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Soluble ion chemistry of the atmospheric aerosol and SO_2 concentrations over the eastern North Atlantic during ACE-2

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ABSTRACT

ACE-2, the second Aerosol Characterization Experiment of the International Global Atmospheric Chemistry Project (IGAC), was conducted in the area between Portugal, Tenerife and Madeira from 15 June to 25 July 1997. We determined the concentration of SO_2 and the soluble ion composition of the atmospheric aerosol in 113 samples collected by aircraft. Comparison between aircraft and ground-based samples collected from the same or similar airmasses showed good agreement (better than 40%) for the fine fraction of the aerosol, but suggests that, for the coarse fraction, the sampling efficiency of the aircraft inlet is only about 35%. During periods when trajectory analysis suggested no recent contact of the airmass with Europe or North America, SO_2 and aerosol ions were at levels comparable to those found over remote ocean regions. The composition of airmasses originating from Europe showed signatures characteristic of the source regions and suggested rapid oxidation of SO_2 during transport over the ocean. The first Lagrangian experiment was conducted in an unpolluted airmass and showed the physical and chemical evolution of a marine boundary layer traversing over increasingly warmer ocean waters. The sulfur cycle in this airmass could be explained based on the emission of DMS from the sea surface. In three other Lagrangian experiments, we investigated the evolution of boundary layers with increasing age since having left the European continent. SO_2 was removed rapidly with lifetimes on the order of half a day in cloud-topped boundary layers. The production of nss-sulfate ceased after SO_2 had declined to background levels, and the aerosol approached a nearly constant composition, with concentrations dominated by physical removal and dilution processes. Aerosol nitrate concentrations suggested that gaseous HNO_3 was taken up by seasalt aerosol and subsequently removed by dry deposition.

1. Introduction

ACE-2 was conducted in summer 1997 over the Atlantic Ocean between Portugal, Tenerife and Madeira. A wide range of aerosol types are present in this area, including marine aerosol containing seasalt particles and sulfates derived from DMS oxidation, European pollution aerosol, and African mineral dust. The central objective of ACE-2 was the study of the chemical and physical properties of these aerosols, their radiative effects, and the processes responsible for controlling and modifying their properties as they are transported over the ocean (Raes et al., 2000).

The composition of the aerosol is one of the key parameters defining its chemical and physical behavior, particularly with regard to the properties

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important for its climatic effects: light scattering and absorption efficiency and cloud droplet nucleating ability. Light scattering and absorption determine the magnitude and sign of the "direct" climate effect, i.e., the amount of solar energy reflected to space by the aerosol. The amount of water-soluble material present in a particle determines at what supersaturation it can become activated, grow into a cloud droplet, and thereby contribute to the "indirect" effect, i.e., the climate forcing due to modification of cloud properties.

In order to understand and model the origin and evolution of sulfate aerosol, the most abundant anthropogenic aerosol species (Andreae, 1995; Tegen et al., 1997), it is essential to know the concentration of its precursor species, SO_2. Previous work in the ACE-2 area has found large variations in atmospheric SO_2 as a result of the diversity of airmass origins typical of this region (Blomquist et al., 1996).

In this paper we discuss the results of the measurements of aerosol chemistry and SO_2 concentration performed on board the MRF C-130 aircraft during ACE-2. Our measurements complement the data obtained on the Citation and Pelican aircraft (Curtius et al., 1998; Schmeling et al., 2000), the research vessel R/V Vodyanitsky (Quinn et al., 2000), at Sagres (Portugal) (Neusüß et al., 2000) and on Tenerife (Bower et al., 2000; Putaud et al., 2000). The results are analyzed in the context of airmass origin and evolution, with an emphasis on the results of the Lagrangian experiments. Further details on the Lagrangian experiments can be found in companion papers (Johnson et al., 2000b; Osborne et al., 2000; Wood et al., 2000).

2. Methods

2.1. Sampling

The aerosol and SO_2 sampling system and procedures are based on a design described in detail previously (Andreae et al., 1988; Talbot et al., 1990). Samples were collected using a system consisting of an isokinetic inlet directly coupled to a 3-stage stacked filter unit. We utilized a thin-walled inlet nozzle with a curved leading edge; the design was based on criteria for aircraft engine intakes at low Mach numbers (Andreae et al., 1988). This design reduces distortion of the pressure field at the nozzle tip and the resulting problems associated with flow separation and turbulence. The sampling system operated at flow rates that averaged 120 liter min^{-1} (at ambient pressure and temperature); the flow was adjusted to maintain slightly subisokinetic sampling conditions.

The aerosol intake system was designed so that rain and large cloud water droplets would be removed from the sampled air stream by inertial separation. At the point where the intake tube begins to curve to bring the air stream inside the aircraft, a bypass tube was connected to the main intake tube and extended back in a straight path from the inlet nozzle. The second tube was of the same diameter initially as the main intake tube (2.5 cm ID), but gradually narrowed to a final internal diameter of about 1 cm. This tube was ca. 20 cm in length and was coupled to another tube of about 1 cm ID that was brought inside the aircraft. There, clear Tygon tubing continued the bypass flow path through a regulating valve and back out of the aircraft through a drain port. Rain drops and large cloud water droplets have too much momentum to follow the sample air stream into the aircraft, therefore they separate from the main air stream and continue in a straight path down the bypass tube. Theoretical calculations show that a separation efficiency of 95% is obtained for droplets larger than 35 μm. Collected water is entrained by the bypass airflow and vented outside. While this droplet removal system does reduce the amount of large droplets potentially impacting on the filters, it was still necessary to close the inlet valves during cloud penetrations to prevent damage to the filter samples due to cloud water.

The filter unit contained three sequential 90 mm diameter filters on polyethylene supports. The aerosol was collected and separated into coarse (> 1.4 μm diameter) and fine particles on the first two filter stages. The first stage held a Nuclepore filter (nominal pore size 8.0 μm), the second a PFTE Teflon filter (Alltech Cat. No. 2564, nominal pore size 1.0 μm). The 50% cut-off aerodynamic diameter of the 8 μm Nuclepore filter is about 1.4 μm at the face velocity used in ACE-2 (ca. 40 cm/s) (John et al., 1983).

Samples for the determination of SO_2 were collected on the third stage with a Whatman 541 filter impregnated with K_2CO_3/glycerol. The preparation, storage, and blank behavior of the impregnated filters have been described in detail previously (Andreae et al., 1988; Berresheim et al., 1989; Ferek et al., 1997; Ferek et al., 1991). Based on determinations of the SO_2 collection efficiency of the impregnated filters in laboratory and field experiments, we conclude that under the sampling and meteorological conditions prevailing during ACE-2, SO_2 was collected with an efficiency $>90\%$ in the boundary layer and $>80\%$ in the free troposphere. No collection efficiency correction was applied to the data presented here.

Laboratory filter handling was done in a clean-air bench fitted with SO_2 and NH_3 scrubbers. Filters were loaded into the filter holders in the lab, and the filter holder assemblies were kept in airtight containers until being inserted in the sampler on the aircraft. After sampling, they were immediately replaced into the airtight containers until being extracted in the lab. Blanks for all filter types were obtained by placing filters in the sampling units in the aircraft and exposing them for a few seconds.

During ACE-2, we collected samples on 21 flights of the MRF C-130 aircraft, including all nine of the Lagrangian missions. A total of 113 filter packs for the determination of aerosol ions and SO_2 were taken, 54 of which were obtained during the Lagrangian experiments.

2.2. *Filter handling and analysis*

The loaded filters were transferred to 30 ml HDPE bottles in the field lab immediately after each flight and stored in a refrigerator until extraction. Depending on the extraction volume, the Zefluor filters were first wetted with 0.5 ml or 1 ml of methanol. For the first aerosol sample sets we used 10 ml milli-Q water for the extraction of soluble aerosol species, but later reduced the extraction volume to 5 ml to obtain higher concentrations in the extract. The K_2CO_3-impregnated filters were treated with 10 ml of 0.06% H_2O_2 whereby all sulfur(IV) species adsorbed on the filter were dissolved and converted to sulfate. After addition of the extraction solutions all samples were shaken vigorously for about 10 min.

2.3. *Analysis*

The first sample sets were analyzed during the campaign in a field laboratory at Tenerife airport, the rest at the MPI for Chemistry (MPIC), Mainz. In Tenerife, analyses were performed on Sykam ion chromatography systems. Anions were determined using Dionex AG4A-SC and AS4A-SC guard and separator columns and an ASRS-1 suppressor in chemical suppression mode. The eluent was 1.1 mM bicarbonate and 1.2 mM carbonate at a flow rate of 2 ml min^{-1}. Cations were measured using a CG12A guard column and CS12 separator column and a CSRS-1 suppressor in autosuppression recycle mode. The eluent was 20 mM methanesulfonic acid (MSA) with a flow rate of 1 ml min^{-1}.

At MPIC, anions were determined using a Shimadzu HIC-6A ion chromatograph with an AS11 column and ASRS-1 suppressor. The temperature of the system was 35°C, the flow rate of the eluent (NaOH, using a gradient mode) was 1 ml min^{-1}. The separation of all ions was optimized by gradient elution (Rocklin et al., 1987). A plateau of high NaOH concentration at the end of the gradient ensured regeneration of the ion exchange capacity of the column after each analysis. For the cation analysis we used a CS14 column, an eluent flow rate of 1.2 ml min^{-1} (10 mM MSA, using isocratic mode), and a CSRS-1 suppressor in autosuppression recycle mode. The detection limits in standard solutions ranged between 0.09 and 0.13 μmol/l for cations and between 0.03 and 0.12 for anions. Aqueous standards were prepared from high-purity reagents with deionized Milli-Q water ($R > 18$ MΩ; Millipore, Bedford, MA, USA). All concentrations are reported in molar mixing ratios in air (ppt = pmol mol^{-1}).

2.4. *Airmass trajectories*

Back trajectories were computed using the HYSPLIT-4 (HYbrid Single-Particle Lagrangian Integrated Trajectory) model (Draxler and Hess, 1997) and the FNL meteorological data set produced by the US National Center for Environmental Prediction (NCEP). The vertical velocities from the FNL data set were used to derive the vertical transport component in the trajectory calculations. Comparison between the trajectories obtained with HYSPLIT-4 and those provided by the Dutch Weather Service (KNMI) and the UK Meteorological Office during the ACE-2 campaign showed good agreement.

