Evaluation of a Chemical Transport Model for Sulfate using ACE-2 Observations and Attribution of Sulfate Mixing Ratios to Source Regions and Formation Processes

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Abstract

High resolution measurements of sulfate during the ACE-2 campaign (June-July 1997) permit detailed evaluation of the performance of a chemical transport models driven by analyzed meteorological data. At Tenerife, Canary Islands, (minimal proximate sources) the median ratio characteristic spread between model and observations, $S_{m/o} \sim 1.3$, was comparable to the spread of three sets of collocated observations and to the spread of observations at stations separated by ~13 km within a single model grid cell (1 ° × 1°). Somewhat greater $S_{m/o}$, ~1.6, at Sagres, Portugal is attributed to nonrepresentativeness of a single measurement site influenced by proximate sources. At Tenerife contributions from European, North American, and biogenic sources to sulfate mixing ratios are comparable, with North American sources dominating (up to ~85%) under conditions of a strong Azores high; thus substantial contributions of sulfate, and by implication other aerosols, can result from long-range midlatitude transport across the Atlantic Ocean.

1. Introduction

Over the industrial era enhanced reflection of solar radiation due to increased atmospheric loading of aerosols is recognized as a substantial climate forcing, but of highly uncertain magnitude [*Houghton et al.*, 2001]. On regional and local scales aerosols have been linked to impairment of health [*Vedal*, 1997], visibility [*U. S. Environmental Protection Agency*, 2001], and ecology [*Kuylenstierna et al.*, 2001]. Governments are debating expensive

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measures to reduce anthropogenic influences on climate; thus it is crucial that aerosol radiative forcing be well quantified and accurately represented in climate models [*National Research Council Panel on Aerosol Radiative Forcing and Climate*, 1996]. Chemical Transport Models (CTMs) are needed to develop representations of aerosol processes for use in climate models, and in view of demonstrable intercontinental transport of aerosols [*Jaffe et al.*, 2003; *Prospero*, 1999] CTMs should be capable of allocating aerosol loadings to source regions and formation processes. Because of the short lifetime of aerosols (ca. one week) high space and time resolution is needed in CTMs and geographically dense, high quality observations are needed for model evaluation.

The Second Aerosol Characterization Experiment (ACE-2), which took place in June and July of 1997 over the eastern North Atlantic [*Raes et al.*, 2000], obtained high space- and time-resolution measurements for aerosols. Sulfate from the oxidation of anthropogenic sulfur dioxide (SO_2) is a major component of aerosols in industrialized regions of the world [*U. S. Environmental Protection Agency*, 2001]. Here we report evaluation of the Brookhaven National Laboratory (BNL) Eulerian CTM for sulfate using ACE-2 measurements and determination of the contributions of source regions and formation processes to sulfate mixing ratios (MRs, in parts per billion, ppb, equal to nmol per mol air) at Tenerife, Canary Islands, and Sagres, Portugal.

2. Model Description

The BNL model represents emissions of the several sulfur species, chemical conversion of sulfur dioxide (SO_2) to sulfate by hydrogen peroxide (H_2O_2) and ozone (O_3) in the aqueous phase and by the hydroxyl radical (OH) in the gas phase, chemical conversion of dimethylsulfide (DMS) to SO_2 and methanesulfonic acid (MSA) by OH, and removal by wet and dry deposition [*Benkovitz et al.*, 1994; 2001]. Analyzed meteorological data from the European Centre for Medium-Range Weather Forecasts (ECMWF) are used, permitting detailed evaluations with observations as a function of time and location. The model tracks SO_2 by source region and sulfate by source region and formation process.

The present version of the model incorporates formation of H_2O_2 from HO_2 and kinetics of the aqueous-phase oxidation of S(IV). Location-dependent monthly averaged oxidant concentrations from Version 2 of the MOZART model [*Horowitz et al.*, 2003] with diurnal cycle are used. Sulfate incorporation into cloud droplets is a function of the liquid water volume fraction, and wet removal is represented by an exponential decay function. The horizontal resolution is 1° with 27 vertical levels to 100 hPa. This model was used to simulate sulfate mixing ratios in the Northern Hemisphere to 81°N for June and July, 1997. Source attribution regions selected were North America (NA), Europe (Eu), and Asia for anthropogenic emissions, biogenic emissions, and volcanic emissions. Sulfate formation processes were gas- and aqueous-phase oxidation and primary emissions.

