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A complex study of Etna's volcanic plume from ground-based, *in situ* and space-borne observations

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Two periods of transboundary transport of volcanic aerosols and debris following recent eruptions of Mount Etna, Italy, were examined using ground-based and satellite spectrophotometric measurements together with Light Detection And Ranging (LiDAR) and aerosol filter observations in Athens and Thessaloniki, Greece. Independent columnar SO_2 measurements from ground and space identified peaks at Greek sites after the volcanic eruptions. LiDAR measurements of the aerosol extinction at Thessaloniki and Athens performed in July 2001 have shown the height of the volcanic plume to be about 3.5 km asl and the optical thickness of the dust layer to be of the order of 3×10^{-3} at 532 nm. Strong ozone depletion observed at the volcano plume level by using ozonesonde ascents may be attributed to the in-plume processes that generate reactive halogens, which in turn destroy ozone. The chemical and elemental composition of aerosol samples, taken at the Earth's surface, was analysed and confirmed the volcanic origin of the dust.

1. Introduction

Mount Etna, located in eastern Sicily (Italy), covers an area of approximately 1200 km^2 and is around 3350 m high. It is a large alkaline stratovolcano that has built upon tensional faults cutting the *ca*. 20-km-thick continental crust, which is made up of carbonate and clastic deposits of the Mesozoic-Pleistocene age (Barberi *et al.* 1974, Chester *et al.* 1985). Etnean volcanism began at 0.5 Ma, related to the break-up of the African plate margin during its collision with the European continental block (Barberi *et al.* 1974). This volcano is an important gas emitter, accounting for approximately 10% of worldwide volcanic emissions of CO_2 and SO_2 (Allard 1997, D'Alessandro *et al.* 1997).

A relatively silent phase of Mount Etna ended in November 1999 and since then, several major outbreaks of Europe's largest and most active volcano have been

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registered. The eruptions in July/August 2001 and the more powerful outbreak in October/November 2002 were observed by different satellite sensors, which provided detailed visual information of the spatial distribution of smoke and ash clouds. Such particle emissions can be measured from space as, for example, described by Holzer-Popp *et al.* (2002), who presented a new technique for aerosol optical thickness retrieval, called the synergic retrieval of aerosol properties. Aerosol observations over the territory of Greece are of special interest because many different aerosol types (desert, marine, volcanic, urban) can be measured in this region under various meteorological conditions and humidity regimes.

This work focuses on Etna's emissions for the two above-mentioned periods using Brewer, Light Detection And Ranging (LiDAR) and aerosol filter measurements in Athens and Thessaloniki, Greece, together with data from satellite overpasses and free balloon ascents. It is complemented by a chemical analysis of rainwater fall at Athens in November 2002.

2. Data analysis and results

A complex field observational experiment was designed to study the chemical composition and physical properties of volcanic aerosols after long-range transport. Two events were analysed: in the first case (July 2001) a volcanic plume was detected with a LiDAR system as it passed over Athens. Soundings were performed to retrieve the vertical profiles of physical characteristics of the aerosol at a wavelength of 532 nm. Back-trajectory analysis confirmed the volcanic origin of the aerosol layer. In the second case (October–November 2002) the volcanic emissions passed over Northern Greece. Based on experience gained from the first event, an observation campaign was organized in Greece, comprising spectroradiometric observations from ground and space as well as LiDAR soundings and chemical composition measurements of the volcanic debris in rainwater and in the volcanic ash fallen at ground level in Eastern Greece.

2.1 *Case 1: July 2001*

The NTUA aerosol LiDAR system (Papayannis and Chourdakis 2002) was operating at 532 nm in the Athens Greater Area in the period 2000–2003, aiming at continuous observation of volcanic dust aerosols originating from the eruption of Mount Etna in the framework of the field observational experiment EARLINET (European Aerosol Research LiDAR Network Project) (Bösenberg *et al.* 2003).