3. Results and discussion

3.1. Comparison between ACE-2 platforms

To assess the internal consistency of the ACE-2 data set and the potential for intake losses during airborne sampling, we compared our airborne measurements taken in the surface mixed layer (SML) with ground-based results from the R/V Vodyanitsky (RVV) (Quinn et al., 2000) and Punta del Hidalgo (PDH) on the coast of Tenerife (Putaud et al., 2000). For this comparison, we selected those samples from each platform that could be most closely linked to a sample collected on the aircraft, e.g., a sample taken at PDH at the time when a forward trajectory from the aircraft indicated that the airmass sampled by the C-130 would arrive at PDH. Obviously, such a comparison is not truly rigorous, since we have to compare samples collected over short intervals on the aircraft (~ 30 min) with ground-based samples collected typically over 12 h, and since the airmasses sampled by the aircraft and at ground level are not always truly identical. In order to avoid bias due to the effect of different size cutoffs for the aircraft and surface samplers, we chose to compare the sums of coarse and fine fractions.

The results of the comparisons are shown in Table 1 in the form of ratios between the aircraft and ground-based measurements. The seasalt elements, Na^+, Cl^-, Mg^{2+}, and K^+, all show ratios of around 0.35, suggesting that only about one-third of the seasalt aerosol present at ground level is collected by the aircraft sampling system, most likely because of losses in the inlet. Our collection efficiency is thus slightly better than that reported for the "community aerosol inlet" used for ACE-1 on the NCAR C-130 (0.18, (Huebert et al., 1998)) or the inlet used on the NCAR Electra aircraft during ASTEX (0.17, (Huebert et al., 1996b)). Vertical gradients in seasalt concentration from the sampling heights of a few tens of meters for the ground-based samplers to a few hundreds of meters for the aircraft may also account for a modest fraction of the difference (20–30%, (Warneck, 1988)).

NH_4^+ concentrations measured on the aircraft were always somewhat higher than those at the ground, but the differences are below or near the statistical confidence limits. For SO_4^{2-}, the agreement between aircraft and PDH is good, but the levels measured on the RVV tend to be higher. For the samples representing the starting points of the three Lagrangian experiments, where an effort was made to sample identical airmasses, the C-130/RVV ratios for fine sulfate are 0.61, 0.93, and 0.59. To put this into perspective, however, we must also look at the variability of measurements on both platforms. Around the starting time of Lagrangian 1 (LAG-1, 3/4 June 1997), fine sulfate on the RVV was quite variable (5, 130, 98, and 8 ppt), while repeated sampling within the same airmass by the aircraft over a period of 24 h gave values of 60, 104, 127, 111, and 106 ppt. A t-test shows the difference between these two groups of samples not to be significant ($p = 0.22$). For LAG-2, a similar comparison of variance is not appropriate, since this airmass was undergoing rapid conversion of SO_2 to SO_4^{2-}. However, the fact that the ship measured 2500, 2175 and 375 ppt in the samples before, during and after the release of the tracking balloon marking the airmass suggests that the good agreement in this case (Table 1) may also be somewhat fortuitous. For LAG-3, the ship measured fairly constant values around 1800–2000 ppt during the 2 days preceding the balloon launch, but, unfortunately, sampling was discontinued immediately following the launch of the last balloon. We conclude that, while there may be a systematic difference in sulfate values between the two platforms, the variability between samples is such that we cannot be confident of its significance. For NO_3^-, finally, we find relatively good agreement between the C-130 and PDH, but

Table 1. *Ratios (means and 95% confidence intervals) between measurements of aerosol species concentrations made on the C-130 aircraft and ground-based measurements made in correlated airmasses at Punta del Hidalgo (PDH) and on the R/V Vodyanitsky (RVV)*

Species	Ratio C-130/PDH avg. ±C.I. (95%)	Ratio C-130/RVV avg. ±C.I. (95%)
Na^+	0.37 ± 0.07	0.34 ± 0.22
NH_4^+	1.16 ± 0.14	1.17 ± 0.59
K^+	0.57 ± 0.30	0.44 ± 0.48
Mg^{2+}	0.39 ± 0.11	0.29 ± 0.25
Cl^-	0.35 ± 0.07	0.27 ± 0.24
NO_3^-	0.81 ± 0.49	0.33 ± 0.21
SO_4^{2-}	0.90 ± 0.31	0.59 ± 0.16
nss-SO_4^{2-}	1.26 ± 0.24	0.63 ± 0.15

much lower values on the aircraft than on the ship. The latter finding would be consistent with NO_3^- being present on seasalt particles. Overall, we conclude that the aircraft systematically undersamples the coarse aerosol (seasalt ions, nitrate) by as much as a factor of three, but that the differences in submicron aerosol species (nss-sulfate, ammonium) between platforms do not exceed 40%, even over the wide range of absolute concentrations sampled during ACE-2.

For SO_2 with its shorter lifetime, there are only a few cases that allow a realistic comparison between platforms. Close agreement is found for flight A555 on 14 July 1997, which was conducted directly offshore of the sampling sites on Tenerife. The C-130 found 23 ± 9 ppt SO_2, while PDH observed 19 ± 2 ppt. On flight A561 (18 July 1997), the C-130 found 48 ± 11 ppt SO_2 ca. 100 km upwind of Tenerife. When this airmass reached Tenerife, SO_2 concentrations between 11 and 42 ppt were recorded at PDH. Flight A562 (19 July 1997) was conducted due north of the island, and the airflow did not connect the sites directly. Here, the aircraft measured 8 ± 6 ppt, while PDH found 20 ± 2 ppt. Overall, the mean SO_2 concentration at PDH was 18 ± 19 ppt, while the averages for the "North Atlantic", "North America" and "European" airmass types sampled on the C-130 was 27 ± 8 ppt. When the "European" airmasses, which were typically sampled 1–3 days upwind of Tenerife, are excluded, the C-130 mean is 21 ± 8 ppt.

Comparison with measurements made on the RVV is also complicated by spatial heterogeneity, and by the high detection limit of 100 ppt SO_2 for the shipborne instrument. On flight A549 (25 June 1997) off the coast of Portugal, the C-130 found 4.3 and 7.7 ppb SO_2 between 1049 and 1203 UT in airmasses immediately upwind of the RVV. During about the same time period, up to about 1115 UT, the ship found values of 4.4–8.8 ppb, which suggested good agreement between the SO_2 measurements on ship and aircraft. The SO_2 levels during LAG-1 were below the ship's detection limit, and for the beginning of LAG-2, only one measurement within several hours of the balloon release is available, which shows 510 ppt SO_2, compared to the aircraft value of 800 ppt. For flights A565 and A566, when the aircraft was over or very close to the ship, the aircraft found values in the range 30–100 ppt, while on the ship values were below the detection limit of 100 ppt. We conclude that, while on one hand there are no obvious conflicts between the ground-based and airborne measurements, our results also cannot provide clear evidence for satisfactory agreement.

3.2. *Meteorological setting and sampling strategies*

The meteorological environment of ACE-2 has been discussed in detail by Verver et al. (2000), and only a brief overview will be given here. Specific information on the meteorological situation during the Lagrangian experiments, as well as trajectory and flight track plots can be found in Johnson et al. (2000a, 2000b), Osborne et al. (2000), Dore et al. (2000) and Wood et al. (2000). The study area, between the Iberian Peninsula and the Canary Islands, lies southeast of the Azores High, the stationary subtropical anticyclone over the North Atlantic. At lower levels, this meteorological situation results in a predominantly northerly and northeasterly flow over the region, bringing relatively clean airmasses into the study area. Trajectory calculations suggest these airmasses may contain some pollution from North America, a situation that prevailed during the first week of ACE-2.

The first Lagrangian experiment (LAG-1) was conducted during a period of northerly flow driven by the Azores High, bringing clean airmasses from the northern North Atlantic to the region. The objective of LAG-1 was to study aerosol and trace gas concentrations and their temporal evolution under clean conditions, as a control case against which to compare the polluted airmasses that were the actual focus of ACE-2. During LAG-1, the C-130 aircraft made three flights into the same air parcel at approximately 12-h intervals. Between flights, the air parcel was tracked by balloons and with chemical tracers.

After the passage of a low-pressure system, the Azores High may ridge over Western Europe, resulting in transport of polluted air from Europe along the southern flank of the ridge. Two such pollution outbreaks were sampled along Lagrangian trajectories during ACE-2 (LAG-2 and LAG-3). The boundary-layer airmasses sampled during LAG-2 traveled over the western coast of France and the coastal regions of the Iberian Peninsula. They probably contained some relatively fresh emissions from the latter region, where a number of power plants with high SO_2 emissions are located (Raes et al., 2000). During LAG-3, the air in the boundary layer had traveled for at least 48 h over the ocean, after having left land in northeastern France. Boundary layer trajectories for this experiment suggest that emissions in the UK, France, Belgium and the Netherlands were responsible for most of the pollutant input into this airmass.

In addition to the Lagrangian experiments, the ACE-2 flights provided an opportunity to sample a large variety of airmasses originating from clean and polluted regions. These include fresh pollution from Iberia sampled just off the Portuguese coast, dust-laden air from the Sahara, and clean mid-latitude marine air from the North Atlantic. We classified the samples according to airmass trajectories into five types: (a) clean marine air that did not make contact with land over the past 10 days, (b) air that had traveled from the North American continent across the Atlantic, (c) airmasses with trajectories over the European continent, but not the Iberian peninsula, (d) airmasses which had come across Iberia, but did not make contact with sulfur emissions along the Portuguese coast, and (e) air that contained fresh pollution from the Portuguese coast.

For the statistical analysis of our results, we further categorized our samples by tropospheric layers. We divided the marine boundary layer (MBL) into two sub-layers: The well-mixed layer between the sea surface and the cumulus cloudbase is referred to as "surface mixed layer" (SML), and the layer between the cumulus cloudbase and the subsidence inversion is categorized as "cloud convection layer" (CCL). Near the Portuguese coast, a polluted layer was present between the newly formed polluted SML and the clean FT proper. This layer represented a remnant of the continental boundary layer (CBL), formed by more intensive convection over land and preserved as a stable layer above the SML.

