IL NUOVO CIMENTO Vol. 27 C, N. 4 Luglio-Agosto 2004
DOI 10.1393/ncc/i2004-10036-8

Ground-based NO_2 measurements at the Italian Brewer stations: A pilot study with Global Ozone Monitoring Experiment (GOME)

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(ricevuto il 29 Novembre 2004; approvato il 3 Gennaio 2005)

Summary. — Ground-based NO_2 total column measurements have been collected since 1992 using Brewer spectrophotometry at Rome, an urban site, and Ispra (semi-rural). These are the only ground-based stations regularly monitoring NO_2 in Italy. The methodology of measurement together with the procedure to control its quality is described. From the analysis of the time series it was found that the mean value of the NO_2 column is 1.63 DU at Rome and 1.60 DU at Ispra. A first attempt to compare NO_2 vertical column densities (VCD) from GOME with those derived from ground-based Brewer measurements, under different atmospheric conditions and measurement time lags is here presented. The results of this pilot study showed unsatisfactory agreement because different atmospheres are probed by GOME and Brewer instruments. The GOME space resolution resulted insufficient to fully characterize the Rome and Ispra highly localized polluted areas.

PACS 92.60.Vb – Solar radiation.
PACS 93.30.Ge – Europe.
PACS 95.75.Rs – Remote observing techniques.
PACS 42.68.Ge – Effects of clouds and water; ice crystal phenomena.

1. – Introduction

The important role of atmospheric nitrogen dioxide (NO_2) in the catalytic destruction of stratospheric ozone was pointed out by Crutzen in early seventies [1]. Several further publications described the role of nitrogen components in the stratospheric chemistry, taken also into account the interaction with ClO_x and HO_x, chlorine radicals and odd hydrogen, respectively [2,3]. The concentration of nitrogen oxides in troposphere is highly variable [4] and controls the concentration of hydroxyl radical and of the tropospheric ozone [5]. Nitrogen dioxide is mainly produced by natural sources (lightning, soil emission and biomass burning) and anthropogenic emissions (*e.g.*, fossil-fuel combustion) [6].

Column densities of NO_2 are monitored by several gauging systems operating from satellite: HALOE on board of UARS since 1991, GOME on board of ERS-2 since 1995, and SCIAMACHY on board the ENVISAT satellite since 2002. The launch of EOS AURA satellite with OMI and HIRDLS instruments successfully took place in 2004, these two instruments will provide high-quality information on atmospheric chemical composition.

In general, satellite nadir-looking instruments provide estimates of total column amounts of atmospheric species; the tropospheric portion can be determined by estimating and subtracting the stratospheric fraction [7].

Ground-based NO_2 measurements are generally based on differential optical absorption spectroscopy technique, DOAS, [8] and the instruments are of the Systeme d'Analyse d'Observations Zenithale, SAOZ, type [9]. Long-term series of stratospheric column of NO_2 are available in the framework of the Network for the Detection of Stratosphere Change, NDSC [10, 11].

First validation of the GOME vertical column amounts of nitrogen dioxide with twilight SAOZ data was not straightforward [12]. A comparison of tropospheric NO_2 column densities [4] showed a good agreement between retrieved data from the GOME observations and *in situ* measurements under clear sky over Austrian regions with very clean tropospheric air.

Ground-based NO_2 total column measurements have been collected since 1992 using Brewer spectrophotometry at Rome, an urban site, and Ispra (semi-rural). These are the only ground-based stations regularly monitoring NO_2 in Italy.

The present study describes a first attempt to compare NO_2 vertical column densities (VCD) from GOME with those derived from ground-based Brewer measurements, under different atmospheric conditions and measurement time lags.

The GOME NO_2 level-2 products (version 2.8) used in our analysis are delivered by ESA in the framework of the CAT-1 project (ID 1152, see `http://eopi.esa.int/esa/esa`). Details on the GOME operation and algorithms can be found in Burrows *et al.* [13].