A distinct aerosol layer was detected over Athens during the period 23–26 July 2001. A typical example of LiDAR measurements is given in figure 1 for 26 July 2001. Here, the derivative of the corrected LiDAR signal at 532 nm with respect to height is shown, as described by Papayannis and Choudakis (2002). The aerosol layer is located at about 3.5–3.8 km asl, and is persistent throughout the whole measurement period (between 0800 and 1200 UT). Taking a LiDAR ratio of 50 sr inside the volcanic dust layer, we estimate a mean value of the corresponding optical thickness of the order of 2.9×10^{-3} at 532 nm. These measurements represent the first detection of volcanic dust aerosols by an aerosol LiDAR system over the Eastern Mediterranean area. This aerosol optical thickness of the dust layer seems low but there are two plausible reasons for this. First, Etna is about 750 km away from the Athens LiDAR station and dry and wet deposition of large particles occurred. As stated by Thomas *et al.* (2005): 'the stronger backscatter at 355 nm

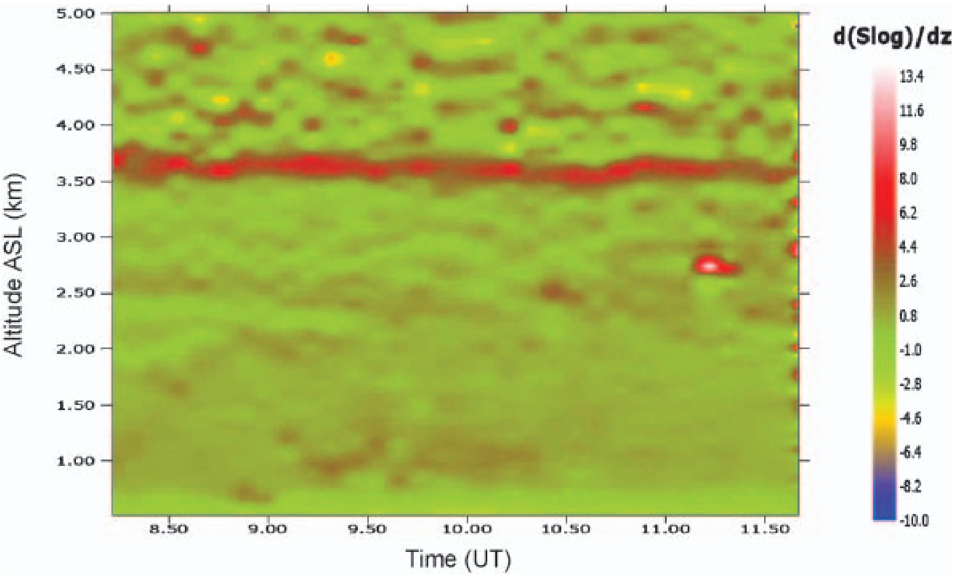

Figure 1. Temporal evolution of the Etna dust layer over Athens, Greece, as observed by the NTUA LiDAR at 532 nm on 26 July 2001, between 0800 and 1200 UT.

compared to 532 nm in the layer between 4500 m and 5500 m indicates an Angstrøm exponent larger than one which is typical for small particles'. Therefore, the aerosol extinction in this layer will be less effective and the optical thickness will remain small. Second, because of the long distance between Etna and Athens, the aerosol plume will no longer be a small plume but will be distributed over a much larger area. The atmospheric dispersion will cause the optical thickness to be much smaller at large distances from the volcano.

To verify the origin of this enhanced dust layer, we performed a back-trajectory analysis using the model HYSPLIT of NOAA (Draxler and Hess 1997, 1998) for air masses ending over Athens on 26 July 2001 at 1100 UT (figure 2). This analysis shows that the air masses between 3.5 and 4 km passed the Etna volcano 24 hours earlier at an altitude of around 4.5–5.5 km. All data gathered show consistently that there was no transport of volcanic emissions to stratospheric levels.