3.3. Measurements in the free troposphere

During most of the ACE-2 flights, samples were collected from the free troposphere at altitudes between 1100 and 7000 m, often during the transit to or from a study area. Sampling times ranged between ca. 0.5 and 2.5 h, to provide enough sample mass at the low aerosol concentrations typical of the FT. In all, 26 valid samples were obtained from the FT; the results are summarized in Table 2. Data are given only for those species that could be detected in at least 10 of the samples. For species that were detectable only in a subset of the samples, the statistics in Table 2 refer to that subset only, therefore the true mean concentrations would be lower than the values reported. Based on the data in Table 2, and ignoring the contribution of species below the detection limit, we estimate FT soluble aerosol mass concentrations of 0.39 ± 0.21 and 0.20 ± 0.10 $\mu g\ m^{-3}$ (STP) in the fine and coarse fractions, respectively.

With only one exception, all FT airmasses sampled came from the west and northwest. 16 of the trajectories crossed North America within the preceding 10 days, 9 had not traveled over land, and one passed at high altitude over the Iberian Peninsula. No significant differences in the concentrations of aerosol species or SO_2 exist between these sample groups. This is consistent with modeling calculations by Tarrasón and Iversen (1992), who predict that, over the ACE-2 region,

Table 2. *Soluble ionic species and SO_2 in the free troposphere (in ppt, except for soluble mass, which is in $\mu g\ m^{-3}$)*

	Fine fraction				Coarse fraction			
Species	N	$x \pm \sigma$	min	max	N	$x \pm \sigma$	min	max
NH_4^+	24	107 ± 55	27	163	12	32 ± 16	6	56
Ca^{2+}	11	53 ± 38	11	130	—	—	—	—
Cl^-	—	—	—	—	11	37 ± 31	14	121
NO_3^-	14	25 ± 7	7	113	19	21 ± 11	7	42
SO_4^{2-}	26	40 ± 12	20	61	10	19 ± 14	3	50
soluble mass ($\mu g\ m^{-3}$)	26	0.39 ± 0.21			26	0.20 ± 0.10		
SO_2	19	15 ± 10	5	32				

SO_2 from North American origin should have declined to levels below the detection limit.

Overall, our results show a rather clean free troposphere, with concentrations somewhat lower than reported by previous investigators from the same or comparable regions. Blomquist et al. (1996) do not provide numerical data for SO_2 in the FT, but values of about 40 ppt can be estimated from their graphs for the FT above 2.5 km. Similar values have been reported by Ockelmann et al. (1987). On the other hand, the SO_2 measurements made on the Citation aircraft during ACE-2 (Curtius et al., 1998) are reasonably consistent with our results: For the altitude range of 4000–7000 m, their average SO_2 concentration is 28 ± 20 ppt, but since their detection limit is 15 ppt, this average is actually an upper limit.

The only other measurements of aerosol composition in the FT made during ACE-2 are from the Izaña station on Tenerife (Putaud et al., 2000). Our aircraft results in Table 2 are in good agreement with the Izaña measurements for nss-SO_4^{2-} (30–50 ppt, depending on airmass origins). On the other hand, our NH_4^+ and NO_3^- values are much higher than the values given by Putaud et al. (2000) for background conditions (10–30 ppt and 6–10 ppt, respectively). Nitrate in the coarse fraction at Izaña was about 2.5 times the amount in the fine fraction, while in our samples there was more nitrate in the fine than in the coarse fraction. Since the mass/size distribution of nitrate often peaks around 1–2 μm, slight differences in the effective size cut between samplers may contribute to the observed discrepancies, but we consider it unlikely that this factor can account for differences of a factor of 3 or more. The fact that in our samples nitrate is more abundant in the fine than the coarse fraction may be related to particle bounce, which can become important with dry particles at the low relative humidities of the FT (John et al., 1983).

Lower concentrations of NH_4^+ and NO_3^- in the Izaña samples may be also due to volatilization from the ground-based samples, which were exposed for much longer times (ca. 12 h) than our aircraft samples (ca. 1 h). Sampling-time dependent losses of NH_4NO_3 have been demonstrated in intercomparison experiments between different samplers and sampling techniques (Slanina et al., 1999). Absorption of HNO_3 or NH_3 to the filter substrate should not have been a problem for either set of samples, since PTFE membranes were used for the collection of the fine fraction in both cases. Finally, the adsorption of NH_3 from air in the aircraft or laboratory onto acidic aerosol (particularly H_2SO_4) collected on the filters is always a possible artefact, even though exposure of the filters during handling was reduced to the minimum possible.

Our FT observations during ACE-2 are in good agreement with previous studies in the region. In the clean FT sampled during ASTEX in a study region just west of ours, Huebert et al. (1996b) found 105 ± 20 ppt NH_4^+, 45 ± 23 ppt NO_3^-, and 99 ± 12 ppt nss-SO_4^{2-}. Also during ASTEX, Harrison et al. (1996) report 140 ppt NH_4^+ and ca. 20 ppt each NO_3^- and nss-SO_4^{2-}. For comparison, the concentrations measured in the FT of the Southern Hemisphere around Tasmania during ACE-1 were 59 ppt NH_4^+, 19 ppt NO_3^-, and 48 ppt nss-SO_4^{2-}. In conclusion, we find that our value of 59 ppt nss-SO_4^{2-} is quite typical for a FT with little or no detectable anthropogenic influence, while our ammonium and nitrate data are somewhat elevated.

Our results, as well as those of Huebert et al. (1996b) and Harrison et al. (1996) suggest that the FT aerosol is almost completely acid-base neutral and that ammonium sulfate predominates. This is, however, in conflict with the results of Putaud et al. (2000) who finds an NH_4^+/SO_4^{2-} ratio of about 1, and with the volatility data of C. O'Dowd (personal communication, 1999) which are more indicative of ammonium bisulfate. To resolve this question it will be necessary to develop very rigorous procedures to eliminate the possibility of adsorption artefacts during sample handling on aircraft, and to conduct carefully designed intercalibrations to ensure that identical airmasses are sampled.

As noted above, soluble ionic species provide an aerosol mass of $0.39 \pm 0.21\ \mu g\ m^{-3}$ and $0.20 \pm 0.10\ \mu g\ m^{-3}$ in the fine and coarse fraction, respectively. From this, we can obtain a rough estimate of the scattering coefficient in the FT if we assume that this fraction accounts for about 50% of the total fine aerosol mass (Putaud et al., 2000), that scattering is dominated by the fine fraction, and that the mass scattering efficiency is about $4\ m^2\ g^{-1}$ (Clarke et al., 1996). The resulting estimate is $\sim 3\ Mm^{-1}$ at STP and 550 nm wavelength, which compares reasonably well with the value of ~1.8 Mm^{-1} at STP and 550 nm observed on the CIRPAS aircraft in the clean FT (S. Gasso, pers. comm., 1998). It is also consistent with the analysis of aerosol optical thickness under background conditions obtained from measurements at 3570 m altitude near the top of Pico de Teide on Tenerife (Formenti et al., 2000).

3.4. The marine boundary layer

3.4.1. SML composition as a function of airmass type. As expected, the concentrations of pollutant aerosol species and SO_2 in the SML are seen to decrease with increasing transport times and distances between pollution sources and the sampling site (Fig. 1, Table 3). However, the patterns of decrease are quite different for the various species. For SO_2, the most short-lived species considered here, there is little difference between European airmasses that have spent only two days over the sea, and airmasses with no land contact for the last 10 days, consistent with an SO_2 lifetime of the order of half a day in the SML (Blomquist et al., 1996; Dore et al., 2000; Johnson et al., 2000a). High SO_2 levels in the SML were only found in airmasses that had come over the Iberian Peninsula, particularly those that had made recent contact with the emission regions along the Portuguese coast (note the logarithmic scale in Fig. 1c).

This presents an interesting contrast to the observations made during ASTEX. While the range of concentrations encountered is quite similar (50–1400 ppt in the BL during ASTEX, (Blomquist et al., 1996)), there is a pronounced difference between the two campaigns in the concentrations measured in airmasses of apparently similar history. During ACE-2, SO_2 levels above 1000 ppt were limited to the region immediately off the SW tip of Portugal, while airmasses that had left the continent some 2 days prior to sampling typically had well below 100 ppt (The somewhat higher concentrations of SO_2 in our "Iberian" airmasses are attributed to emissions from power plants along the western coast of Spain and Portugal). During ASTEX, on the other hand, SO_2 levels of ca. 600 ppt were seen even two days after the airmasses had left Europe. These differences are probably not due to faster SO_2 oxidation during ACE-2, but to higher initial pollution loadings in the ASTEX airmasses. This is supported by comparison of the initial conditions of ASTEX Lagrangian 2 (~600 ppt SO_2 and ~4000 ppt SO_4^{2-}), and ACE LAG-3 (~100 ppt SO_2 and 1000 ppt SO_4^{2-}). In spite of similar airmass trajectories and source regions for these two

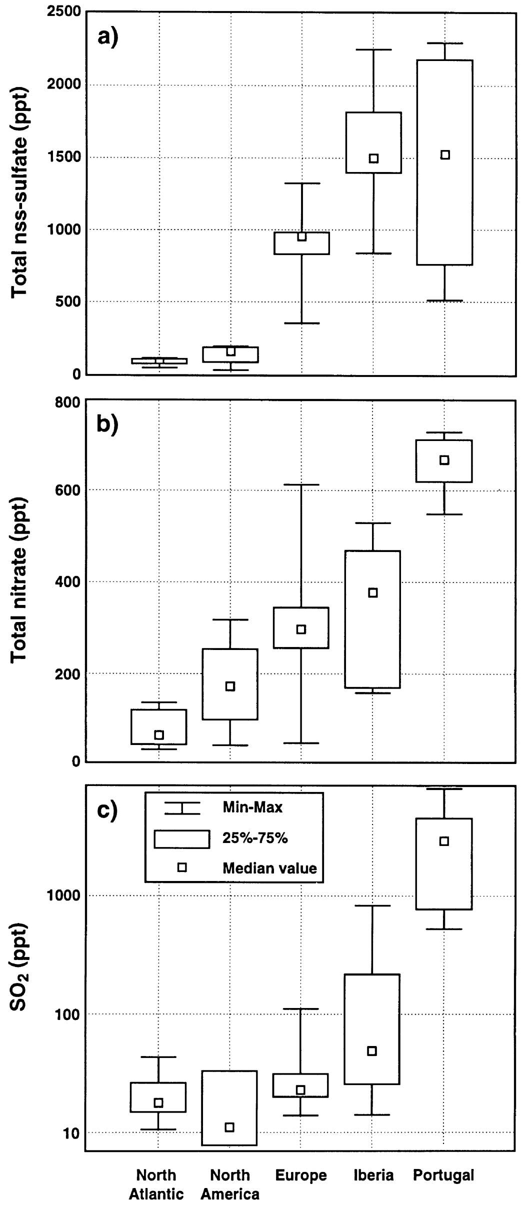

Fig. 1. Concentrations of total aerosol nss-sulfate (a), nitrate (b), and SO_2 (c) in the surface mixed layer as a function of airmass origin.