2. – The Brewer series of NO_2 measurements at the Italian stations

Since 1992 the two Italian stations of Rome (latitude 41.9° N, longitude 12.5° E, altitude 60 m) and Ispra (latitude 45.8° N, longitude 8.6° E, altitude 240 m) have been providing estimates of atmospheric ozone and nitrogen dioxide total columns by means of two Brewer MKIV spectrophotometers (SCI TEC, 1998). Both stations were included in several WMO/GO_3OS (World Meteorological Organization/ Global Ozone Observing System) ozone monitoring campaigns. Total ozone data are delivered to the World Ozone and Ultraviolet Radiation Data Centre (WOUDC), and to the Laboratory of Atmospheric Physics of the Aristotle University of Thessaloniki.

Brewer no.067 is located on the roof of the Fermi Building of the Physics Department at University of Rome "La Sapienza"; Brewer no.066 is located on a terrace at 20 m above the ground at the Joint Research Centre. More details on the two sites are described in Casale *et al.* [14].

The Brewer MKIV instrument is a single monochromator spectrophotometer designed to measure ground-level intensities of the attenuated solar radiation at five specific wavelengths in the Huggins absorption spectra of ozone and sulphur dioxide [15, 16] and in the NO_2 absorption bands between 430 and 460 nm [17]. Aerosols characteristics can be also investigated using this type of instrument [18].

TABLE I. – *The five operational wavelengths in the NO_2 mode and the related absorption coefficients.*

Wavelength (nm)	NO_2 absorption coefficient ($\times 10^{-19}$ cm^2)
431.42	6.127
437.34	4.749
442.82	4.226
448.10	6.610
453.22	4.612

The two Brewer spectrophotometers operating in Italy are mainly used for the ozone and UV irradiance measurements [14], but they can also perform measurements aimed at the estimate of NO_2 VDC (depending on the season and the working programme). Diffuse radiation during sunset and sunrise sky can be used to determine the stratospheric and tropospheric NO_2 components [19].

The total columns of the atmospheric quantities from direct sun (DS) measurements are estimated by applying the Lambert-Beer to a set of five wavelengths. The DS measurements are carried out at different times of the day and collected in the form of raw photon counts. The five operational wavelengths used to determine the column amount of NO_2 with the related absorption coefficients [17] are reported in table I.

In the official Brewer MKIV algorithm [20] the dark count signal (*i.e.* the instrumental noise) is subtracted from the photon counts (*i.e.* the atmospheric signal) measured at the five operational wavelengths; afterwards, corrections for the dead time and for the temperature dependence of the nickel sulfate filter effects are applied.

After signal correction, the measured radiance I, for each of the five wavelengths, can be approximately expressed in the following form:

$$\log I \approx \log I_0 - \alpha X \mu - \beta m \,. \tag{1}$$

In eq. (1) I_0 is the intensity of light at the top of the atmosphere, α is the absorption coefficient (cm^2/molecules), X is the column amount of nitrogen dioxide in molecules/cm^2, μ is the NO_2 air mass, β is the Rayleigh scattering coefficient and m is the ratio of the slant path through the atmosphere to the vertical path.

By linearly combining the five equations, using coefficients that eliminate ozone absorption and Rayleigh scattering, eq. (1) takes the following expression:

$$F - F_0 = \Delta\alpha X \mu \,, \tag{2}$$

where F, F_0, and $\Delta\alpha$ are a linear combination, respectively, of $\log I$, of $\log I_0$ (Extraterrestrial Constant, ETC) and of the NO_2 absorption cross-sections, with combination coefficients 0.1, −0.59, 0.11, 1.2, −0.82. X is given now in Dobson units. The accuracy of the Brewer NO_2 column amount measurements is close to 1% for nominal instrument performances. Further details on the algorithm used to estimate NO_2 amounts are described in Kerr [17].