3. Observations at ACE-2 Stations

Here we focus on near-surface measurements of sulfate MRs (Table 1). Observations used were from Sagres, Portugal (8.95°W, 36.98°N), a location influenced by proximate sources, and two sites separated by 13 km in Tenerife, Canary Islands, a location with minimal influence by proximate sources: Punta del Hidalgo (PdH, 16.32°W, 28.57°N) and Taganana (16.2°W, 28.53°N). The Sagres data were obtained from Prof. Harmut Herrmann, University of Leipzig, Germany; all the Tenerife data were obtained from the ACE-2 data

CDs released by the Environment Institute of the Joint Research Centre of the European Commission, 2001.

Time series of modeled sulfate mixing ratios in the lowest model level (surface to ~170 m above sea level, asl) at Tenerife (Figure 1) are presented by source region and formation process, and observations are presented for each measurement site. In general the observed MRs agreed quite closely; however observations by ULA and at Taganana 100 m (3 hr sampling interval) showed features, such as peak values at certain times, that are not captured in the observations by JRC and UCO because of their longer sampling interval. Overall, the model results agreed quite closely with the observations, albeit with some minor displacements in time or magnitude that are most likely caused by errors in representation of the transport and chemical transformation. Model error could result as well from erroneous magnitudes or locations of sources.

Time series data were quantitatively evaluated using the ratio characteristic spread (S), a measure of the ratios of the MRs [*Benkovitz and Schwartz*, 1997]. For two observed MRs, $S_{o/o}$, or for model observation evaluation, $S_{m/o}$, S = greater MR/lesser MR. For more than two observations this definition is generalized as $S = \exp\{2 \text{ s.d.}(\ln \text{MR})\}$ where s.d. (ln MR) is the standard deviation of the natural logarithm of the observations. As a measure of the spread of the observations due to analytical uncertainties, different measurement techniques, sampling protocols, and/or subgrid variation, $S_{o/o}$ is indicative of the agreement that might be achievable between the model and the observations. Thus it is very important to have multiple observations within a model grid cell.

Because of the different sampling intervals of the measurements $S_{o/o}$ values were calculated for three time intervals, 6, 12, and 24 hr. Two sets of $S_{o/o}$ values were calculated, one using the collocated measurements and a second using the Taganana 100 m measurements and the average of the collocated measurements at PdH. All S values were calculated using only time periods for which there are no missing data; results are presented in Table 2. Median values for the subgrid $S_{o/o}$ are within the range of $S_{o/o}$ for the collocated measurements, indicating the homogeneity of the Tenerife model grid cell.

4. Evaluation of Model Results

Values of $S_{m/o}$ were calculated at three locations: Tenerife model level 1 (surface to average 170 m asl), Tenerife model level 3 (average 340 to 590 m asl) using the Taganana 500 m observations, and Sagres; results are presented in Table 2. At Taganana 500 m the observations were averaged to the 6 hr model time interval; at Sagres the model results were averaged to the time periods of the observations.

Median values of $S_{m/o}$ at Tenerife were within the range of the subgrid $S_{o/o}$, indicating that model results were within the variation of the observations and thus accurately represented sulfate MRs at this location. Median $S_{m/o}$ at Sagres is somewhat larger; this increase is attributed to the nonrepresentative sampling by a single station at this location where greater subgrid variation is expected because of the influence of proximate sources. This influence was seen in the plume-type behavior of SO_2 measurements at this site (C. Neusüß, Bruker Saxonia Analytik GmbH, personal communication, 2002).

5. Influence of Source Regions and Formation Processes on Sulfate Mixing Ratios

The median relative contributions of source regions and formation processes to the sulfate MRs over the simulation period are presented in Table 3. Because of the geographic position of Sagres, sulfate from Eu sources dominated at this location; however, at Tenerife, located further away from the European continent, the relative contributions of Eu sources were much lower and comparable to contributions from NA and biogenic sources. At this location the relative contribution of NA sources exceeded that of Eu sources ~ 48% of the simulation time period and the combined contributions of NA and biogenic sources exceeded that of Eu sources ~ 68% of the period.