Table 3. *Soluble ionic aerosol species and SO_2 in surface mixed layer samples with different airmass origins (averages and standard deviations, in ppt)*

	N. Atlantic		N. America		Europe		Portugal			
					Iberia					
Fraction	fine	coarse	fine	coarse	fine	coarse	fine	coarse	fine	coarse
N	8		4		9		7		6	
Na^+	111 ± 48	670 ± 233	199 ± 120	904 ± 404	—	1230 ± 1220	—	1270 ± 1000	—	584 ± 202
NH_4^+	235 ± 53	—	354 ± 53	24 ± 11	2020 ± 690	—	2070 ± 400	127 ± 120	2822 ± 1337	181 ± 74
K^+	—	19 ± 8	—	26 ± 10	—	39 ± 27	—	35 ± 25	—	—
Mg^{2+}	18 ± 9	67 ± 19	23 ± 8	101 ± 54	17 ± 11	138 ± 146	33 ± 21	137 ± 98	26 ± 10	74 ± 17
Ca^{2+}	—	22 ± 12	—	—	—	57 ± 41	87 ± 55	122 ± 107	108 ± 28	237 ± 87
Cl^-	157 ± 62	586 ± 237	149 ± 22	750 ± 280	171 ± 159	875 ± 1106	197 ± 156	825 ± 900	91 ± 18	157 ± 107
NO_3^-	48 ± 23	46 ± 20	141 ± 117	68 ± 38	81 ± 48	255 ± 79	174 ± 124	213 ± 114	201 ± 76	451 ± 66
SO_4^{2-}	103 ± 24	44 ± 16	143 ± 70	71 ± 34	815 ± 238	174 ± 118	1350 ± 440	284 ± 70	1320 ± 690	173 ± 62
nss-SO_4^{2-}	98 ± 22	6 ± 3	131 ± 70	27 ± 15	807 ± 233	101 ± 46	1340 ± 430	211 ± 27	1310 ± 690	137 ± 51
MSA	—	3.1 ± 1.0	—	—	—	2.7 ± 2.0	—	4.8 ± 1.5	—	11.4 ± 3.4
$EF_{(Cl/Na)}$	1.00 ± 0.09	0.95 ± 0.10	0.89 ± 0.42	0.99 ± 0.12	0.64 ± 0.35	0.72 ± 0.15	0.66 ± 0.31	0.65 ± 0.17	0.38 ± 0.12	0.28 ± 0.17
SO_2	22 ± 11		17 ± 14		36 ± 30		170 ± 280		3120 ± 2670	

Values are given only if the species was detectable in more than half of the samples in a given category. The data are not corrected for inlet losses.

Lagrangians, concentrations of both short-lived (SO_2) and long-lived (SO_4^{2-}) sulfur species are 4–6 times higher in the airmass sampled during ASTEX, presumably due to differences in initial pollution loadings.

In contrast to the rapid decrease of SO_2 levels with the dwell time of the airmass over the ocean, the concentrations of particulate pollutants show a more gradual change. The differences between "North Atlantic" and "North American" airmasses are statistically significant ($p < 0.05$) only for ammonium, but the consistently higher concentrations for all pollutant species in the "North American" samples suggests that even the statistically less significant differences in other species are not due to chance. The amount of nss-SO_4^{2-} found in the "North American" airmasses is in reasonable agreement with the model predictions of Tarrasón and Iversen (1992), who predict about 40 ppt of sulfate of North American origin to be present in summer off the western coast of Europe.

Somewhat surprisingly, the largest differences between "North Atlantic" and "North American" airmasses are in fine ammonium and nitrate, suggesting the presence of ammonium nitrate aerosol in the fine fraction of the "North American" airmasses. These samples are also unusual for SML aerosols in that they show high nitrate in the fine relative to the coarse fraction, in contrast to the other samples taken during ACE-2 and to most previous observations made by us and other groups (e.g., Andreae et al., 1999; Berresheim et al., 1990; Huebert et al., 1996b; Savoie and Prospero, 1982). However, NH_4^+/SO_4^{2-} ratios of 2.0 and greater were found both in the boundary layer and in the free troposphere in polluted airmasses off the east coast of the United States during WATOX-86 (Whelpdale et al., 1987). Interestingly, these airmasses also contained substantial amounts of fine particulate nitrate, suggesting that observations of elevated concentrations of NH_4NO_3 may not be limited to European sites (Slanina et al., 1999). High NH_4^+ concentrations (ca. 500 ppt) and high NH_4^+/SO_4^{2-} ratios have also been observed in measurements spanning over a decade at the North Atlantic sampling sites Heimaey (Iceland) and Mace Head (Ireland) (J. M. Prospero and D. L. Savoie, pers. comm., 1999).

The "North Atlantic" SML airmasses during ACE-2 were very clean, with sulfate and nitrate levels well below those observed in the "clean" airmasses sampled during ASTEX (ca. 200 ppt NO3- and 350 ppt nss-SO_4^{2-}, Huebert et al., 1996b), and comparable to the lowest values found previously over the North Atlantic (Berresheim et al., 1991; Church et al., 1991; Galloway and Whelpdale, 1987; Harrison et al., 1996). The total NO_3^- concentration of ca. 100 ppt in these airmasses is only about twice that measured at remote island sites in the South Pacific (ca. 40–50 ppt; (Huebert et al., 1998; Prospero and Savoie, 1989)) and is comparable to values from island sites in the remote North Pacific (Prospero and Savoie, 1989) and to the background nitrate level at Barbados (Savoie et al., 1989). The total nss-SO_4^{2-} concentrations (ca. 150 ppt) are only slightly higher than summer levels from the cleanest temperate sites, such as from Cape Grim (Andreae et al., 1999; Ayers et al., 1991; Huebert et al., 1998) and from remote islands in the South Pacific (Savoie and Prospero, 1989).

In sharp contrast to these very clean airmasses are the samples collected in the SML influenced by the European pollution plume. Sulfate and nitrate concentrations are about one order of magnitude above the background, while SO_2 in the samples recently advected from Portugal is elevated more than two orders of magnitude. Still, as mentioned above, the pollution levels found over the Atlantic during ACE-2 are well below those measured during ASTEX, where nss-SO_4^{2-} and NO_3^- reached 4900 ppt and 2500 ppt, respectively, compared to the highest SML values during ACE-2 of 2300 and 720 ppt, respectively. Overall, however, our results from polluted airmasses over the North Atlantic are in good agreement with previous observations both on the eastern and western sides of the Atlantic (Berresheim et al., 1991; Duce et al., 1991; Galloway and Whelpdale, 1987; Whelpdale et al., 1987).

3.4.2. The cloud convection layer. In the CCL, the altitude region between cloudbase and the subsidence inversion, we were able to obtain 11 valid samples, representing either airmasses without land contact for the preceding 6–10 days, or airmasses that had passed over the European continent (Table 4). Comparison with the SML data in Table 2 shows that the composition of the CCL aerosol is nearly identical with that of the SML, when airmasses of the same type are com-

Table 4. *Soluble ionic aerosol species and SO_2 in cloud convection layer (CCL) samples with different airmass origins (averages and standard deviations, in ppt)*

	N. Atlantic		Europe	
N	5		6	
fraction	fine	coarse	fine	coarse
Na^+	179 ± 88	535 ± 302	—	540 ± 160
NH_4^+	197 ± 62	—	1420 ± 620	32 ± 5
K^+	—	—	—	44 ± 47
Mg^{2+}	25 ± 6	60 ± 33	13 ± 10	51 ± 20
Ca^{2+}	—	24 ± 9	—	62 ± 20
Cl^-	199 ± 80	395 ± 260	109 ± 74	280 ± 136
NO_3^-	43 ± 20	50 ± 37	81 ± 119	128 ± 45
SO_4^{2-}	94 ± 26	40 ± 20	760 ± 520	139 ± 51
nss-SO_4^{2-}	81 ± 26	17 ± 9	750 ± 520	110 ± 50
$EF_{(Cl/Na)}$	0.95 ± 0.12	0.87 ± 0.05	0.49 ± 0.21	0.56 ± 0.16
SO_2	12 ± 10		30 ± 23	

Values are given only if the species was detectable in more than half of the samples in a given category. The data are not corrected for inlet losses.

pared. The main exception is the seasalt component, which is significantly lower in the CCL than the SML, especially in the European airmasses. This may be a result of either seasalt removal by settling or drizzle formation, or of the entrainment of free tropospheric air (in the case of the N. Atlantic airmasses) or air from a polluted residual CBL (in the case of the European airmasses) into the CCL from above. We also find that the chloride enrichment factor, $EF_{(Cl/Na)}$, is lower in the CCL, suggesting that more chloride has been lost from the seasalt particles by reaction with SO_2 and HNO_3. These reactions may have occurred during cloud processing of air as it is being transported from the SML into the CCL. In the N. Atlantic CCL samples, SO_2 is lower than in the SML, which may also be a consequence of wet removal during cloud processing. Overall, we find that cloud processing had a relatively minor impact on the average composition of the boundary layer aerosol. A specific example where the effect is more pronounced will be presented below in the discussion of LAG-2.