On 26 July 2001 ozone vertical profile measurements were also carried out by means of free balloon ascents at Athens at 1200 UT (figure 3). Details concerning the operation principle and the specific characteristics of the ozone sensor can be found in Varotsos *et al.* (1994). Figure 3 shows a remarkable reduction in ozone partial pressure at the height level between 650 and 700 hPa that almost coincides with the altitude of the aerosol plume (*ca.* 4 km) depicted in figure 2. The latter is of potential important for the evidence of halogen (X)-catalysed ozone destruction and suggests that the Etna either directly emits XO or emits X species that are rapidly converted to reactive X in volcanic plumes. In-plume processes that generate reactive halogens may contribute significantly to ozone destruction in volcanic plumes.

In this context, recent investigations during eruptions of the Soufriere Hills volcano, Montserrat, reported mixing ratios of bromine monoxide (BrO) reaching 1 ppb in the plume 4–7 km downwind of the summit (Gerlach 2004). In addition, Gerlach (2004) noted that: (1) shallow magma degassing generates emissions with ppb to ppm levels of reactive radicals Br, Cl, H and HO but no significant BrO or

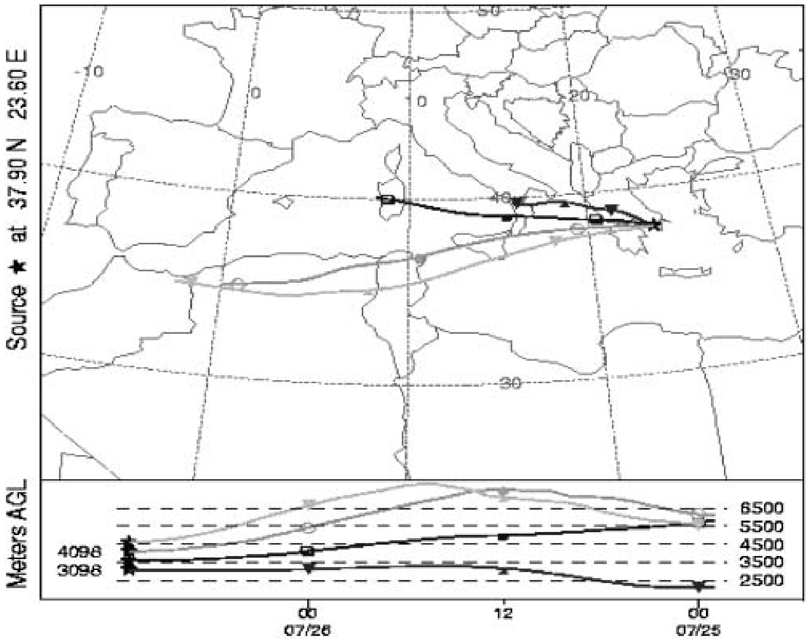

Figure 2. Backward trajectories ending at 1100 UT on 26 July 2001 at Athens.

chlorine monoxide (ClO). (2) The conversion of volcanic Br and Cl by reaction with ozone in gas-phase catalytic reaction cycles in the plume can lead to secondary BrO and ClO at mixing ratios of a ppt and higher, possibly approaching a ppb for especially halogen-rich volcanic gases, several kilometres downwind of degassing sources. In general, however, ppb BrO and ClO levels in volcanic plumes at a certain distance to the volcano require near-vent, high-temperature reaction of magmatic gases with air and/or in-plume heterogeneous chemical processes involving aerosols during plume transport. (3) These processes oxidize bromine and chlorine in HBr and HCl, giving rise to increased levels of reactive Br, Cl and HO, in addition to NOx. In addition, Keys *et al.* (1998), studying the plume of the active Antarctic volcano, Mount Erebus (77.5° S, 167.2° E, height 3794 m), reported that there is no evidence of rapid tropospheric scavenging of HCl, as might be expected for more explosive events and a less dry atmosphere.

Enhanced levels of HOx and NOx in volcanic emissions may trigger non-halogen catalytic cycles, depleting ozone in tropospheric volcanic plumes. To this end, estimations of BrO emission performed by Bobrowski *et al.* (2003) revealed that local ozone depletion and small ozone ‘holes’ may occur in the vicinity of active volcanoes.