For the period July 12 to July 15 the sulfate MRs at Tenerife were 0.5 ppb or less (Figure 2). For this period meteorological conditions were dominated by a strong Azores High, as illustrated in Figure 3 for July 14 0000 UTC, which shows the synoptic features that drove long-range transport across the North Atlantic at midlatitudes and resulted in large relative contributions of NA sources at this distant location. Strong westerly winds ascended on the western side of the Azores high, as seen in the isentropic analysis on the 300K and 305K surfaces. These winds continued across the Atlantic Ocean and on the northern side of the high they intensified and proceeded into Europe. However, near the center of the high, winds turned north along the eastern branch and acquired a descending motion. Approaching the trade winds regime, the winds turned northeast passing over Tenerife and finally turned east. On this date the model indicated that the relative contribution of NA sources to the sulfate MR was ~ 85%, with the aqueous-phase oxidation of NA sources contributing ~ 60% of the total sulfate.

Transport of sulfate from North America to Europe during ACE-2 has previously been inferred on the basis of trajectory analyses [*Andreae et al.*, 2000; *Putaud et al.*, 2000; *Verver et al.*, 2000]. However, such analyses can yield substantially different results depending on the methodology used (isobaric, isentropic, etc.) and in any event cannot quantify the contributions of different source regions and formation processes. The present calculations, while supporting those previous inferences, allow the paths taken by the sulfur species from source to receptor to be determined by isentropic analyses, allow the formation mechanism to be apportioned, and provide quantification of the North American influence.

Aqueous-phase oxidation was the most important contributor to sulfate at both locations. This agrees with general conclusions of previous global-scale modeling studies as reviewed by Rasch et al. [2000] and Barrie et al. [2001]. In this study the median contribution of aqueous-phase oxidation was larger at Tenerife (73%) than at Sagres (51%) because the greater distance from sources allowed more transit time and likelihood of encountering clouds. Sulfate formed by aqueous-phase oxidation predominated at Tenerife during the whole simulation period; however, at Sagres there were several periods when gas-phase oxidation predominated, usually associated with stagnant high pressure conditions over the European continent. At Sagres, because of its proximity to emission sources, the median relative contribution of primary sulfate was larger; at certain periods this contribution was almost 25%. At Tenerife the contribution of primary sulfate was always less than 5%.

6. Summary and Conclusions

An Eulerian chemical transport model was used to simulate sulfate during the ACE-2 experimental period, June-July 1997, and results have been evaluated using high space- and time-resolution observations necessary to set a level of expectation for model performance. At Tenerife, Canary Islands (minimal influence from proximate sources) median ratio characteristic spread characterizing the variation of concurrent observations and that characterizing the departure between model and observations were both 1.3, indicative of the ability of the model to represent sulfate mixing ratios at this location within the inter-measurement and subgrid variations. At Sagres (influenced by proximate sources) the median ratio characteristic spread between model and observations was 1.6; this increase is attributed to the nonrepresentativeness of a single measurement site at a location where considerable subgrid variation can be expected.

Although Tenerife is much closer to European sources, the median relative contributions of European and North American sources were comparable (32 and 27%). The fractional contribution of North American sulfate was greatest when meteorological conditions were dominated by a strong Azores High, which resulted in long-range transport of North American emissions across the North Atlantic at midlatitudes. Overall aqueous-phase oxidation dominated at the two locations; however the relative contribution of each formation processes varies day-to-day depending on meteorological conditions.

Evaluation of model results at distances well removed from source areas lends confidence in these results at scales that are relevant for climate influence. These results indicate substantial contributions of sulfate, and by implication other aerosol components, resulting from long-range midlatitude transport across the Atlantic Ocean. Thus it is important that this transport be accurately represented in models used to assess the influence of these aerosols on climate and air quality.

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Table 1. Details of Measurements Used for Evaluation of Model Results

Site	Altitude (m asl [f])	Institution	Particle Diameter (μm)	Instrumentation	Analysis Method	Interval (hr)
Tenerife Punta del Hidalgo	42	JRC [a]	< 1	Virtual impactor PM$_{10}$ inlet	IC [g]	~ 12
		ULA[b]	< 2.5	4-stage filter pack	IC	~ 3
		UCO [c]	< 2.5	6-stage Sierra impactor		~ 24
Taganana	100	UBI[d]	< 2.5	Filter pack	IC	~ 3
Taganana	500	UBI	< 2.5	Filter pack	IC	~ 3
Sagres	50	UL[e]	0.05 - 1.2	Impactor	CE [h]	~ 12