3.4.3. Residual continental boundary layers (CBL). When continental airmasses are advected over the ocean, especially over relatively cold water, the weaker convective activity over water cannot sustain vertical mixing to the same height as over land. Consequently, a new, shallower SML evolves at the base of the CBL, and the residual CBL between the top of this new SML and the inversion at the top of the CBL becomes disconnected both from the FT and the sea surface (Johnson et al., 2000a). This evolution was most clearly observed during LAG-3 (Wood et al., 2000), but residual CBLs in their earliest stages of development were also encountered several times during the "Clear Lagrangian" (Flight A549 on 25 June) and CLEARCOLUMN experiments off the Portuguese coast (Flights A563 and A565 on 20 and 22 July).

The residual CBL airmasses (Table 5) are of particular interest in the context of ACE-2, insofar as they represent samples of the European plume that have not interacted to a measurable degree with the marine atmosphere. Evidence for this is the absence of significant amounts of seasalt elements in the coarse fraction. Comparison of the CBL and SML data from European airmasses shows that the fine fractions are not significantly different, with the exception of Ca^{2+}, which is higher in the CBL. In the coarse fraction, there is obviously an additional seasalt component in the SML, but NO_3^- and possibly nss-SO_4^{2-} are also elevated, indicating nitrate and sulfate formation or deposition on the seasalt particles. SO_2 may also be somewhat lower in the SML, but this difference is only marginally significant. The elevated CBL concentrations of Ca^{2+} in both size fractions may be due to a higher soil dust component in this layer.

In the Iberian airmasses, there is a much higher nss-SO_4^{2-} content in the SML (1350 ± 440 ppt)

Table 5. *Soluble ionic aerosol species and SO_2 in samples from residual continental boundary layers with different airmass origins (means and standard deviations, in ppt)*

	Europe		Iberia	
N	8		6	
fraction	fine	coarse	fine	coarse
Na^+	—	60 ± 24	—	—
NH_4^+	1310 ± 500	72 ± 28	1360 ± 510	105 ± 62
K^+	—	25 ± 15	—	24 ± 13
Mg^{2+}	4 ± 3	7 ± 7	25 ± 10	32 ± 20
Ca^{2+}	64 ± 47	141 ± 155	227 ± 93	354 ± 146
Cl^-	111 ± 91	26 ± 10	—	41 ± 34
NO_3^-	69 ± 70	54 ± 16	223 ± 184	114 ± 92
SO_4^{2-}	610 ± 262	71 ± 41	480 ± 280	76 ± 26
SO_2	54 ± 40		290 ± 320	

Values are given only if the species was detectable in more than half of the samples in a given category. The data are not corrected for inlet losses.

than in the overlying CBL (480 ± 280 ppt) samples. Conversion of SO_2 to sulfate in the SML can only explain part of this difference, since there is only 120 ppt more SO_2 in the CBL than in the SML. The higher sulfate concentrations in the lower layer may be explained by the existence of large emissions of SO_2 in the coastal region of Spain and Portugal (Raes et al., 2000), which would be trapped in the incipient SML at the coast, and therefore would not affect the CBL.

The composition of the CBL aerosol in Iberian airmasses closely resembles that found in air of continental origin sampled at the Portuguese coast (Pio et al., 1996). While our mean concentration is about half of Pio et al.'s long-term average, the proportions of the major ions are very similar. In both data sets, nitrate and sulfate are nearly fully neutralized by ammonium, and there is a substantial amount of submicron nitrate. In fact, in our samples there even appears to be slight excess of NH_4^+ over NO_3^- and SO_4^{2-}. This may be due to the unusual fact that they contain considerable amounts (400–600 ppt) of formate, an aerosol component that is only stable in the presence of high levels of ammonia or other alkaline substances. High NH_4^+ levels and a high ratio of submicron nitrate to sulfate has also been observed in the Netherlands (ten Brink et al., 1996), particularly when sampling techniques were used that eliminated ammonium nitrate evaporation losses during sampling. Preliminary data collected during ACE-2 at Sagres with the same techniques also show high NH_4^+ (up to 4000 ppt) and NO_3^- (up to 1500 ppt) concentrations (ten Brink, personal communication, 1999; Slanina et al., 1999). The mean nitrate/sulfate ratio at Sagres was 0.61 ± 0.28, identical to our ratio in the Iberian airmasses.

Overall, we find that, besides the obvious addition of seasalt aerosol, the effect of the transition from a continental to a marine boundary layer is rather subtle. The most obvious difference is the much higher concentration of non-seasalt Ca^{2+} in the CBL (204 and 581 ppt in 'European' and 'Iberian' airmasses, respectively) compared to the MBL with the same airmass origins (28 and 181 ppt, respectively). This suggests that soil dust is removed relatively rapidly, possibly by incorporation into drizzle or by dry deposition. There is a tendency for reduced sulfate content in the European airmasses, possibly also due to dry deposition, while coastal sources may add SO_2 and consequently nss-SO_4^{2-} to air flowing out of Iberia. SO_2 decreases rapidly in the SML, probably due to cloud processing, and NO_3^- and nss-SO_4^{2-} condensed or formed on the seasalt particles.

3.5. *The Clear-Air Lagrangian experiment off Sagres (25 June 99)*

The objective of this experiment was to characterize the initial phase of the transition from a continental to a marine boundary layer, and the chemical and aerosol microphysical changes that accompany this transition (Johnson et al., 2000a). In an attempt to conduct a Lagrangian experiment by following an airmass from the coast to the RVV, the ship was positioned about 200 km downwind of the instrumented sites near Sagres on the southwestern tip of Portugal. The aircraft conducted measurements along a presumed airmass trajectory from the Sagres site to the RVV. It executed a sawtooth pattern (20–1100 m altitude) from the ship to the coast, a stack of box patterns halfway between Sagres and the ship (Table 6), and flew vertical profiles over the coastal site and the ship. The airborne measurements showed a polluted CBL over land from the surface up to 2000 m MSL, which over the sea decreased in thickness towards the ship's position due to subsidence in the FT. In this layer, a moist SML

Table 6. *Submicron aerosol and SO_2 measurements from the Clear-Air Lagrangian Experiment off Sagres, 25 June 99 (in ppt); aircraft measurement from LAG-2 SML sampled at 200 m included for comparison*

			Aircraft				Aircraft
	Sagres 90 m	Sawtooth 20–1100 m	SML 30 m	CBL 430 m	FT 1900 m	R/V Vodyanitsky	LAG-2 200 m
Na^+	330	267	180	460	—	220	640
NH_4^+	2690	3100	706	5210	300	2270	2360
K^+	29	—	—	—	—	—	—
Mg^{2+}	47	31	21	54	—	—	73
Ca^{2+}	31	123	79	282	—	—	180
Cl^-	3	103	63	55	—	108	290
NO_3^-	29	194	126	483	<70	46	156
SO_4^{2-}	1950	1620	2120	2370	97	2500	1660
nss-SO_4^{2-}	1930	1600	2110	2340	97	2500	1630
MSA	—	—	—	—	—	63	—
neutralization ratio	0.69	0.90	0.16	1.0	<1.5	0.45	0.69
SO_2	3600–24000	4340 ± 260	7670 ± 460	3890 ± 240	42 ± 10	4420–8840	800

gradually developed, growing in depth from zero at the coast to 230 m at the ship's position, 200 km offshore.

Trajectory calculations for the morning of 25 June show that airmasses arriving at the ship up to about 0900 UT had left the coast near Sagres about 6 h earlier. At the time of the sawtooth pattern (0900–0930 UT), both the aircraft and the ship were still in the pollution plume, and the aircraft sampled the SML and the overlying CBL between 20 and 1100 m altitude. Beginning about 1000 UT, however, the flow shifted more to the west, and the airmasses sampled by the ship had left the western coast of Portugal at about 38.5°N and more than 12 h before, ending the conditions for a true Lagrangian experiment involving Sagres, the C-130, and the RVV. However, the aircraft's box patterns, being to the northeast of the ship's position, were still downwind of the coastal site, allowing an internally consistent analysis of the plume evolution over a range of up to about 200 km from the coast based on the aircraft data. The lowest sample in the stack of box patterns represents the SML, the sample at 430 m is in the uncoupled CBL above the newly formed SML, and the uppermost sample at 1900 m is from the FT above the pollution layer. The airflow at this level is unrelated to the flow below the inversion and suggests a North Atlantic airmass with some potential pollution inputs over southern Iberia.

The initial chemical composition of the airmass leaving the Portuguese coast was determined at the Sagres site (Table 6; C. Neusüß, pers. comm. 1999). Two aerosol samples were collected at Sagres around the time of the Clear-Air Lagrangian experiment, one from 24 June 1845 UT to 25 June 0750 UT, the other on 25 June between 1025 and 1414 UT. The value shown in Table 6 is the average concentration from these two samples. The coastal site was subjected to high levels of pollution from the power plants at Sines (80 km N of Sagres) and the urban plume of Lisbon, resulting in rapidly fluctuating SO_2 concentrations. Between 0600 and 0800 UT, when the airmass sampled by the aircraft left the coast, SO_2 fluctuated between 3600 and 24,000 ppt.

Because of this high variability in the initial airmass, we cannot identify a clear gradient in SO_2 between platforms. The surface SO_2 concentrations at Sagres, at the box pattern $\sim$100 km offshore ($\sim$8000 ppt), and at the ship $\sim$200 km offshore (4000–9000 ppt) are not significantly different. The lack of a pronounced gradient is consistent with the slow SO_2 oxidation expected under the prevailing cloud-free conditions and low relative humidity in the CBL, limiting SO_2 oxidation to homogeneous processes. Furthermore, the values in the SML sample may have been influenced by emissions from ship traffic, as numerous ship plumes were observed during this flight leg.