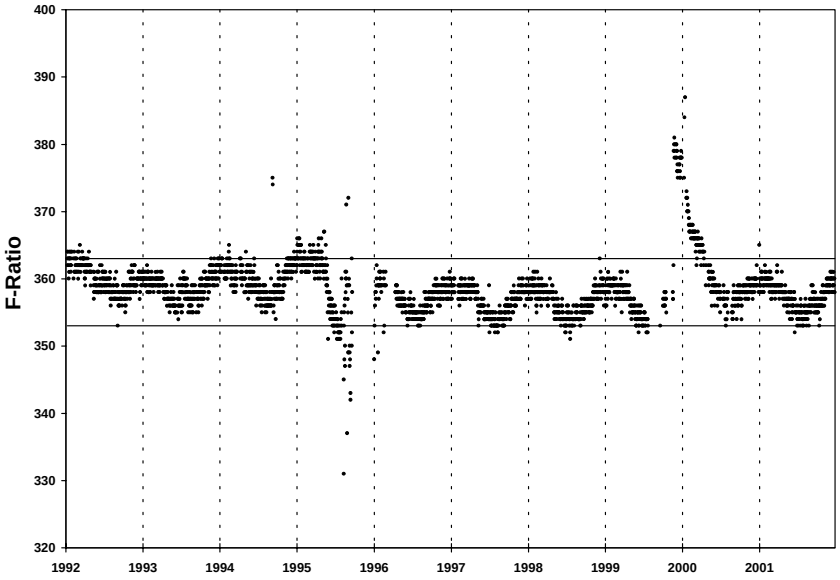

Fig. 1. – Rome: Time series of the F-ratio. The horizontal solid lines indicate the lower and upper limits (353–363) corresponding to the acceptance interval.

Tests are carried out on regular basis to monitor the performance of the instrument. The wavelength stability is assured by a "mercury lamp" test, while the stability of spectrophotometer is checked through the analysis of an internal control parameter, the "F-ratio", from a standard lamp test. The latter is performed using an internal quartz-halogen standard lamp emitting a continuous spectrum. Raw photon counts are recorded at the five operating wavelengths and dark-counts channels; afterwards the F-ratio is calculated as a linear combination of decimal logarithms of lamp light intensity at the five operating wavelengths. The stability of the instrument is assured when the F-ratio is within $\pm$ 1.5% of the reference value [21]. Figures 1 and 2 show the time evolution of the control parameter (F-ratio) for the Brewers located in Rome and Ispra, respectively. The seasonal variation in the F-ratio can be attributed to the temperature dependence of nickel sulfate filter. The estimated impact of this affect is below 3% on Brewer accuracy.

On the basis of the F-ratio test, data outside the acceptance interval were rejected for this study (reference value is 358 for Brewer no.067 and 321 for Brewer no.066). Moreover, a further quality control procedure was applied to the NO_2 values, data showing uncertainties higher than 0.2 Dobson units (10% of the mean value under clear-sky conditions) were rejected.

The final homogeneous data set of daily direct-sun (DS) NO_2 measurements covers the periods 1992-2001 for Rome's Brewer, and 1992-1999 for Ispra Brewer data. Although the F-ratio test for the Ispra Brewer instrument was not performed during 1998 and 1999, daily DS measurements were also included in the data set because the daily mean values are within $\pm$1 standard deviation of the mean value of the whole series.

The percentage of rejected data was 23% for Rome and 28% for Ispra.

The time sequences of daily total NO_2 DS values from 1992 to 2001 estimated at Rome, and from 1992 to 1999 for Ispra, are plotted in fig. 3 and fig. 4, respectively.

The mean value of the NO_2 column is 1.63 DU at Rome and 1.60 DU at Ispra.

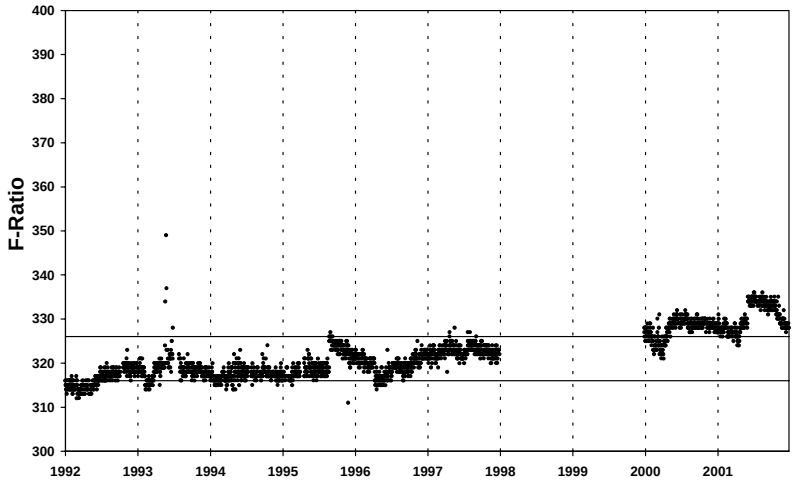

Fig. 2. – Ispra: Time series of the F-ratio. The horizontal solid lines indicate the lower and upper limits (315–320) corresponding to the acceptance interval.