[a] JRC=Environment Institute, EC Joint Research Centre, EI-JRC, Ispra, Italy

[b] ULA=Lancaster University, Lancaster, UK

[c] UCO=University of Colorado, Boulder, CO, USA

[d] UBI=University of Birmingham, Birmingham, UK

[e] UL=University of Leipzig, Leipzig, Germany

[f] asl=above sea level

[g] IC=ion chromatography

[h] CE=capillary electrophoresis

Table 2. Median Values of Ratio Characteristic Spread for Model and Observations

Interval (hr)	$S_{o/o}$ Observations/Observations at Tenerife					$S_{m/o}$ Model Observations		
	Collocated Measurements PdH			Subgrid[a] PdH/Taganana		Tenerife Surface	Taganana 500 m	Sagres
		No. Values	Components		No. Values			
6	ND[b]		ULA	1.3	86	1.36	1.34	
12	1.3	45	ULA, JRC	1.3	44	1.41		1.62
24	1.5	21	ULA, JRC, UCO	1.3	20	1.22		

[a] Calculated using the average of collocated measurements at PdH and the measurements at Taganana 100 m

[b] ND=only one set of collocated measurements available.

Table 3. Median Relative Contribution of Source Regions and Formation Processes to Sulfate Mixing Ratios (%)

Location	Source Regions			Formation Processes		
	Europe	North America	Biogenic	Aqueous	Gas	Primary
Sagres	88	3	6	51	37	12
Tenerife	32	27	22	73	24	3