Much the same applies to the aerosol measurements. The fine sulfate concentrations from the surface samples (Sagres 90 m, Aircraft SML, and RVV) are quite similar (Table 6). The higher NO_3^- concentrations in the airborne samples may be in part due to the somewhat higher and less sharp size cut of our filter pack compared with the Berner impactor used on the ship and at Sagres (50% cutoff at 1.0–1.2 µm). The coarse nitrate concentrations at the Sagres site and on the ship were quite high (ca. 1300 ppt and 2700 ppt, respectively), and a relatively small leakage of this amount onto the fine stage of the filter pack could easily account for the amount found in the fine fraction. In the CBL, NO_3^- is considerably higher than in the SML, which could be due to the presence of NH_4NO_3, as suggested above. Some of the nitrate found in the CBL could also be adsorbed to mineral particles (Wolff, 1984).

On the other hand, NH_4^+ in the SML sample is considerably lower than in the surface samples. This results also in a lower neutralization ratio $\{NR = [NH_4^+]/(2 \cdot [SO_4^{2-}] + [NO_3^-])\}$ in the aircraft sample, for unknown reasons. The CBL, in contrast, shows much higher NH_4^+ levels, in agreement with our other CBL data of Iberian airmasses (Table 5), and the results of other investigators, who find an almost completely neutralized aerosol and high levels of fine NH_4^+ and NO_3^- in airmasses of continental origin at the Portuguese coast (Pio et al., 1996; Slanina et al., 1999). The sample from the sawtooth profile approximated the mean composition of the SML and CBL samples, except that SO_4^{2-} is relatively low. This may be related to inhomogeneities in the pollution layer along the flight track. As mentioned above, the air at 1900 m is completely disconnected from the flow below the inversion, and the chemical composition of the aerosol suggests a slightly polluted FT.

The composition and development of the CBL and SML advecting off the Portuguese coast in this experiment is of particular interest in the context of ACE-2, since the resulting boundary layer may be a prototype for the airmass that is encountered at the beginning of the second Lagrangian experiment (Table 6). As will be further discussed below, we find there a nearly identical aerosol composition, albeit with a somewhat higher seasalt fraction and lower SO_2 concentrations.

3.6. *Lagrangian 1 (3–5 July 1997)*

During this experiment, clean air masses from the temperate and northern North Atlantic were flowing into the study region. Backtrajectories show no contact of these airmasses with land for some 10 days before sampling. Subsidence compressed the boundary layer during the measurement period from about 1.5 to 0.9 km thickness (Fig. 2). Initially, the MBL consisted of two distinct sublayers, a SML up to 0.5 km and an overlying CCL up to 1.5 km that contained scattered cumulus and stratocumulus. During the experiment, the air was moving at increasing

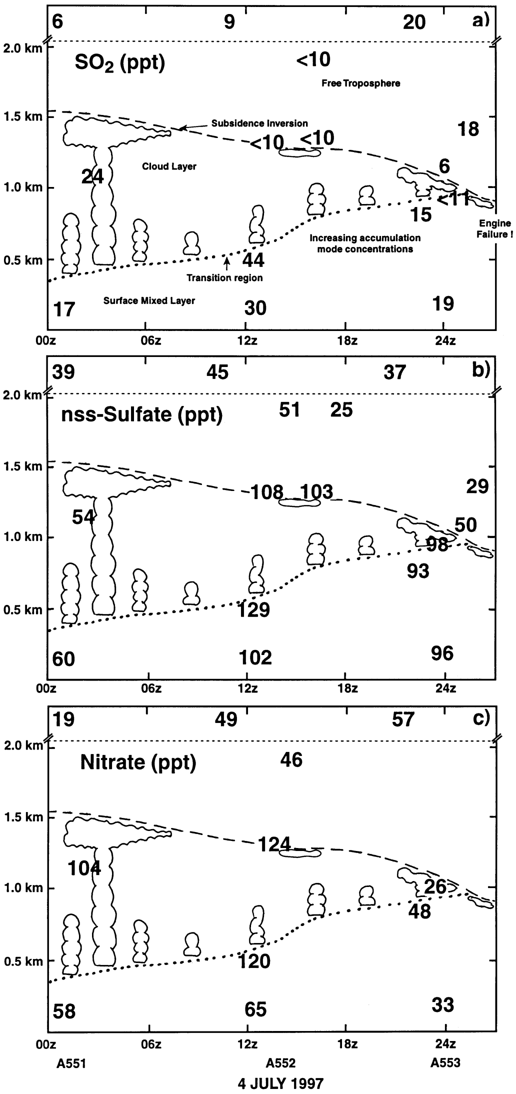

Fig. 2. Concentrations of SO_2 (a), nss-sulfate (b), and nitrate (c) during the 1st Lagrangian experiment.

windspeed over gradually warmer surface waters, which led to a heightening of the SML from 0.5 to 0.8 km. Simultaneously, the thickness of the CCL was reduced to some 100–200 m by the end of the experiment.

MBL SO_2 concentrations ranged from 15 to 44 ppt, with no systematic differences between SML and CCL (Fig. 2a). They were highest during mid-day, consistent with photochemical SO_2 production from DMS, but the data set is too small to prove that this temporal trend is significant. The SO_2 values during LAG-1 were typical of the clean MBL airmasses sampled during ACE-2, and comparable to the lowest SO_2 concentrations observed during ASTEX (Blomquist et al., 1996). They are similar to SO_2 measurements from clean remote oceanic regions, such as the Pacific and the Southern Ocean (Andreae et al., 1988; Ayers et al., 1997; Berresheim et al., 1990; De Bruyn et al., 1998; Thornton and Bandy, 1993), where they have been shown to be supported by DMS oxidation without significant anthropogenic inputs.

During the first five days of July, average DMS concentrations of 84 ppt were measured on the RVV. At a DMS lifetime of 19–29 h with respect to oxidation by OH in the MBL (K. Suhre, personal communication, 1999), we estimate a DMS oxidation rate of 70–104 ppt day^{-1}. Even at an SO_2 yield as low as 50%, this would correspond to a SO_2 production of ca. 35–52 ppt day^{-1}, enough to sustain the observed SO_2 concentrations if we assume SO_2 lifetimes of about 12 h. Neglecting SO_2 deposition to the sea surface, DMS oxidation via SO_2 could thus provide a nss-sulfate production rate of about the same magnitude, i.e., 30–50 ppt day^{-1}.

This rate of sulfate production corresponds roughly to the observed temporal trend of nss-sulfate in the MBL during LAG-1 (Fig. 2b). The initial concentrations of nss-SO_4^{2-} in the MBL are 60–80 ppt, in good agreement with the value of 85 ppt measured on the RVV around the time of balloon release. By midday, about 12 h later, nss-SO_4^{2-} in the MBL had grown to 100–130 ppt, and by the following midnight, it had decreased again slightly to 90–100 ppt, most likely due to entrainment of clean air from the FT (Johnson et al., 2000a). Overall, the nss-sulfate values measured during LAG-1 are of the same order as measurements over the remote Pacific, where they have been shown to be due to the oxidation of biogenic sulfur (Andreae et al., 1999; Huebert et al., 1996a).

The modest increase in nss-SO_4^{2-} during LAG-1 is accompanied by a 4-fold increase in the number concentration of accumulation mode particles detected by the PCASP probe (>0.12 μm diameter) from 50 to 200 cm^{-3} (Johnson et al., 2000a). A considerable part of this increase may be due to enhanced seasalt particle production as a result of increasing windspeeds during LAG-1 (Hoell et al., 2000). This suggestion is supported by the observation that coarse Na^+ rises from 440 to 800 ppt through the experiment. However, since over 90% of nss-sulfate was present in the fine fraction during LAG-1, the observed increase in this species must have also contributed to an increase in the mass concentration of the accumulation mode, and therefore possibly to an increase in its number concentration as well. Due to the low CCN concentration in the initial phase of LAG-1, a large fraction of particles down to relatively small sizes (ca. 0.06 μm) were activated during cloud cycling (Johnson et al., 2000a). Therefore, uptake of SO_2 and H_2SO_4 by cloud droplets and subsequent re-evaporation would have resulted in particle growth affecting also the size class between the nucleation threshold and the detection threshold of the PCASP, i.e., the range between ca. 0.06 and 0.12 μm. As a result, cloud cycling would produce an increase in the number of particles detected in the smallest size bins of the PCASP, as was in fact observed during LAG-1.

MBL nitrate concentrations during LAG-1 were in the range typical of unpolluted marine regions. There is some indication that concentrations in the CCL were higher than in the SML, and that concentrations of NO_3^- increased during the first half of the experiment, followed by a decrease during the second half to values below the initial ones (Fig. 2c). Most of the observed differences occur in the coarse fraction, while the concentrations in the fine fraction remain at about 30–50 ppt throughout the experiment.

3.7. *Lagrangian 2 (16–18 July 1997)*

In contrast to LAG-1, which investigated an essentially pristine airmass, LAG-2 was conducted under polluted conditions. The surface level trajectories (up to 500 m) originated over the open Atlantic and moved eastward toward the western coast of France, but then turned southwestward over or near the French coast without making prolonged contact with the European continent. Most important for the sulfur chemistry in the lowest layer was probably the subsequent brief transit over the northwestern tip of the Iberian Peninsula, where substantial point sources of SO_2 (power plants) are located (Raes et al., 2000). In addition to these stationary point sources, the air traveled also over the ocean region off the western coast of Iberia, which is one of the world's most densely traveled marine shipping corridors, and therefore has a high density of SO_2 and NO_x emissions from ships.

The CBL samples collected above the subsidence inversion are from airmasses originating over western Europe, which have complex trajectories. The trajectories in the altitude range from 1000 to 2000 m pass over Spain, France, Belgium and Germany, while at slightly higher altitudes (up to 3000 m) some trajectories curve back from Spain to North Africa. Of particular interest are a set of trajectories from the altitude range of 1100 to 1800 m. These cross Iberia and then pass over the western Mediterranean in the time period 12–15 July 1997, a time when an intense dust storm was visible in the same region on Meteosat imagery (F. Dulac, pers. comm., 1997). Overall, the trajectory analyses suggest the interaction of an initially clean MBL, to which recent SO_2 pollution has been added, with a CBL containing aged pollution from Central and Western Europe.