3. – GOME products

The NO_2 vertical column density can be derived from Global Ozone Monitoring Experiment (GOME) measurements. This instrument has been flying on board of the European research satellite ERS-2 since April 1995 [22, 13]. The GOME instrument is a 4-channel double monochromator measuring light scattered by the atmosphere and re-

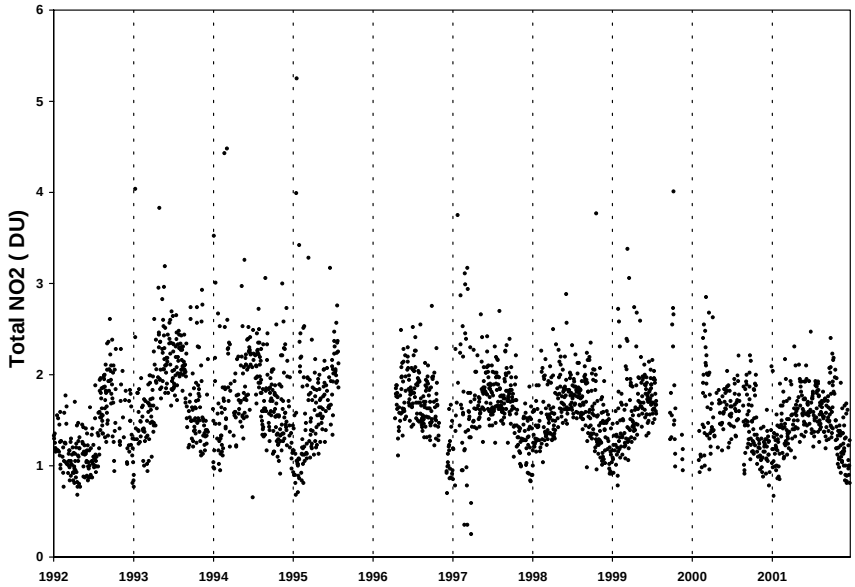

Fig. 3. – Total NO_2 data at Rome from January 1992 to December 2001.

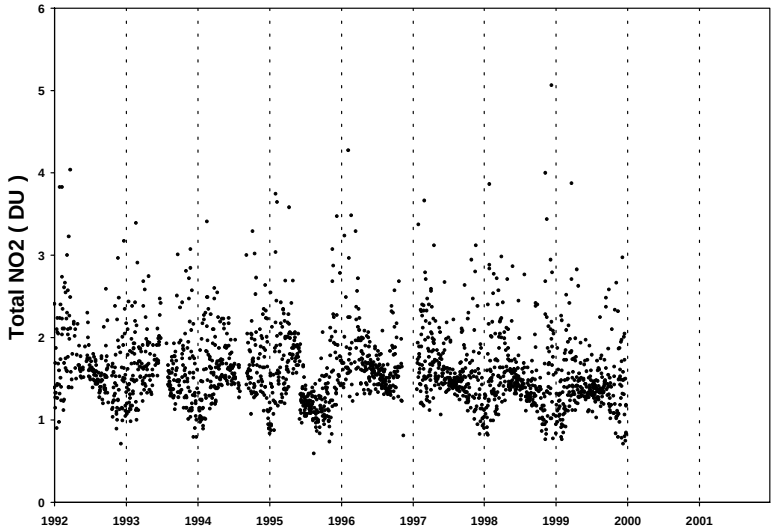

Fig. 4. – Total NO_2 data at Ispra, from January 1992 to December 1999.

flected by the Earth's surface in the wavelength range 280–790 nm. The GOME ground pixel size can vary between 40×40 km^2 to 960×40 km^2. Typical size (nominal forward scan mode) is 320×40 km^2.

Column density data of NO_2 from GOME are determined in the visible range (423–450 nm) through the application of a Differential Optical Absorption Spectroscopy (DOAS) algorithm [13]. This type of satellite product has been extensively validated during the GOME lifetime [23]. In this work data for the period April 1995- December 2001 were analysed.