2.2 *Case 2: November 2002*

2.2.1 Spectroradiometric observations from ground and space as well as LiDAR measurements. Columnar SO_2 measurements are performed routinely at Thessaloniki, Greece, with a single Brewer spectrophotometer (Zerefos *et al.* 2000). The Brewer instrument was initially designed to measure the atmospheric content of ozone while the retrieval of SO_2 is a side-effect of these measurements. As ozone and SO_2 absorption bands overlap in the UV region where retrievals are

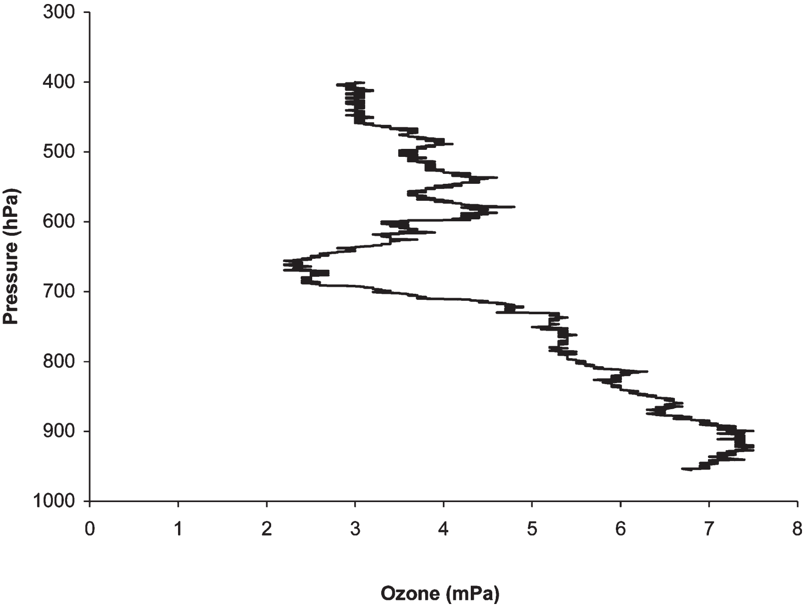

Figure 3. Ozone vertical distribution derived from ozonesonde ascent performed at Athens on 26 July 2001 (1200 UT).

performed, it is necessary to know the SO_2 content in order to retrieve reliable ozone data. A larger uncertainty in SO_2 amounts retrieved from Brewer data is, however, expected, as discussed in detail by Fioletov *et al.* (1998).

After the October 2002 eruption of Etna, relatively high SO_2 values of 6–7 Dobson Units (DU) were detected over Thessaloniki. Figure 4 shows the Brewer measurements for the period October–November 2002. The high values observed are well above the background conditions for Thessaloniki, ranging between 2 and 4 DU. The relative increase in SO_2 levels is of the order of 3 DU.

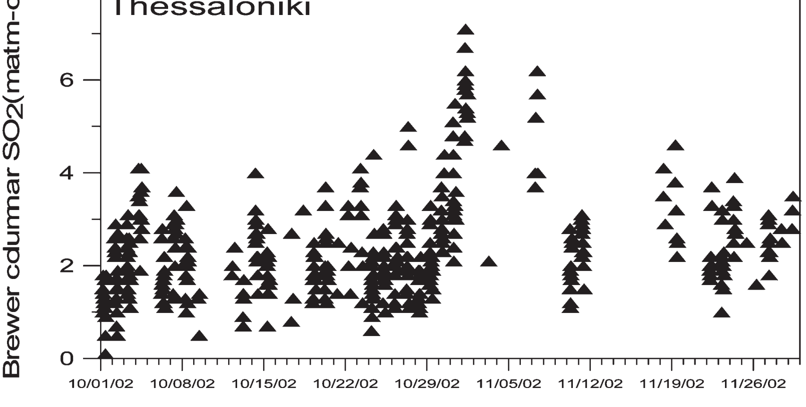

Figure 4. Ground-based columnar SO_2 measurements over Thessaloniki for the period October–November 2002.