The chemical characteristics of the MBL and CBL at the beginning of LAG-2 are consistent with this analysis (Fig. 3). SO_2 concentrations are elevated in the MBL (ca. 800 ppt), and the nss-sulfate concentration is about 3 times that of SO_2. Data from the RVV suggest considerable internal inhomogeneity of the airmass; in the 6 h preceding the balloon launch, SO_2 varied between 200 and 2000 ppt, with a mean of 950 ppt. Aerosol composition from the RVV is available only in the form of one sample collected over the 9 h preceding the balloon launch. Fine nss-sulfate measured on the ship agrees very well with the aircraft measurements (1750 and 1630 ppt, respectively), while the coarse aerosol concentrations from the ship are significantly higher, as discussed above. In the overlying CBL, SO_2 is at background levels, and nss-sulfate is slightly elevated at about 200–300 ppt. Nitrate is initially fairly low in both layers.

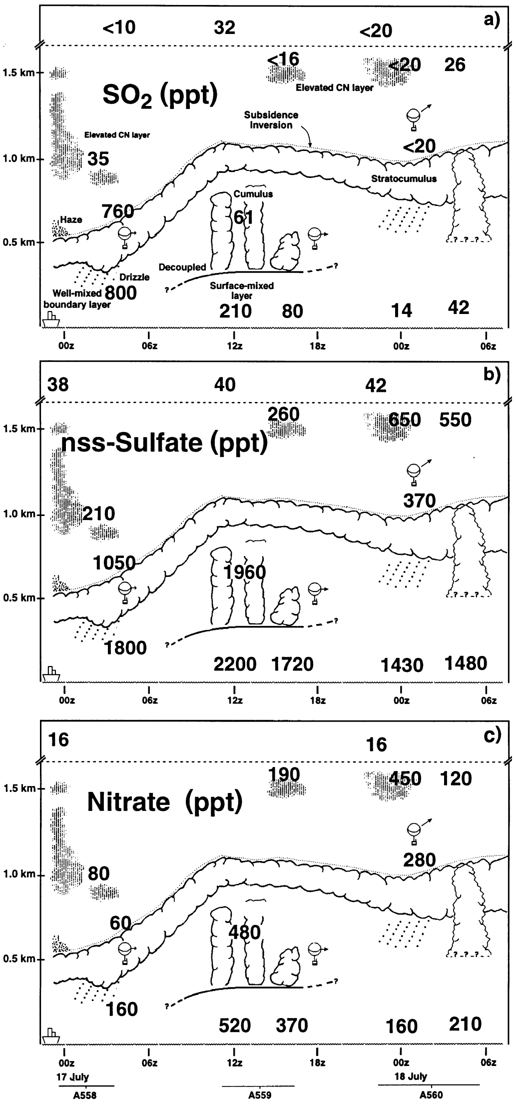

Fig. 3. Concentrations of SO_2 (a), nss-sulfate (b), and nitrate (c) during the 2nd Lagrangian experiment.

Since the relatively clean CBL cannot be the source of the enhanced sulfur species concentrations in the MBL, recent input of SO_2 (as suggested by the trajectories) and its oxidation to SO_4^{2-} is the most likely explanation. We can use the ratio of SO_2 to nss-SO_4^{2-} of about 1:2.5, observed on both aircraft and ship, for a rough estimate of the

SO_2 lifetime in the MBL during its travel from the source region. If we assume that all sulfur (nss-SO_4^{2-} plus SO_2) in this airmass above the background level of ca. 150 ppt present in clean airmasses was added as SO_2 over northern Spain, the initial SO_2 concentration would have been ca. 2250 ppt. From this estimated initial value over northern Spain, the SO_2 concentration dropped by about a factor of 2.8 during transport, to arrive at the beginning of LAG-2 with a SO_2 concentration of about 800 ppt. As this ratio is numerically almost identical to e (2.72), we estimate the lifetime of SO_2 to be about the same as the travel time of ca. 12–18 h, a reasonable value for a shallow MBL capped by stratocumulus. Since we have ignored SO_2 losses due to dry deposition in this calculation, our lifetime estimate represents an upper limit, and would be reduced proportionately to the fraction of SO_2 removed by dry deposition.

SO_2 decreased further during the first 12 h of LAG-2 to about 60–210 ppt, with the lowest value in the CCL. This drop is probably due to a combination of liquid phase oxidation and dilution with CBL air, implied by the increasing thickness of the MBL. Osborne et al. (2000) have shown that most cloud processing during LAG-2 took place during this period, in which the depth of the MBL increases from 500 to 1000 m and a decoupled cloud layer developed over the SML. Model calculations of the chemical evolution in the MBL suggest a SO_2 lifetime of only 6.5 h due to oxidation and dilution during this period (Dore et al., 2000). At the same time, while most of the SO_2 was being removed, nss-sulfate remained approximately constant around 2000 ppt. This suggests that the production of nss-sulfate from SO_2 oxidation was balanced by dilution due to the entrainment of less sulfate-rich air from the overlying residual CBL air. After the supply of SO_2 was practically exhausted by the time of the second flight (A559), dilution by entrainment continued, resulting in a reduction of the nss-sulfate concentration in the MBL by about 25%. Deposition probably played a minor rôle, as drizzle did not reach the surface except during the very beginning of the experiment (Osborne et al., 2000) and dry deposition of submicron sulfate would be too slow to make a noticeable difference over the 30-h duration of the experiment. At the end of LAG-2, SO_2 concentrations were down to 15–40 ppt, the levels found in the clean North Atlantic airmasses.

The neutralization ratio in the fine fraction in the MBL is a relatively low 0.68, consistent with a preponderance of SO_2 over NH_3 sources in northern Iberia, whereas the aerosol in the CBL is almost completely neutralized (NR = 0.96), as is typical of aged pollution in Western Europe. Particulate nitrate in the MBL was initially at ca. 160 ppt, increased during the daytime to about 500 ppt during the second flight, and decreased to near 200 ppt near the end of the experiment. This could be explained by photochemical production of HNO_3 from NO_x emitted by the dense ship traffic in the ACE-2 region (Lawrence and Crutzen, 1999), subsequent attachment of HNO_3 on the seasalt aerosol, and relatively rapid deposition of the coarse nitrate.

During LAG-2, the presence of mineral dust aerosol was evident from high amounts of soluble calcium in the samples from the CBL. The soluble Ca^{2+} concentrations in this layer ranged from 280 to 850 ppt, with a mean of 500 ± 230 ppt. These high Ca^{2+} values are most likely due to the fact that the air in the layer between 1100 and 1900 m passed through the region of a dust storm over the western Mediterranean. In the same layer, aerosol nitrate is also elevated in several samples (Fig. 3c). This may be related to the uptake of HNO_3 on the mineral dust surfaces, a phenomenon that has been observed previously in the Saharan dust plume (Andreae and Crutzen, 1997, and references therein). The presence of considerable amounts of Ca^{2+} in the first MBL sample of LAG-2 (530 ppt) suggests that either dust was settling into this layer from above, or that considerable entrainment of CBL air into the MBL was taking place at this time.

3.8. *Lagrangian 3 (23–24 July 1997)*

Whereas the airmass studied in LAG-2 had experienced a recent addition of SO_2, the third Lagrangian experiment investigated an airmass containing a mature aerosol with no recent pollution inputs. The 10-day backtrajectories for boundary layer airmasses sampled below 1400 m during LAG-3 originated in the high Arctic, then followed a generally southwesterly path through the Baltic region and Scandinavia. About 3–4 days before arriving at the sampling region, they passed over northern Germany, the Netherlands, Belgium and northern France. Air sampled between 1500 and 2100 m also originated in the Arctic, but passed over England rather than over Germany and the Low Countries. All these airmasses left the European continent about 2 days before the beginning of LAG-3 and did not make contact with land again prior to sampling.

The boundary layer evolution during LAG-3 is dominated by two phenomena, large-scale subsidence reducing the thickness of the BL from ~2100 m at the beginning to ~1200 m at the end of the experiment, and the growth of a marine internal boundary layer (MIBL) within the residual CBL (Fig. 4). At the beginning of LAG-3, the MIBL is about 500 m thick, and reaches about 1000 m by the end of the experiment. Within the MIBL, cumulus and stratocumulus developed in the CCL, above a relatively thin SML (300–400 m cloudbase).

The chemical composition of the airmass at the beginning of LAG-3 reflects its history. The entire BL, including the MIBL and the overlying residual CBL are strongly polluted, with SO_4^{2-} concentrations of 1120 ppt within the MIBL, somewhat lower levels in the residual CBL, and the highest concentrations (1900 ppt) in a layer near 2000 m (Fig. 4b). This layer, which also showed the highest number concentrations of accumulation mode particles, has a different origin from the underlying airmass. It received pollution inputs in the UK, rather than the region from northern Germany to Belgium.

The chemical composition of the aerosol is consistent with these differences in airmass origin (Table 7). Northern Germany and the Netherlands are prolific emitters of ammonia as a result of intensive animal husbandry, resulting in a very ammonium-rich aerosol in the samples taken below ca. 1000 m. The UK, on the other hand, has lower ammonium emissions, but strong sources of SO_2 from power plants, producing an aerosol with a substantially lower neutralization ratio. The upper pollution layer was only found during the first flight of LAG-3. Given the significant amount of wind shear between the upper layer and the main pollution layer below, it most likely was removed from the sampling area by advection.