The GOME data set relevant for our study was selected adopting a criterion based on the pixel area (S) and the distance between the centre of the pixel and the station ($D < 50$ km). Pixels covering an area of 80×40 km^2 and 320×40 km^2 were chosen, because of their relatively high space resolution. Being interested in very localized lower tropospheric atmospheric composition only cloud-free (cloud fraction, CF, < 0.3) cases were considered, in order to avoid cloud shading effects. This will also reduce the possible impact of uncertainties on the GOME measurements, which mainly result from cloud cover and air mass factors [24]. The overall satellite NO_2 uncertainty is estimated to be in the order of 1.5×10^{15} molec/cm^2 [4].

4. – Intercomparison methodology and results

The comparison was made at different levels in terms of the correlation coefficient (r) and mean percentage difference, MPD, ((Brewer-GOME)/Brewer) at Ispra and Rome stations.

The procedure consisted in four separate steps.

1) Only the Brewer daily means and the selected late morning GOME values were considered. The mean percentage difference is high in both stations (MPD = 85%; $r = 0.48$ and $r = 0.46$ at Rome and Ispra, respectively): the Brewer NO_2 daily

TABLE II. – *Summary of the results of the pilot study.*

Selection based on S, D and CF	Correlation coefficient	(Brewer-GOME)/Brewer
Rome NO_2 daily means	0.48	85%
Ispra NO_2 daily means	0.46	85%
Selection based on ETC		
Rome NO_2 daily means	0.60	85%
Ispra NO_2 daily means	0.50	85%
Rome NO_2 daily means corrected by the ETC	0.40	60%
Rome quasi-simultaneous corrected measurements	0.40	50%

means range between 1 DU and 2 DU, while the GOME NO_2 data are between 0.1 and 0.2.

2) As second step, the daily mean value of Extraterrestrial Constant (ETC), determined by the Brewer software, was assumed as a good indicator of clear-sky conditions (when it is comprised within 718 ± 79). The GOME-Brewer agreement with the new selection of Brewer data has not improved and the percentage difference is still high (MPD = 85%; $r = 0.60$ at Rome and 0.50 at Ispra).

3) The third step consisted in adopting the daily ETC value to determine the Rome Brewer NO_2 data instead of using the standard fixed value. The correction rendered some improvements without eliminating the large discrepancy between the two sets of data. The mean percentage difference is 60% with $r = 0.40$.

4) Finally, the comparison for data acquired quasi-simultaneously was carried out for the Rome station. Direct-sun Brewer measurements in the time interval 9.30–11.30 (UTC) were considered, while the GOME overpass time is around 10:00 UTC. The ETC correction was also applied to the Brewer morning data. The mean percentage difference is 50% and the correlation coefficient is 0.40.

A summary of the results of the pilot study is given in table II.

The detailed analysis of the GOME-Brewer intercomparison exercise revealed that the apparent inconsistency of the two NO_2 estimates is neither due to instrument malfunctioning, nor to algorithms deficiencies. The large discrepancies are most probably due to the different air masses probed by the two instruments. GOME measurements are related to a rather broad area, which, in the case of the intercomparison with the Brewer located in Rome, covers a region from the Adriatic Sea to the Tyrrhenian Sea. This implies that the contribution to GOME NO_2 from the very polluted but restricted urbanized area of Rome is highly diluted. Actually, the Tiber Valley area (41.6° N-42.2° N latitude) is roughly 1–2% of the total GOME pixel area.

The characterization of this effect was attempted by selecting SCIAMACHY NO_2 products [25, 26]. SCIAMACHY (Scanning Imaging Absorption Spectrometer for Atmospheric CHartographY) is a spectrometer designed to measure sunlight, transmitted,