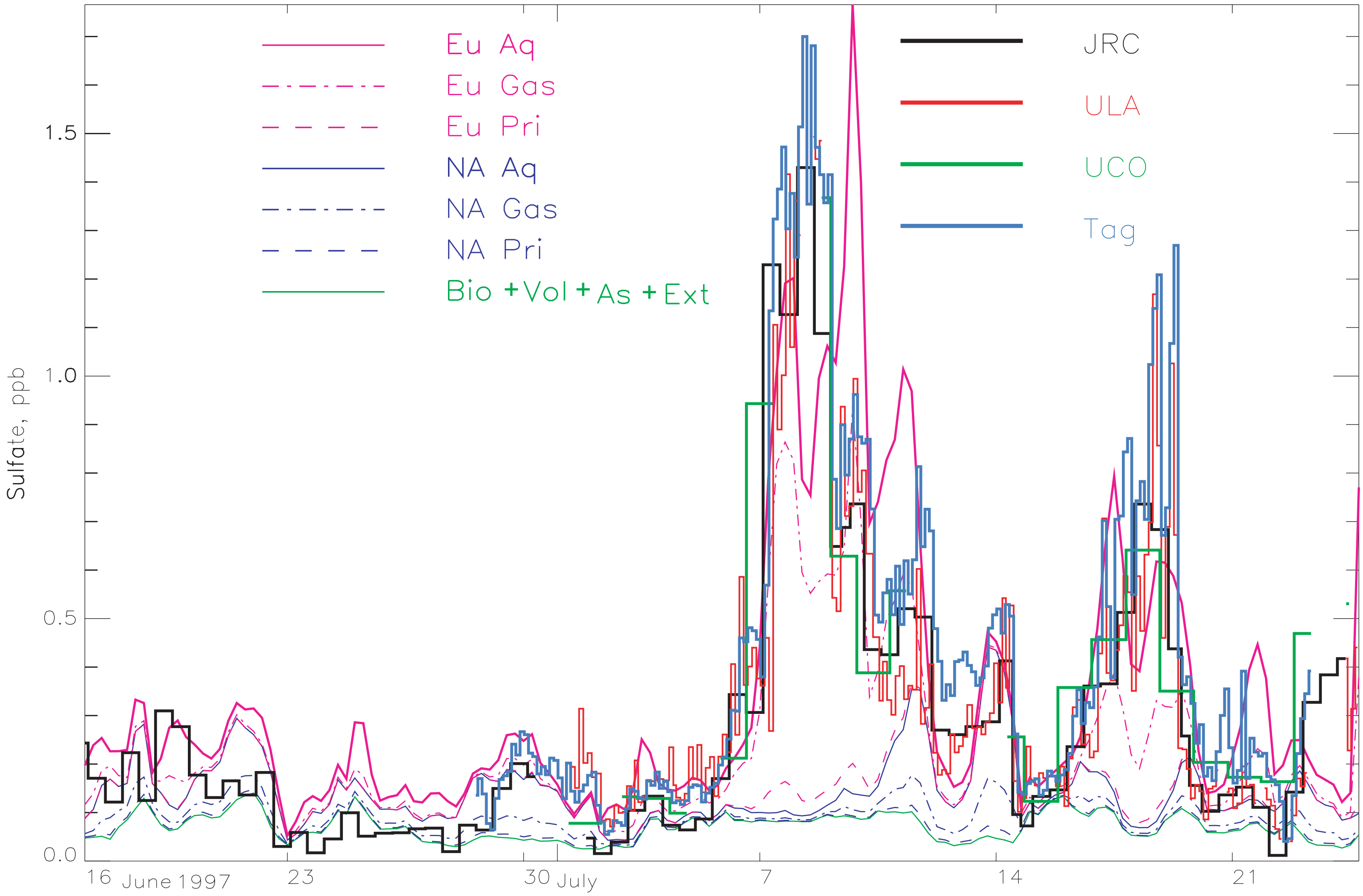

Figure 1. Time series of surface sulfate mixing ratios at Tenerife, Canary Islands. Curves represent model results by source region and formation process (NA=North America; Eu=Europe; As=Asia; Bio=biogenic; Vol=volcanos; Aq=aqueous-phase conversion; Gas=gas-phase conversion; Pri=primary emissions). Curves are cumulative; contribution of source region/formation process indicated by a given label is represented by the vertical distance between that curve and the one immediately below it. Cityscape curves represent observations; measurement details appear in Table 1.

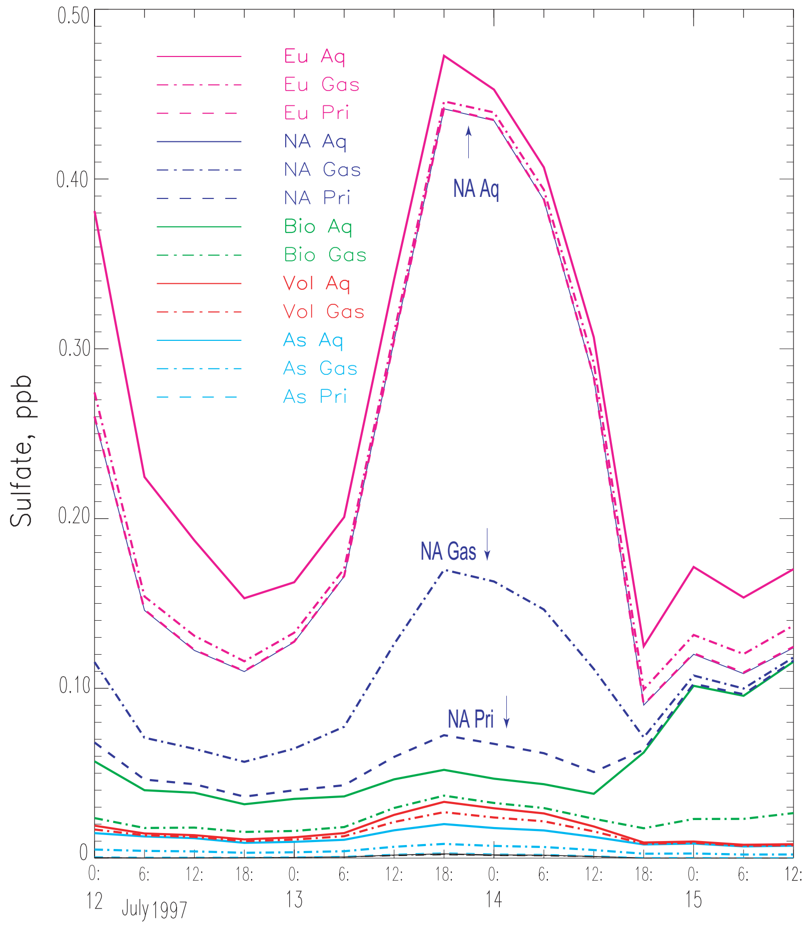

Figure 2. Detail of the time series of the surface sulfate mixing ratios at Tenerife, Canary Islands showing one period with large relative contributions of North American sources. North American sources contribute ~ 85% of the sulfate on 7/14/97 at 00UT when the mixing ratio was ~ 0.47 ppb. Source regions are differentiated by color; formation processes are differentiated by line style.