A notable feature of the pollution layer during LAG-3, is the presence of considerable amounts of Cl^- in the submicron fraction. The low concentrations of Mg^{2+} found in these samples show that this Cl^- cannot be accounted for by seasalt aerosol (unfortunately, no fine fraction Na^+ data are available for the flights after 11 July). We propose that fine nss-chloride may be due to emissions from coal-fired power plants, which release substantial amounts of HCl (Meij, 1994). In the presence of alkaline dust or ammonia, HCl can become incorporated into the particulate phase (Tomza et al., 1982). Fine nss-chlorine was especially abundant in the samples from the upper levels of the pollution layer with airmass origins

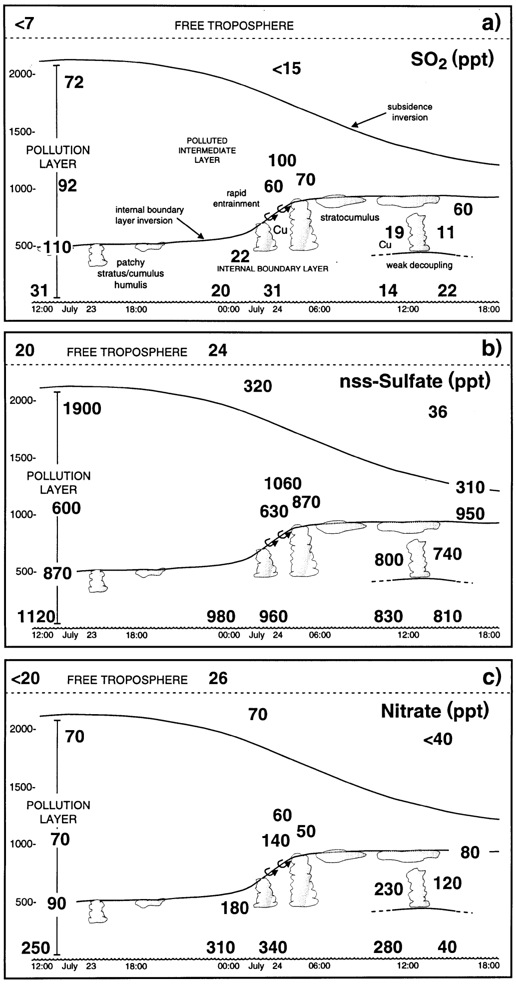

Fig. 4. Concentrations of SO_2 (a), nss-sulfate (b), and nitrate (c) during the 3rd Lagrangian experiment.

Table 7. *Submicron aerosol and SO_2 measurements from the first flight of the 3rd Lagrangian Experiment (ppt)*

	SML, 120m	CBL, 520 m	CBL, 1000 m	CBL, 1920 m
Na^+	—	—	—	—
NH_4^+	2190	1640	1240	2060
Mg^{2+}	10	<1	1	<1
Ca^{2+}	<30	<30	<30	<30
Cl^-	77	150	45	204
NO_3^-	63	87	66	27
SO_4^{2-}	1040	810	560	1630
nss-SO_4^{2-}	1030	810	560	1630
MSA	—	—	—	—
neutralization ratio	1.0	0.96	1.0	0.63
SO_2	31	110	92	72

in the UK, where coal accounted for almost 40% of electricity generation in 1997 (UK Government Statistical Service, 1998).

The chemical evolution of the BL aerosol during LAG-3 is constrained by the fact that SO_2 had almost reached background levels at the beginning of the experiment (Fig. 4a). In the SML, the initial SO_2 concentration around mid-day is 31 ppt, the same as the mid-day values measured during the clean LAG-1. The concentrations in the residual CBL are somewhat higher at 60–110 ppt, presumably because of the longer SO_2 lifetime in the absence of wet oxidation and dry deposition. As the MIBL grows into the CBL during the experiment, SO_2 is removed from the entrained CBL air, and at the end SML and CCL both show levels of 10–20 ppt, comparable to clean MBL air with transatlantic trajectories. If we take the difference between initial and final SO_2 concentrations in the MIBL (ca. 70 ppt) and a rate of ca. 40 ppt day^{-1} as an estimate for the possible sulfate production from DMS, we find that some 110 ppt SO_4^{2-} could have been produced during LAG-3 and added to the pre-existing aerosol population.

This sulfate production did not lead, however, to an observable increase in the mass concentration of sulfate or the number concentration of accumulation mode aerosol during LAG-3. Rather, the accumulation mode particles in the MIBL drop from about 1000 cm^{-3} at the beginning of the experiment to ca. 880 cm^{-3} at the end (Wood et al., 2000), while nss-SO_4^{2-} decreases from 1120 to 830 ppt (Fig. 4b). The aerosol size spectra show no evidence for new particle formation and no change in the number/size distribution during LAG-3. This suggests that the aerosol population has reached a steady state with respect to its size distribution, and the observed slow decrease in the MIBL is the result of a combination of dry deposition and dilution with the overlying CBL. Accordingly, the sulfate concentration averaged over the BL column (excluding the high altitude layer present only on the first flight) did not show any significant change during the experiment (Fig. 4b).

Particulate nitrate in the polluted CBL (50–70 ppt) is lower than in the MBL (120–340 ppt), presumably due to partitioning of gaseous HNO_3 to the particulate phase at the higher humidities and seasalt concentrations in the MIBL. In contrast to sulfate, there is no significant decrease of aerosol nitrate in the MIBL, and the column-averaged concentration actually increases. Since the ACE-2 region contains numerous intensively used shipping lanes, it is possible that emissions from ships result in elevated NO_x levels in the MIBL (Lawrence and Crutzen, 1999) and consequently contribute to aerosol nitrate production.

4. Conclusions

The flight experiments on the MRF C-130 aircraft during the Second Aerosol Characterization Experiment (ACE-2) offered opportunities to characterize the distribution of SO_2 and the chemical composition of aerosols in polluted and clean airmasses over the North Atlantic. During a series of Lagrangian experiments, the chemical evolution of polluted continental airmasses over the ocean was investigated.

In those cases where the airmasses had not made contact with land for some 6–10 days, the SO_2 levels and aerosol ion concentrations approached values typical for the clean marine troposphere, in spite of the proximity of the sampling region to the European and African continents. During the first Lagrangian experiment (LAG-1), the evolution of such an airmass was followed over some 24 h. The chemical changes in this airmass were consistent with a scenario dominated by the conversion of biogenic DMS to SO_2 and sulfate aerosol.

Analysis of the results of the "Clear-Air" Lagrangian and the polluted Lagrangian experiments LAG-2 and LAG-3 provided insight into the different phases of the transition of a polluted continental airmass into a marine one. The evolution of the thermodynamic structure of the boundary layer is accompanied by changes in chemical composition and aerosol size spectra. In the initial phase of the transition, SO_2 is rapidly converted to sulfate, predominantly by oxidation in cloud droplets and in the liquid phase of seasalt aerosol particles. SO_2 lifetimes of about half a day or less are consistent with the observed rate of decrease in SO_2 concentration during LAG-2. This phase or airmass evolution is completed after about 2 days of transport over the ocean, at which time SO_2 has dropped to near-background levels.

This situation was encountered at the beginning of LAG-3, when only a small amount of anthropogenic SO_2 was left over. Together with the SO_2 derived from DMS, and in the absence of significant wet removal, SO_2 oxidation was able to stabilize column-average sulfate aerosol concentrations during LAG-3. At the end of LAG-3, however, there was no SO_2 left beyond what can be supplied by DMS oxidation. From this time on therefore, about 3–4 days after the airmass left the continent, sulfate levels are expected to decrease.

Particulate nitrate was formed whenever alkaline surfaces were available in the form of seasalt or dust aerosol. In several instances, this was followed by a decline in particulate nitrate concentrations consistent with the dry deposition of nitrate associated with coarse particles.

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REFERENCES

Andreae, M. O. 1995. Climatic effects of changing atmospheric aerosol levels. In: A. Henderson-Sellers (ed.), *World Survey of Climatology*, vol. 16: *Future climates of the world*. Elsevier, Amsterdam, pp. 341–392.

Andreae, M. O., Berresheim, H., Andreae, T. W., Kritz, M. A., Bates, T. S. and Merrill, J. T. 1988. Vertical distribution of dimethylsulfide, sulfur dioxide, aerosol ions, and radon over the northeast Pacific Ocean. *J. Atmos. Chem.* **6**, 149–173.

Andreae, M. O. and Crutzen, P. J. 1997. Atmospheric aerosols: biogeochemical sources and role in atmospheric chemistry. *Science* **276**, 1052–1056.

Andreae, M. O., Elbert, W., Cai, Y., Andreae, T. W. and Gras, J. 1999. Non-seasalt sulfate, methanesulfonate, and nitrate aerosol concentrations and size distributions at Cape Grim, Tasmania. *J. Geophys. Res.* **104**, 21,695–21,706.

Ayers, G. P., Ivey, J. P. and Gillett, R. W. 1991. Coherence between seasonal cycles of dimethyl sulphide, methanesulphonate and sulphate in marine air. *Nature* **349**, 404–406.

Ayers, G. P., Cainey, J. M., Gillett, R. W., Saltzman, E. S. and Hooper, M. 1997. Sulfur dioxide and dimethyl sulfide in marine air at Cape Grim, Tasmania. *Tellus* **49B**, 292–299.

Berresheim, H., Andreae, M. O., Ayers, G. P. and Gillett, R. W. 1989. Distribution of biogenic sulfur compounds in the remote southern hemisphere. In: E. S. Saltzman and W. J. Cooper (eds.). *Biogenic sulfur in the environment*. ACS Symposium Series, Washington, D.C., pp. 352–366.

Berresheim, H., Andreae, M. O., Iverson, R. L. and Li, S.-M. 1991. Seasonal variations of dimethylsulfide emissions and atmospheric sulfur and nitrogen species over the western North Atlantic Ocean. *Tellus* **43B**, 353–372.

Berresheim, L., Andreae, M. O., Ayers, G. P., Gillett, R. W., Merrill, J. T., Davis, V. J. and Chameides, W. L. 1990. Airborne measurements of dimethylsulfide, sulfur dioxide, and aerosol ions over the Southern Ocean south of Australia. *J. Atmos. Chem.* **10**, 341–370.

Blomquist, B. W., Bandy, A. R. and Thornton, D. C.

1996. Sulfur gas measurements in the eastern North Atlantic Ocean during the Atlantic Stratocumulus Transition Experiment/ Marine Aerosol and Gas Exchange. *J. Geophys. Res.* **101**, 4377–4392.

Bower, K. N., Choularton, T. W., Gallagher, M. W., Beswick, K. M., Flynn, M., Allen, A. G., Davison, B. M., James, J. D., Robertson, L., Harrison, R. M., Hewitt, C. N., Cape, J. N., McFadyen, G. G., Martinsson, B. G., Frank, G., Swietlicki, E., Zhou, J., Berg, O. H., