatterplot of y' ($y - \langle y \rangle$) versus x' ($x - \langle x \rangle$), corresponding to the best pair (*a*, *b*).

3.2. Retrieval of the Best (*a*, *b*) Pair Using W_c Estimations (Surface Humidity Method)

[32] Before applying the in situ procedure using the surface humidity method, the reliability of the numerical approximation of *Choudhury* [1996] was checked by performing a comparison between simultaneous values of precipitable water content W_{RDS} from the radiosonde measurements and values of W_C determined by equation (7). The comparison was made in the (V, W_C) common ensemble for the summer periods of 2007 and 2008. The evaluation was problematic because of the very low number of data including simultaneous values of W_{RDS}, W_C, and V, given the scarcity of regular daily RDS measurements at SPC. However, the monthly values of ratio N_{good}/N_{tot} computed using (i) the number N_{good} of W_{RDS} measurements that agree within 10% with the estimates of W_C, and (ii) the total number N_{tot} of W_{RDS} values obtained from the available radiosonde measurements, were found to vary between 0.14 and 0.77 during the two summer periods (Table 3). The table does not give the value of ratio N_{good}/N_{tot} relative to

Table 2. Monthly Best-Fit Values of the Retrieval Parameters Obtained Through the Present In Situ Procedure for Determination of the Monthly Pairs of Parameters a and b[a]

Year	Month	a	Δa	b (Δb = 0.005)	R^2	N_{good}	N_{tot}	$V_0 \times 10^{-4}$	$\frac{\Delta V_0}{V_0}$ (%)	Average
2007	Jun	0.1653	0.0033	0.57	0.9384	157	167	**2.2558**	3.3	2.1552 ± 0.0710
	Jul	0.1498	0.0020	0.58	0.9521	276	292	**2.1217**	1.9	2.1552 ± 0.0710
	Aug	*0.0914*	*0.0015*	*0.68*	*0.9491*	*182*	*192*	**2.1480**	2.8	2.1552 ± 0.0710
2008	Jun	0.1794	0.0036	0.56	0.9621	92	96	**2.4210**	3.8	2.2946 ± 0.1613
	Jul	*0.1288*	*0.0020*	*0.61*	*0.9666*	*141*	*148*	**2.1129**	2.7	2.2946 ± 0.1613
	Aug	*0.2347*	*0.0039*	*0.53*	*0.9560*	*156*	*166*	**2.3499**	3.3	2.2946 ± 0.1613
2009	July	0.1886	0.0024	0.57	0.9981	12	14	2.4289	3.6	–

[a]Here Δa is the absolute error found in the best-fit procedure; R^2 is the correlation coefficient; N_{good} and N_{tot} are the numbers of points after and before, respectively, the preliminary quality check on the (x', y') data set; V_0 is the calibration constant, relative to each of the 7 summer months; and $\frac{\Delta V_0}{V_0}$ is the percent error where ΔV_0 is the error found by the best-fit procedure. The average column shows the seasonal average of V_0 and its standard deviation. Bold text is for average values a = 0.1648 and b = 0.57. Italic text indicates the rejected months in the calculation of the best average (a, b) pair using the "surface humidity method."

August 2008, as no RDS measurements were available for that month.

[33] The results in Table 3 indicate substantially good agreement between W_{RDS} and W_C in June 2007, June 2008, and July 2007, albeit based on a limited number of measurements and precipitable water content estimates performed at noon of each day. Conversely, no accordance was found between the noon data measured in the other months (August 2007 and July 2008) with values of ratio $N_{\mathrm{good}}/N_{\mathrm{tot}}$ worse than 0.25 or not available (August 2008). The findings indicate that the numerical values of coefficients c_1 and c_2 of *Choudhury* [1996] in these months are likely to fail in providing reliable estimates of precipitable water content also during the early morning and late afternoon hours of the day, when the vertical distribution of water vapor mass concentration is likely to assume quite different profiles from the exponential one. In the morning, this is due to the more stable conditions characterizing the low atmosphere after the nocturnal cooling period, while in the afternoon to the gradual decrease of the convective vertical transport of humid air from the surface up to the entrainment region of the mixed layer. Thus, it can be reasonably assumed that no reliable estimates of pairs (a, b) are achieved with the proposed method from the monthly data sets of August 2007, July 2008, and presumably, August 2008. The best pairs of (a, b) for the monthly data sets of summers 2007 and 2008, are shown in Table 2. As expected, the monthly values of a and b were found to be quite in accordance in June 2007, July 2007, and June 2008, with mutual differences smaller than 0.015 for a and 0.01 for b. On the contrary, the three remaining summer months (indicated by footnote h in Table 2) present larger variability features.

[34] Considering the above remarks, the average values a = 0.1648 ± 0.0148 and b = 0.57 ± 0.01, obtained by averaging the (a, b) pairs over June 2007, July 2007, and June 2008, were assumed to be the most suitable pair from the surface humidity method. Uncertainty in a and b is given by their standard deviation, differently from the case when W_{RDS3} data are used for starting the procedure. The (a, b) pairs retrieved in August 2007, July 2007, and August 2008 were rejected. Figure 3 shows the scatterplot of y' versus x' corresponding to each monthly best (a, b) pair. The rejected months are shown in Figure 3.

[35] Very encouraging results appear in the comparison between (a, b) pairs retrieved using real measurements of W_{RDS3} and the surface humidity method. Both cases agree in retrieving b = 0.57. With regard to the best-fit values of a, the difference is about 0.03, although, as explained in the next section, the value of a does not affect the subsequent retrieval of V_0.