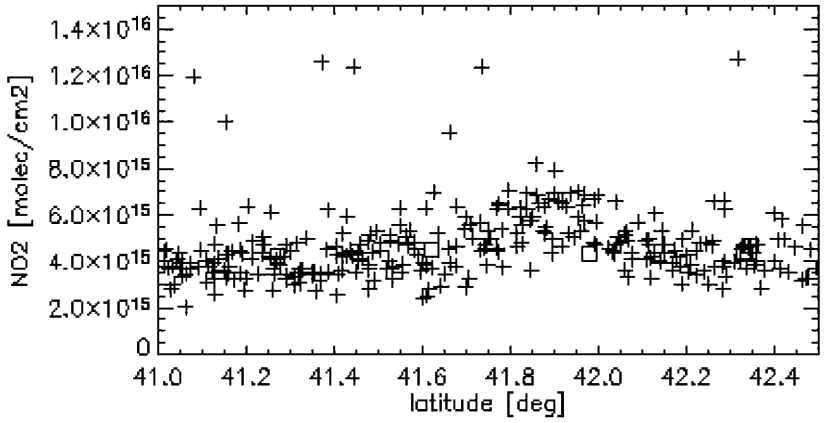

Fig. 5. – SCIAMACHY (crosses) and GOME (squares) NO_2 vertical column density (VCD) *vs.* latitude for the 20-27 November 2003 time period.

reflected and scattered by the Earth's atmosphere or surface in the ultraviolet, visible and near-infrared wavelength region. It flies on board the ESA ENVISAT-1 satellite, successfully launched in 2002. This instrument operates in nadir, limb and occultation modes, and its maximum nadir space resolution is 26×15 km^2, which could be sufficient for the purposes of this study.

Unfortunately, the availability of SCIAMACHY products to the community suffered from distribution problems, and only very few data are accessible from which it is not possible to carry out meaningful statistical analyses. Nevertheless, SCIAMACHY NO_2 products for three orbits over passing the area of Rome in the period 20-27 November 2003 were analysed. The NO_2 concentrations *vs.* latitude are shown in fig. 5: crosses indicate SCIAMACY NO_2, while squares are relative to GOME NO_2 products relative to the same days but of year 2002, since GOME data after June 2003 are no more available due to ERS-2 satellite downlink problems.

As can be easily seen, the relatively high resolution of SCIAMACHY allows a better determination of the NO_2 content for the Tiber Valley, providing concentration values that are, on average, 30% higher than those estimated by GOME. It should also be noted that for regions distant from Rome, SCIAMACHY and GOME NO_2columns coincide almost perfectly. Most important still, some NO_2 values from SCIAMACHY reach values larger than 1.0×10^{16}, *i.e.* in the range of those estimated from Brewer measurements. No cloud fraction discrimination was applied to the plotted data in order to keep the number of observations sufficiently high.

This result is an eloquent indication that probing highly localized polluted areas from the space is only possible if satellite instruments are characterized by a very high space resolution and that ground-based instruments are still the best to provide valuable data for this type of sites.

These considerations could apply to the Ispra site too.

5. – Conclusions

The preliminary investigation on operational Brewer and GOME NO_2 data showed unsatisfactory agreement. A marked difference is present, which did not disappear even

when nearly simultaneous data and cloud-free GOME and Brewer data were used, showing that a "scale" problem exists. The impact of possible errors in the estimate of some key Brewer parameters has been investigated. Of this, the Extraterrestrial Constant (ETC) reference value seems to play a major role in the quality of the retrieval.

The large discrepancies, once excluded eventual instrument and algorithm deficiencies, can be explained by the consideration that different atmospheres are probed by GOME and Brewer instruments. The GOME space resolution resulted insufficient to fully characterize the Rome and Ispra highly localized polluted areas.

This pilot study demonstrated that the use of SCIAMACHY products will certainly improve the Brewer-Satellite NO_2 intercomparison results, thanks to a better space resolution of this satellite instrument.

In any case, the use of ground-based instruments to characterize highly localized polluted areas is still the only acceptable choice.

List of used acronyms and abbreviations

ERS-2: European Remote Sensing-2 (satellite)
EOS AURA: Earth Observing System AURA
GOME: Global Ozone Monitoring Experiment
HALOE: Halogen Occultation Experiment
HIRDLS: High Resolution Dynamics Limb Sounder
OMI: Ozone Monitoring Instrument
SCIAMACHY: Scanning Imaging Absorption Spectrometer for Atmospheric CHartographY
UARS: Upper Atmospheric Research Satellite

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The authors thank J. Kerr (Meteorological Service of Canada), J.-C. Lambert (Belgian Institute for Space Aeronomy) for their helpful comments and the Joint Research Centre of Ispra for provision of the NO_2 data. GOME data are provided by ESA in the framework of the CAT-1 project (ID 1152, see `http://eopi.esa.int/esa/esa`).

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