Brewer measurements are not appropriate to detect the height level of volcanic emissions but Thomas *et al.* (2005) showed by means of trajectory analysis that aerosols and gaseous emissions were located in the troposphere below 6 km asl.

The presence of high SO_2 values over Athens is also evident from satellite measurements. We used data from the Total Ozone Mapping Spectrometer (TOMS/ Earth-Probe) and the Global Ozone Monitoring Experiment (GOME) sensor on board ESA's European Remote Sensing Satellite ERS-2.

The distinct TOMS spectral channels with a band width of about 1 nm are partly sensitive to SO_2, allowing the so-called Sulfur Index (S.I.) to be calculated. It is retrieved from a ratio approach of radiances sensitive and insensitive to gaseous absorption by SO_2. Figure 5 shows a time series of the TOMS S.I. for the period October–November 2002. The values observed in late 2002 reach a relative maximum in the seasonal cycle of the S.I. and occurred during the active period of Mount Etna. Zerefos *et al.* (2000) previously showed the good correlation between the TOMS S.I. and ground-based measurements of columnar SO_2 amounts.

The GOME spectrometer resolves the SO_2 and ozone absorption bands in the UV region between 315 and 330 nm at a spectral resolution of about 0.2 nm. The GOME retrieval is based on the Differential Optical Absorption Spectroscopy (DOAS) technique that was successfully applied to GOME data in the past (Burrows *et al.* 1999). A recent application of the GOME Data Processor (GDP), the latter described in Spurr *et al.* (2005), to the retrieval of SO_2 from volcanic emissions is presented in Thomas *et al.* (2005). The main uncertainties of retrieved SO_2 columns are with the typically unknown aerosol profile (loading and optical properties) and the shape of the trace gas profile, especially the height of the SO_2 plume. In addition, GOME is not sensitive to SO_2 in the lowest atmospheric layers under low albedo conditions. However, for the outbreaks in Autumn 2002 it was shown that the relative increase in SO_2 levels in the atmosphere after the Etna outbreaks was similar for GOME and the ground-based Brewer instrument.

We therefore conclude that satellite instruments can be generally used to detect and, to a lesser extent, to quantify SO_2 emissions of volcanic origin.

2.2.2 Chemical composition of the rainwater at Athens. Rainwater was sampled from two prototype automatic samplers (Dikaiakos and Nastos 1987, Dikaiakos

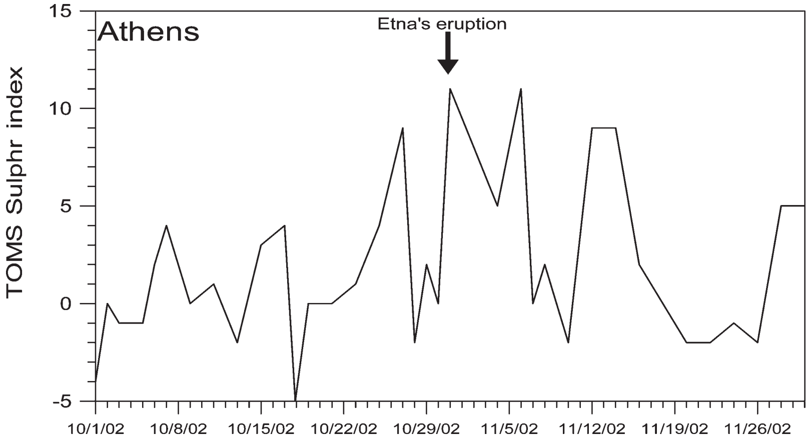

Figure 5. Satellite time series of the Suphur Index, based on TOMS overpasses in October–November 2002 over Athens.

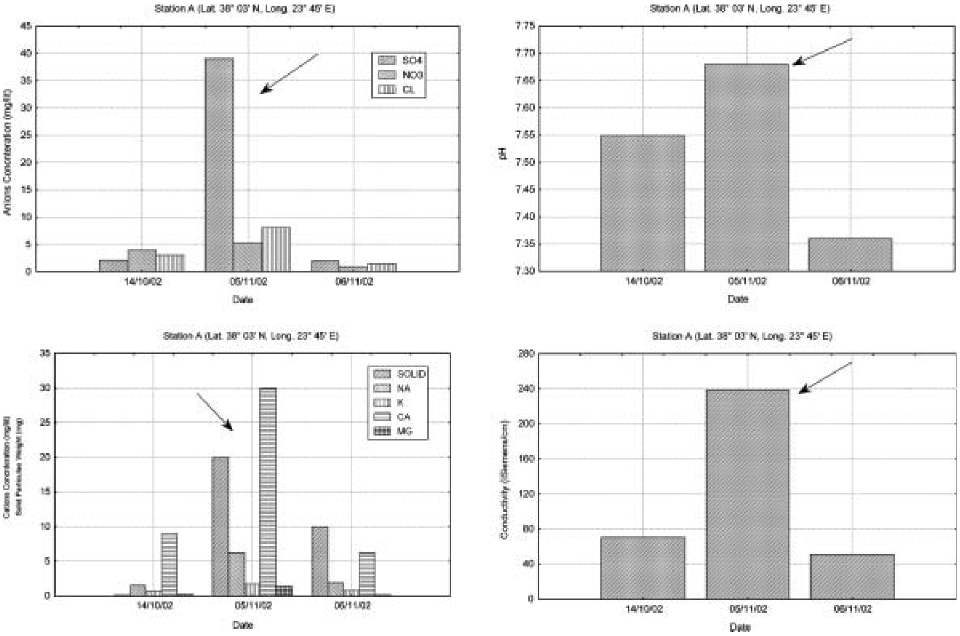

Figure 6. Anion, cation and solid particulate concentrations (mg/l), as well as pH and conductivity for wet deposition, for Station A.

et al. 1990), to study the wet deposition of volcanic material in the region of Athens. The chemical composition, pH and conductivity of the rainwater on 14 October and 5 and 6 November 2002 from the Athens Station A are depicted in figure 6. It is clear that on 5 November 2002 (when the precipitation at the station under consideration was the first after Etna's eruptions), the concentrations of SO_4^{2-} (39 mg/l) were very high compared to those of previous wet deposition on 14 October (2.1–4.0 mg/l) and subsequent wet deposition on 6 November (1.0–2.0 mg/l). The concentration of Cl^- reached a maximum of 8.1 mg/l on 5 November, while it was 3 mg/l on 14 October and 1.5 mg/l on 6 November.

A recent rainwater geochemical study performed by Bellomo *et al.* (2003) showed that chlorine measured in rainwater collected at the sampling station at Catania city located about 20 km away from Etna ranges from 2.38 to 335.10 mg/l. Even higher concentrations of chlorine were detected in rainwater samples collected close to the crater of Etna, ranging from 3.47 to 1408 mg/l.

With regard to cation concentrations, Ca^{2+} showed a highly variable concentration with a peak at 30 mg/l on 5 November, while it was 9.0 mg/l on 14 October and 6.3 mg/l on 6 November. Similarly, the concentration of Mg^{2+} increased from 0.2 to 1.3 mg/l on 5 November but decreased to zero afterwards. The concentration of Na^+ increased from 1.5 to 6.3 mg/l and then fell to 2.0 mg/l. The concentration of K^+ showed a higher value of about 1.7 mg/l on 5 November.