3.3. Determination of V_0

[36] Once the best pair of parameters (a, b) was determined, the type 2 modified Langley approach was applied to retrieve V_0. In order to demonstrate how much the type 2 modified Langley improves the capability of retrieving V_0 when the time patterns of W are not stable, the calibration constant was calculated using both type 1 and type 2 modified Langley approaches separately for each day of June 2007. Only days with a wide range of $m_w \cdot W$ were used. The results showed that when type 1 is used, the daily values of V_0 exhibit a larger dispersion (~9%) than that obtained using type 2 (~5%). Dispersion was calculated as the ratio between standard deviation and average value over the entire month. Moreover, the mean monthly value of V_0 retrieved using type 1 (1.9742×10^{-4}) is 13% lower than that retrieved using type 2 (2.2635×10^{-4}). The increased dispersion and the discrepancy between the average values of V_0 confirm that the large day-to-day changes in the retrieved calibration constants is strongly reduced using type 2 modified Langley.

[37] Type 2 modified Langley was applied using the following (a, b) pairs: a = 0.1886 ± 0.0024, b = 0.570 ± 0.005 for the entire summer period of 2009; and a = 0.1648 ± 0.0148, b = 0.57 ± 0.01 for the summer periods of 2007 and 2008.

[38] In this regard, it is important to point out that even if the variability of a causes a shift in the values of x, the shift is not relevant to the application of the type 2 modified Langley plot used to obtain V_0, since it is retrieved by extrapolating the variable $a{\cdot}x$ to the null value. Thus, the value of a does not affect the retrieval of V_0. Conversely, calibration constant V_0 is very sensitive to variations in b. In the present work, it was evaluated that a variation of 0.01 in b leads to a variation in the retrieved value of V_0 corresponding to a percentage within 3%. In other words, an uncertainty of 0.01 in retrieving parameter b is the maximum error allowed in order to obtain V_0 with an accuracy better than 3%. Also worthy of note is the need to determine the maximum value of R^2 with precision to the fifth digit,

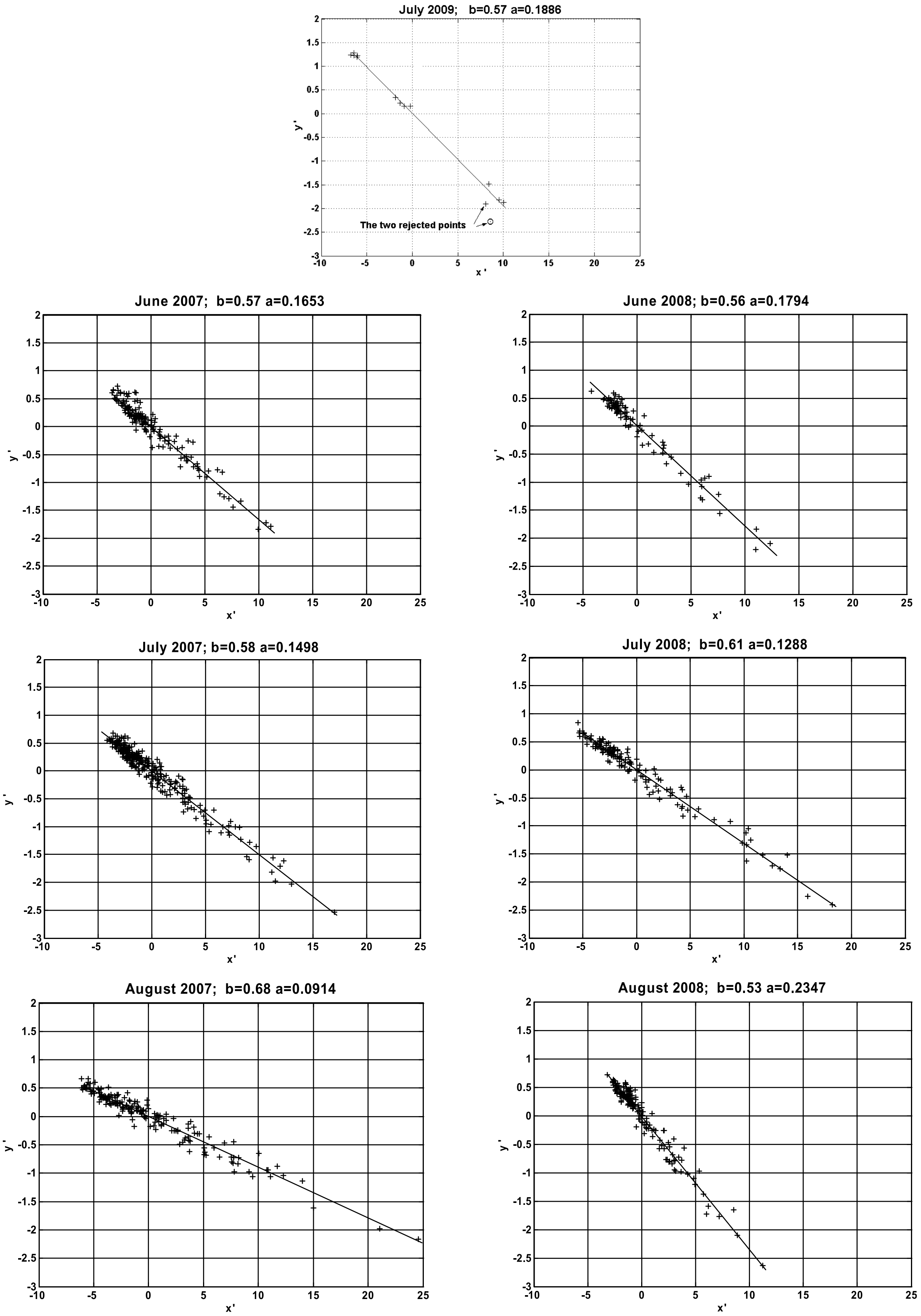

Figure 3. Scatterplots of y' $(y - \langle y \rangle)$ versus x' $(x - \langle x \rangle)$ as in equation (5a) for each month.