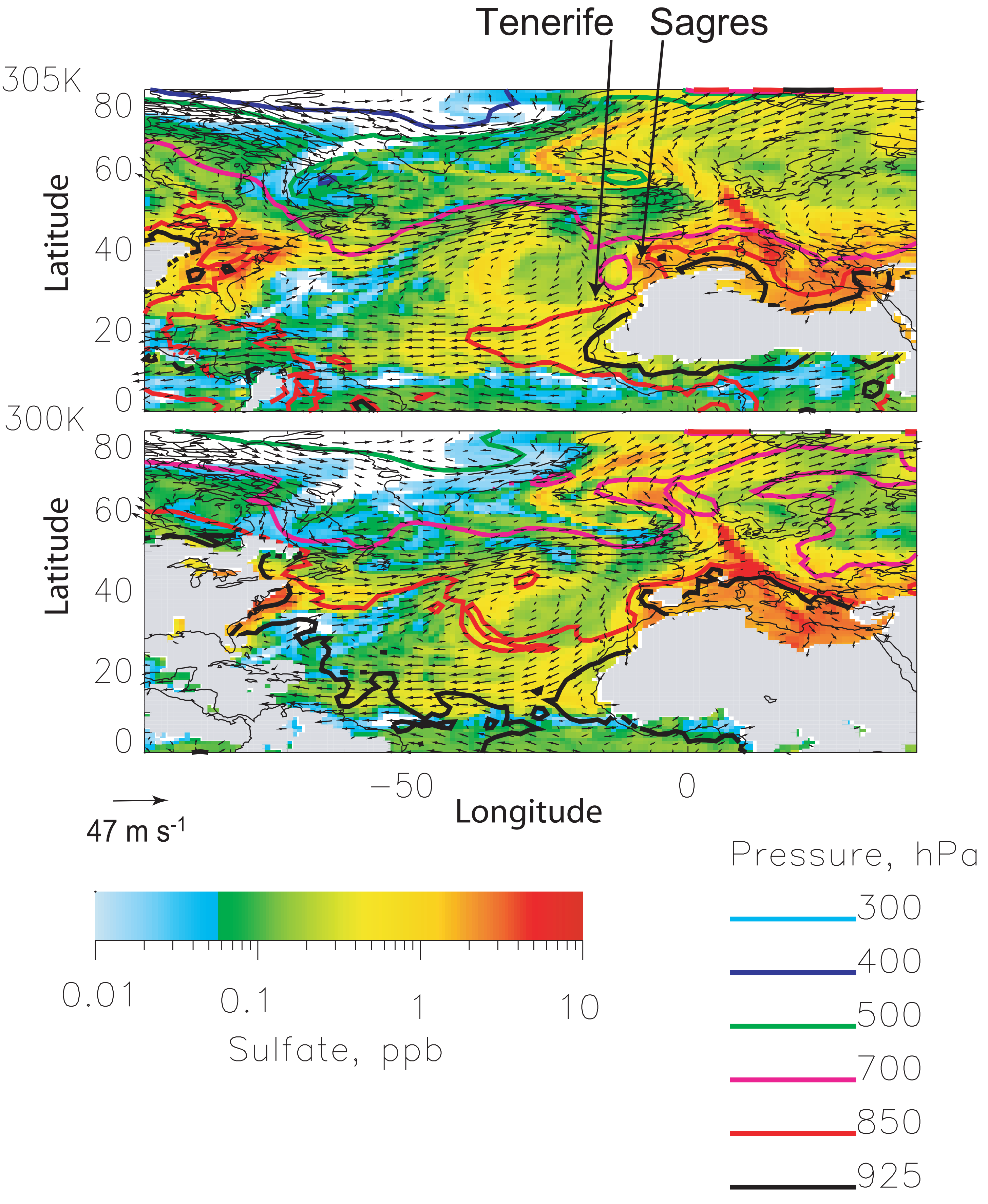

Figure 3. Isentropic analysis for July 14 0000 UT at the 300K and 305K surfaces. The potential temperature is constant at all points on each chart and the contours represent constant barometric pressures. The colors denote the sulfate mixing ratio on the isentropic surface. Gray areas denote the intersection of isentropic surfaces with the ground; white areas denote regions where the sulfate mixing ratio was < 0.01 ppb.