Note also the remarkably abrupt change in the weight of the particulates remaining in the filter, a process that took place before the chemical analysis started. The weight of the particulates increases from zero to 20 mg on 5 November and decreased to 10 mg on 6 November. The neutralization of the rainwater samples collected is reflected in the pH value of the probes. These values, however, do not vary much (from 7.36 to 7.68) and are close to the mean value reported for this region (Station A: $pH_{mean}=7.41$; Station B: $pH_{mean}=7.25$). By contrast, the conductivity of the rainwater increased from 70 to 239 μS/cm and then reduced back to 51 μS/cm. The peak conductivity on 5 November differed considerably from the mean value reported for this region (Station A: 79 μS/cm; Station B: 70 μS/cm) (Kelepertsis *et al.* 2002, Nastos and Kanellopoulou 2000). Similar results were obtained from Athens Station B. In particular, the chemical analysis of the ion content of the inorganic compounds revealed that SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, Ca^{2+} and Mg^{2+} concentrations were higher on 5 November than the corresponding values on 14 October and 6 November, respectively. Based on the chemical composition of rainwater and on trajectories at 3 and 5 km asl (model HYSPLIT NOAA) over Etna (figure 7), we can conclude that the rainwater composition was altered by the presence of volcanic material.

3. Conclusions

The impact of the volcanic eruptions of Mount Etna on the atmospheric composition in the larger environment is manifold and can be monitored even in remote places. Our study has confirmed the long-range transport of volcanic SO_2 and aerosols from Etna's eruption in 2001 and 2002 to Greece. We analysed spectrophotometric measurements from ground-based equipment and space-borne sensors as well as LiDAR measurements at Athens and Thessaloniki. We showed that the geometrical thickness of the volcanic plume was of the order of 300 m, having an aerosol optical depth of about 3×10^{-3} at 532 nm, and being present 4 km

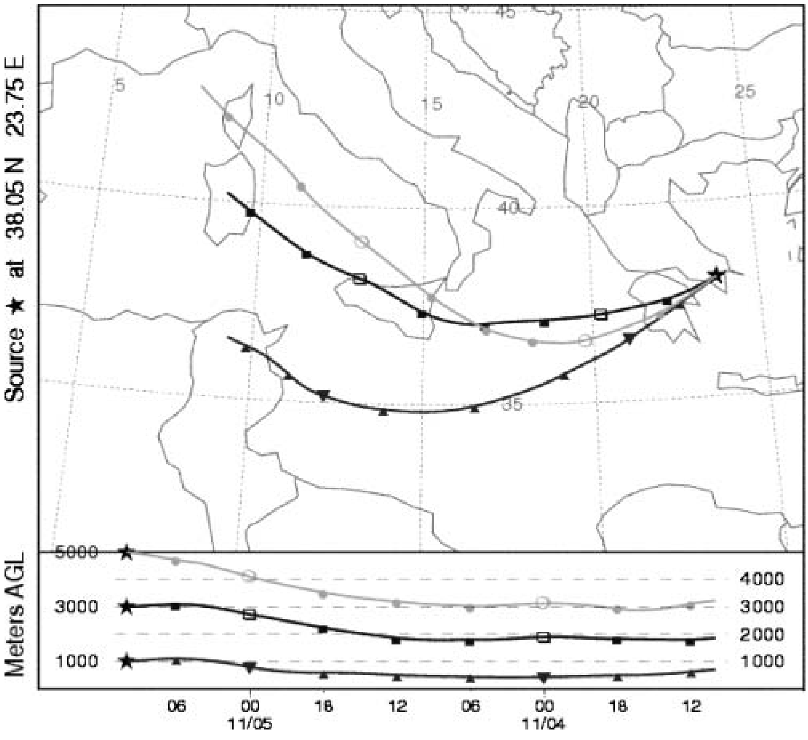

Figure 7. Backward trajectories ending at 1000 UTC on 5 November 2002 (Case 2).

asl. A significant reduction in ozone partial pressure between height levels 650 and 700 hPa over Athens was seen, coinciding with the altitude of the aerosol plume (*ca.* 4 km). This highlights the important role of halogen and non-halogen catalytic cycles depleting ozone in tropospheric volcanic plumes. Enhanced SO_2 levels were similarly measured from ground (Brewer) and space-based sensors (TOMS, GOME). All SO_2 records from this period are in good qualitative agreement, while GOME results and Brewer data show a similar quantitative increase in SO_2 levels after the eruptions in late 2002. Chemical analysis of rainwater and ash samples confirmed that material of volcanic origin was deposited over Athens.

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