Table 3. Monthly Values of the $N_{\mathrm{good}}/N_{\mathrm{tot}}$ Ratio Between the Number N_{good} Values of W_{RDS} Measurements Differing by Less than 10% From the Estimates of W_{C} and the Total Number N_{tot} Values of W_{RDS} Obtained From Radiosonde Measurements for the 6 Summer Months of 2007 and 2008

Year	Month	$N_{\mathrm{good}}/N_{\mathrm{tot}}$
2007	Jun	0.77
	Jul	0.50
	Aug	0.25
2008	Jun	0.60
	Jul	0.14
	Aug	na[a]

[a]Here na means not available.

given that a variation of 10^{-5} in R^2 corresponds to a variation of 0.01 in b. On the basis of this evaluation, the value of 0.01 must be assumed as the maximum uncertainty acceptable on b.

[39] The retrieved monthly values of V_0 using type 2 modified Langley are shown in Table 2 together with the percentage uncertainty in their evaluation, intended to represent the statistical error associated to the retrieval of the intercept (ΔV_0 / V_0).

[40] V_0 time patterns are presented in Figure 4. It is evident that there is an oscillation in the values of V_0 during the three summer months of 2007, and that this oscillation was even greater in 2008. This behavior was expected because the retrieval of V_0 depends on the dispersion features of the scatterplot of y versus x, and on the slope of its best-fit line. Therefore, the retrieval of V_0 is affected by the uncertainty (not quantifiable) in estimating W_C. The values of V_0 calculated in 2007 turn out to be more stable than in 2008, because there was a better agreement between W_C and W_{RDS} in the first year (see Table 3), probably due to the occurrence of a greater number of atmospheric conditions with vertical water vapor distributions more closely resembling the ideal exponentially decreasing profile. The evaluation of the monthly values of V_0 is also affected by the capability of retrieving stable monthly values of (a, b). As showed before, in 2007 similar pairs (a, b) were estimated for 2 months (June and July) out of 3, whereas in 2008 2 months out of 3 were rejected (July and August). In this sense, it can be stated that the monthly oscillation of V_0 is due to the uncertainty (not quantifiable) affecting the estimations of W_C, which leads to a decrease in the (a, b) estimation precision.

Table 4. Percentage Uncertainty on the Precipitable Water Content Values Retrieved for Each Summer by PREDE Sun-Sky Radiometer, Radiosonde, and MODIS/Terra-Aqua

Year	PREDE (%)	RDS[a] (%)	MODIS/Terra-Aqua[b] (%)
2007	20	10	5–10
2008	25	10	5–10
2009	10	10	5–10

[a]According to *Miloshevich* [2006].

[b]According to *Gao and Kaufmann* [2003].

[41] Accordingly, the following values of V_0 were assumed for the calculation of W_P: the 2007 summer average value equal to $(2.1552 \pm 0.0710) \times 10^{-4}$, the 2008 summer average value equal to $(2.2946 \pm 0.1613) \times 10^{-4}$, and the 2009 July value to $(2.4289 \pm 0.0870) \times 10^{-4}$.

3.4. Retrieval and Validation of Time Patterns of Precipitable Water Content W_{P}

[42] Using equation (6), the time patterns of W_P were determined for each of the seven summer months. The uncertainty of W_P (ΔW_P /W_P) was estimated by means of propagation error formulas, considering that the quantities affected by errors in equation (6) are V_0, τ_A, a, and b. In particular, the following uncertainties were used in the propagation error formula: For 2007 Δa = 0.0148, Δb = 0.01, $\Delta\tau_a$ = 0.0014, $\Delta V_0 = 0.071 \times 10^{-4}$; for 2008 Δa = 0.0148, Δb = 0.01, $\Delta\tau_a$ = 0.0014, $\Delta V_0 = 0.1613 \times 10^{-4}$; and for 2009 Δa = 0.0024, Δb = 0.005, $\Delta\tau_a$ = 0.005, $\Delta V_0 = 0.0087 \times 10^{-4}$.

[43] The results are shown in Table 4 for each season. The uncertainty for the PREDE-based retrievals of precipitable water content in 2009 is comparable with that of the radiosonde measurements and the Aqua and Terra satellite estimations, but it strongly increases in 2007 and 2008 because of the problems arising from the use of the surface humidity method. This point will be more fully discussed in the next section.

[44] The comparison among the time patterns of W_P, W_{RDS}, W_{TERRA}, and W_{AQUA} was made in terms of their trends and median percentage differences. The time patterns

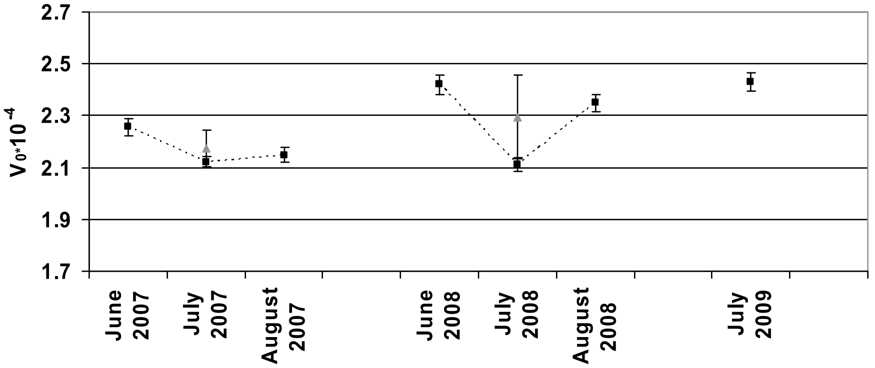

Figure 4. Sequence of monthly values of calibration constant V_0 retrieved from the data sets for June–August of 2007 and 2008 and for July 2009 (squares), as given in Table 2. Triangles give the mean summer values and standard deviations are indicated by vertical bars.

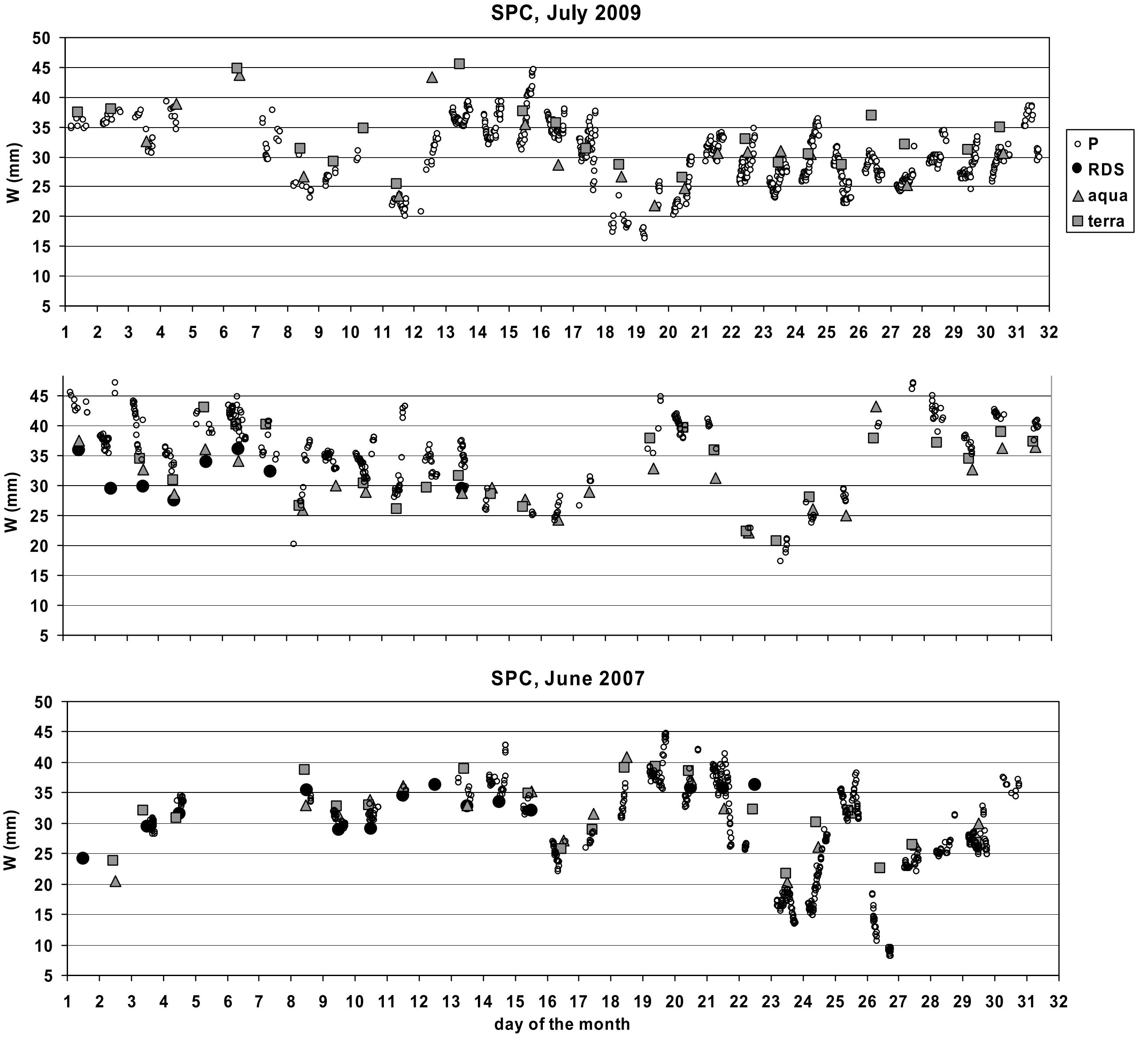

Figure 5. Time patterns of precipitable water content retrieved from the PREDE Sun-sky radiometer (P), San Pietro Capofiume radiosonde (RDS), and Aqua and Terra satellite Moderate Resolution Imaging Spectroradiometer (MODIS).

of W_P were found to agree very closely with the evaluations of W_{RDS}, W_{TERRA}, and W_{AQUA} for all the years, as shown in Figure 5 for the 3 months presenting a greater number of available common measurements.

[45] The correlation coefficients R^2 (see Table 5) between simultaneous measurements of W_P and W_{RDS} were calculated for the entire summer seasons 2007 and 2008. In cases where simultaneous measurements were not available, those within 1 hour around the W_{RDS} measurement time were used to interpolate W_P at the W_{RDS} time. Monthly values of R^2 in 2007 and 2008 could not be calculated because of the low number of measurements collected in the common (W_P, W_{RDS}) ensemble. Parameter R^2 was found to assume high values (about 0.79) in all summer seasons, and the median percentage difference between W_P and W_{RDS} was 8% in 2007, which is within the percentage uncertainty presented in Table 4. In 2008, the difference increased up to 23%, certainly due to the error made in determining V_0 for the year in question.

[46] The correlation between W_P, W_{AQUA} and W_{TERRA} performed also in summer 2009 was found to yield higher monthly and seasonal values, greater than 0.8 for the majority of cases. This is also because the common data set covers a larger time interval than those of the (W_P, W_{RDS}) ensemble ((W_P, W_{AQUA}) ranges between 1145 and 1315 UT, and (W_P, W_{TERRA}) between 1000 and 1115 UT), so that the correlation between the time patterns are better.

[47] Concerning the median percentage difference, summer 2008 also shows a greater disagreement (by 13%) with respect to W_{AQUA} than the other years, whereas the difference with respect to W_{TERRA} seems to be indifferent to this effect. A better average agreement was found between W_P and W_{AQUA}, all the data sets being within the percentage uncertainty defined in Table 4. These results are comparable

Table 5. Comparison of Simultaneous Measurements[a]

Year	Month	R^2 (N_{points})			Percent Difference (Median Value)		
		W_{RDS}-W_{P}	W_{AQUA}-W_{P}	W_{TERRA}-W_{P}	W_{RDS}-W_{P}	W_{AQUA}-W_{P}	W_{TERRA}-W_{P}
2007	Jun	–[c]	0.81 (10)	0.9 (13)			
	Jul	–	0.85 (21)	0.89 (20)			
	Aug	–	0.84 (15)	0.72 (13)			
	Summer	0.78 (8)	0.84 (46)	0.86 (46)	8	7	9
2008	Jun	–	0.95 (7)	0.77 (12)			
	Jul	–	0.94 (16)	0.89 (14)			
	Aug	–	0.85(17)	0.79 (15)			
	Summer	0.79 (6)	0.88 (40)	0.84 (41)	23	13	9
2009	Jun	–	0.93 (9)	0.88 (10)			
	Jul	–	0.77 (13)	0.83 (17)			
	Aug	–	0.82 (6)	0.91 (7)			
	Summer	–	0.85 (28)	0.89 (34)	–	7	10

[a] R^2 is the correlation coefficient, N_{points} is the number of available points, and the dashes indicate that too few points were available for R^2 calculation.

with the AERONET findings, where errors made in deriving the precipitable water content values varies from 5 to 15% when compared to in situ measurements with radiosondes and ground-based microwave radiometers for variable water vapor amounts between 1 and 5 cm, at locations varying from high-latitude boreal forest to tropical rain forest and from urban area to desert [*Halthore et al.*, 1997; *Holben and Eck*, 1990].

[48] Figure 6 shows the scatterplots between W_P and W_{AQUA} or W_{TERRA} for the entire summer data set. The regression line assumes values close to 1; in particular, it is 0.961 for the comparison with W_{TERRA} and 0.947 for the case of W_{AQUA}. Overestimation of precipitable water content retrieved from Terra (intercept value −0.13 mm) and underestimation of W retrieved from the Aqua satellite (2.55 mm) are consistent with retrieval errors.

4. Discussion

[49] It was claimed in section 1 that the improvement and innovation of the proposed technique arise from the capability of avoiding errors due to transmittance simulation. However, simulation errors are only reduced and not deleted. In fact, when the surface method is used the procedure relies heavily on a linear parameterization of precipitable water content based on the surface relative humidity (see equation (7)). A parameterization is a simple model, and, hence, is a simulation of the real physical process. Although in this case the procedure does not rely wholly on a simulated, a priori, water vapor column (as happens in methods using atmospheric transmittance simulation), it does incorporate independent observations of surface relative humidity. However, the diagnosed water vapor column used to start the procedure is a hybrid of observation and modeling and, hence, an element of simulation error still creeps into the procedure. This is also partially true for the 2009 retrievals, where, although the precipitable water contents used to start the procedure are derived wholly from radiosonde observations, the Rayleigh-scattering optical thickness is derived from a model.

[50] The proposed in situ procedure for retrieving precipitable water content from radiometric measurements taken at 940 nm was found to provide very good results when it was applied to summer monthly data sets. The time patterns of the estimates of W_P agree very well with the measurements of W_{RDS}, W_{AQUA}, and W_{TERRA}, while the obtained median percentage differences were also within the estimation errors.

[51] However, Sun-sky radiometers rely on clear-sky conditions and both direct and diffuse irradiance observations cannot be made through clouds. Recently, a cloud screening procedure was set up only for direct solar irradi-

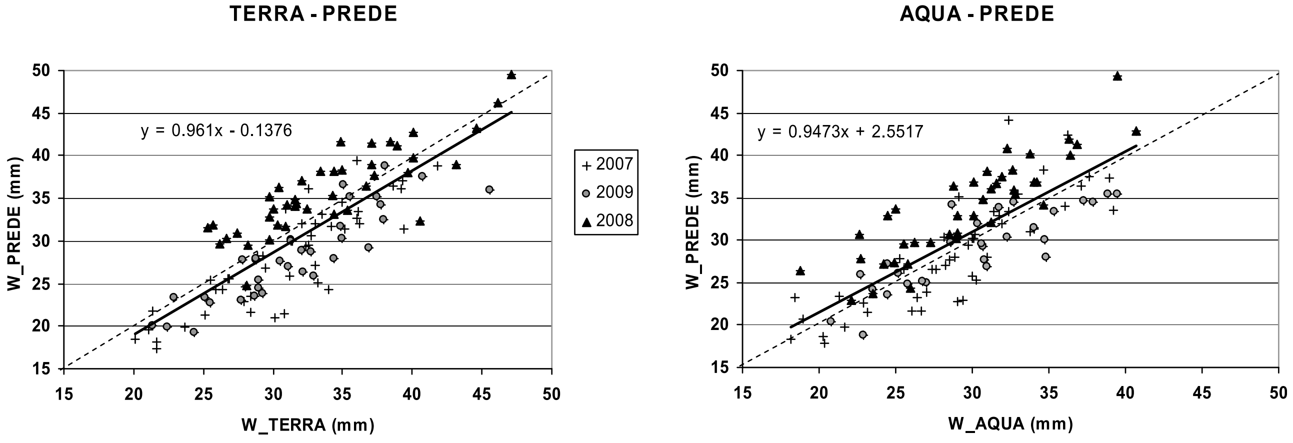

Figure 6. Scatterplots between precipitable water content retrieved from the PREDE Sun-sky radiometer (*W*_PREDE) and the Aqua or Terra MODIS (*W*_AQUA, *W*_TERRA) for the entire summer data set.

ance measurements taken by PREDE equipment [*Khatri and Takamura*, 2009], but before this paper, cloud screening was usually performed on the basis of the degree of agreement between the sky diffuse irradiance measured in the optical visible region and the almucantar geometry, and that reconstructed by the ESR.pack inversion code.

[52] In particular, the present study selected only measurements whose RMS deviation between measured and reconstructed diffuse sky irradiance was lower than 8%. This criterion assured the rejection of cloud-contaminated direct and diffuse irradiance measurements, but it could not exclude the contamination of high and thin cirrus clouds. For this reason, the possibility of ice crystals being mistaken for precipitable water content cannot be eliminated. A further development of the proposed methodology will be its implementation with the new cloud screening procedure [*Khatri and Takamura*, 2009], and the comparison with the one used in this study.

[53] The presented method requires a wide range of $m_w W$ data derived from independent measurements (e.g., radiosonde or microwave radiometer measurements) performed over a number of days (at least 1 week), in order to retrieve confidently the best (a, b) pair suitable for instrument calibration. The most important outcome of the present work is that, when independent measurements are not available, estimates of W made in terms of equation (7) (the “surface humidity method”) can be used, and the in situ methodology can be applied to achieve satisfactory results, as demonstrated here for the 2007 and 2008 summer seasons.

[54] Undoubtedly, the calculation of precipitable water content W_C is questionable, since it is calculated using a linear parameterization of precipitable water content based on surface relative humidity. The surface humidity method works well when vertical humidity profile is exponential, and this assumption is generally verified at SPC during summer. The goodness of the surface humidity method has also been discussed by comparing W_C and W_{RDS} simultaneously estimated at noon (Table 3). An error in W_C estimation can affect the validity of equation (5), but actually this is not an important point, as the equation is merely used to derive the (a, b) coefficients in equation (6). The precipitable water content amount (W_P) can be derived accurately by Sun photometric observations through equation (6), unless a and b coefficients are too far from reality. In the present work, using the simple propagation error formula of equation (6), it was estimated that an error of 9% in a (as occurs here, when the surface humidity method is applied) leads to an error of 15% in W_P, while an error of 3% in estimating V_0 (that needs a determination of b with an uncertainty of 0.01, as happens here when applying the surface humidity method) leads to an additional uncertainty of 4% in W_P. Therefore, although the present W_C estimation at SPC fails to evaluate the real precipitable water content, the method is still able to retrieve the best (a, b) pair with an uncertainty such that W_P has an error of about 20%. At the present state of the art, this error is certainly greater than the error calculated when radiosonde measurements are used to start the in situ procedure. It is also greater than the uncertainty officially given by satellite retrievals. However, the surface humidity method can be of great benefit to users who do not have radiosonde measurements, and as such, it requires further validation at several sites and for different seasons.

[55] A problem connected with the use of surface humidity method, is that the uncertainty in estimating W_C can be also reflected in the calculation of V_0, which may be subject to large oscillations. To overcome the problem, it is necessary to apply the present method using a data set of $m_w W$ estimated for each summer month, and not only for a period of at least 1 week as above when radiosonde measurements were only examined. In this way, a seasonally average value of V_0 can be calculated and the problem related to the time oscillations of V_0 can be reduced.

[56] The present study also highlighted (see Figure 2) that the vertical profile of absolute humidity can often differ greatly from the exponential curve. In such cases, systematic deviations of the scale height from the average value implicitly assumed in equation (7) may arise, causing a dispersion of data with respect to the average atmospheric model configuration of equation (7). Thus, the preliminary check on the quality of the (x', y') scatterplot, employed in this paper, needs to be improved with the aim of automatically rejecting the data presenting anomalous vertical profiles.

5. Conclusion

[57] Direct solar irradiance measurements were taken using a PREDE POM-02L Sun-sky radiometer at the San Pietro Capofiume station (SPC) (44°23′N, 11°22′E, 11 m asl) in the Po valley (Northern Italy) during the period from May 2007 to August 2009.

[58] A new in situ technique for the retrieval of precipitable water content from measurements taken at the 940 nm wavelength in the three summer seasons of 2007, 2008, and 2009 was set up, developed, and tested in this paper. The in situ procedure, to be started, needs at least 1 week of independent measurements of precipitable water content (such those by radiosondes, microwave radiometers or GPS receivers) taken over a large range of solar zenith angle simultaneously with radiometric measurements, but it was also tested for the case when such independent measurements are not available. The new methodology is aimed to determine precipitable water content by Sun-sky radiometers with some improvements with respect to the traditional techniques: (1) the capability of retrieving the best values of constants (a, b), characterizing the atmospheric water vapor transmittance, reducing simulation errors and potentially containing information on seasonal changes in vertical profiles of temperature, air pressure, and moisture occurring at each measurement site; (2) the development of a surface humidity method that can allow the estimation of precipitable water content, starting the procedure with only measurements of surface temperature and relative humidity, which are much more common than those performed with radiosondes or microwave radiometers; and (3) the development of a type 2 modified Langley method to determine the calibration constant V_0. All these points allow the use of Sun-sky radiometers for estimating precipitable water content, even when these instruments are not part of a federated network (mainly for economic reasons).

[59] The in situ procedure described in this work is a preliminary development of the retrieval procedure provid-

ing the precipitable water content from measurements performed with PREDE Sun-sky radiometers, employed as standard instruments in the SKYNET network, where the inversion of the output voltage at the 940 nm wavelength is not yet officially used. The procedure will be included in the ESR.pack, a complete package of free open source programs and control scripts developed within the frame of the European SkyRad users network, to provide Sun photometer users with independent calibration and processing of radiometric raw data.

[60] Validation of the precipitable water content, W_P, retrieved from summer dataset of 2007, 2008, and 2009 was done through comparison with measurements of precipitable water content determined from radiosonde measurements and from MODIS-Terra and MODIS-Aqua observations.

[61] Both time patterns and absolute values of W_P showed a good agreement with the retrievals from MODIS radiance measurements and radiosonde records (high correlation coefficients in the 0.8–0.9 range and low percentage median differences varying between 7% and 13%). A larger median difference (23%) was found when the solar calibration constant V_0 could be accurately retrieved (Table 5, June–August 2008).

[62] The new in situ procedure provided good results in the summer season by using as starting dataset both a record of W radiosonde measurements (provided that they are taken over a wide optical air mass range) and estimates of W derived from surface observations. In the latter case it was generally found that greater uncertainties affect the evaluations of (a, b) pair and calibration constant V_0. To study such aspects, the present in situ procedure needs to be applied to a series of monthly data sets recorded in all seasons and over at least one year, in an attempt to verify whether the V_0 oscillations observed in the present study are occasional or systematic. The analysis of a yearly data set will also allow the estimation of the variation in the (a, b) pair arising from seasonal changes in the vertical profiles of temperature, air pressure and moisture. For this reason, a paper is under preparation making use of two different data sets: A one year set of simultaneous measurements taken by a microwave radiometer and a PREDE-SKYNET Sun-sky radiometer located at Chiba University, Japan; and a one year set of simultaneous measurements taken by GPS receivers and a PREDE-ESR Sun-sky radiometer located at Valencia, Spain.

[63] **Acknowledgments.** This research was supported by the "Fondo Integrativo Speciale per la Ricerca" strategic program, "Sustainable Development and Climate Changes," sponsored by the Italian Ministry of University and Scientific Research (MIUR), and developed as a cooperative project between CNR and MIUR Study of the Direct and Indirect Effects of Aerosols and Clouds on Climate (AEROCLOUDS). Data analysis was performed as part of a cooperative activity with the SKYNET network. The data giving the vertical profiles of water vapor mixing ratio were collected during the BASE-ALFA campaign. ARPA-Servizio IdroMeteoClima, Bologna, Italy, is acknowledged for collecting and providing data. The authors thank Christian Lanconelli, Mauro Mazzola, and Vito Vitale for the management of the PREDE POM-02 Sun-sky radiometer measurement campaigns at the San Pietro Capofiume site.

References

Alexandrov, M. D., B. Schmid, D. D. Turner, B. Cairns, V. Oinas, A. A. Lacis, S. I. Gutman, E. R. Westwater, A. Smirnov, and J. Eilers (2009), Columnar water vapor retrievals from multifilter rotating shadowband radiometer data, *J. Geophys. Res.*, *114*, D02306, doi:10.1029/2008JD010543.

Anderson, G. P., S. A. Clough, F. X. Kneizys, J. H. Chetwynd, and E. P. Shettle (1986), AFGL atmospheric constituent profiles (0–120 km), *Environ. Res. Pap. 954*, 43 pp., Opt. Phys. Div., Air Force Geophys. Lab., Hanscom Air Force Base, Mass.

Bolton, D. (1980), The computation of equivalent potential temperature, *Mon. Weather Rev.*, *108*, 1046–1053.

Cachorro, V. E., C. Toledano, M. Sorribas, A. Berjón, A. M. de Frutos, and N. Laulainen (2008), An "in situ" calibration-correction procedure (KCICLO) based on AOD diurnal cycle: Comparative results between AERONET and reprocessed (KCICLO method) AOD-alpha data series at El Arenosillo, Spain, *J. Geophys. Res.*, *113*, D02207, doi:10.1029/2007JD009001.

Campanelli, M., T. Nakajima, and B. Olivieri (2004), Determination of the solar calibration constant for a Sun-sky radiometer: Proposal of an in situ procedure, *Appl. Opt.*, *43*, 651–659, doi:10.1364/AO.43.000651.

Campanelli, M., V. Estellés, C. Tomasi, T. Nakajima, V. Malvestuto, and J. A. Martínez-Lozano (2007), Application of the SKYRAD improved Langley plot method for the in situ calibration of CIMEL sun-sky photometers, *Appl. Opt.*, *46*, 2688–2702, doi:10.1364/AO.46.002688.

Choudhury, B. J. (1996), Comparison of two models relating precipitable water to surface humidity using globally distributed radiosonde data over land surfaces, *Int. J. Climatol.*, *16*, 663–675, doi:10.1002/(SICI)1097-0088(199606)16:6<663::AID-JOC29>3.0.CO;2-O.

Estellés, V., M. Campanelli, T. J. Smyth, and M. P. Utrillas (2009), Development of an open source package for the processing of sky-Sun photometric data in the European Skyrad users network (ESR), *Geophys. Res. Abstr.*, *11*, abstract EGU2009-10952.

Gao, B.-C., and Y. J. Kaufman (2003), Water vapor retrievals using Moderate Resolution Imaging Spectroradiometer (MODIS) near-infrared channels, *J. Geophys. Res.*, *108*(D13), 4389, doi:10.1029/2002JD003023.

Glahn, H. R. (1973), Comments on "On the correlation of the total precipitable water in a vertical column and absolute humidity at the surface," *J. Appl. Meteorol.*, *12*, 1411–1414.

Goody, R. M. (1964), *Atmospheric Radiation I: Theoretical Basis*, chap. 4, pp. 122–170, Clarendon, Oxford U. K.

Halthore, R. N., T. F. Eck, B. N. Holben, and B. L. Markham (1997), Sun photometric measurements of atmospheric water vapor column abundance in the 940 nm band, *J. Geophys. Res.*, *102*(D4), 4343–4352, doi:10.1029/96JD03247.

Hay, J. E. (1970), Precipitable water over Canada: Part I. Computation, *Atmosphere*, *8*, 128–143.

Holben, B. N., and T. F. Eck (1990), Precipitable water in the Sahel measured using Sun photometry, *Agric. For. Meteorol.*, *52*, 95–107.

Holben, B. N., et al. (1998), AERONET—A federated instrument network and data archive for aerosol characterization, *Remote Sens. Environ.*, *66*, 1–16.

Kasten, F. (1966), A new table and approximation formula for the relative optical air mass, *Arch. Meterol. Geophys. Bioklimatol. Ser. B*, *14*(2), 206–233.

Kasten, F., and A. T. Young (1989), Revised optical air mass tables and approximation formula, *Appl. Opt.*, *28*, 4735–4738.

Khatri, P., and T. Takamura (2009), An algorithm to screen cloud-affected data for sky radiometer data analysis, *J. Meterol. Soc. Jpn.*, *87*, 189–204, doi:10.2151/jmsj.87.189.

Liu, W. T., W. Tang, and F. J. Wentz (1992), Precipitable water and surface humidity over global oceans from special sensor microwave imager and European center for medium range weather forecasts, *J. Geophys. Res.*, *97*(C2), 2251–2264, doi:10.1029/91JC02615.

Miloshevich, L. M., H. Vomel, D. N. Whiteman, B. M. Lesht, F. J. Schmidlin, and F. Russo (2006), Absolute accuracy of water vapor measurements from six operational radiosonde types launched during AWEX-G and implications for AIRS validation, *J. Geophys. Res.*, *111*, D09S10, doi:10.1029/2005JD006083.

Reitan, C. H. (1963), Surface dew point and water vapor aloft, *J. Appl. Meteorol.*, *2*, 776–779.

Schmid, B., et al. (2001), Comparison of columnar water vapor measurements from solar transmittance methods, *Appl. Opt.*, *40*, 1886–1896.

Schwarz, F. K. (1968), Comments on "Note on the relationship between total precipitable water and surface dew point," *J. Appl. Meteorol.*, *7*, 509–510.

Smirnov, A., B. N. Holben, A. Lyapustin, I. Slutsker, and T. F. Eck (2004), AERONET processing algorithms refinement, paper presented at AERONET Workshop, AERONET, PHOTON, El Arenosillo, Spain, 10–14 May.

Smith, W. L. (1966), Note on the relationship between total precipitable water and surface dew point, *J. Appl. Meteorol.*, *5*, 726–727.

Takamura, T., and T. Nakajima (2004), Overview of SKYNET and its activities, *Opt. Pura Apl.*, *37*, 3303–3308.

Tomasi, C. (1977), Precipitable water vapor in atmospheres characterized by temperature inversions, *J. Appl. Meteorol.*, *16*, 237–243, doi:10.1007/BF00874671.

Tomasi, C., and T. Paccagnella (1988), Vertical distribution features of atmospheric water vapor in the Po valley area, *Pure Appl. Geophys.*, *127*, 93–116, doi:10.1007/BF00878693.

Tomasi, C., V. Vitale, B. Petkov, A. Lupi, and A. Cacciari (2005), Improved algorithm for calculations of Rayleigh scattering optical depth in standard atmospheres, *Appl. Opt.*, *44*, 3320–3341, doi:10.1364/AO.44.003320.

Tuller, S. E. (1977), The relationship between precipitable water content and surface humidity in New Zealand, *Arch. Meteorol. Geophys. Bioklimatol. Ser. A*, *26*, 197–212.

M. Campanelli and V. Malvestuto, Institute of Atmospheric Science and Climate, Consiglio Nazionale delle Ricerche, via Fosso del Cavaliere 100, I-00133, Rome, Italy. (m.campanelli@isac.cnr.it)

V. Estellés, Departamento Fisica de la Tierra y Termodinamica, Facultat de Fisica, Universitat de València, Dr. Moliner 50, E-46100, Burjassot, Valencia, Spain.

A. Lupi and C. Tomasi, Institute of Atmospheric Science and Climate, Consiglio Nazionale delle Ricerche, via Gobetti 101, I-40129, Bologna, Italy.

T. Nakajima, Center for Climate System Research, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8568, Japan.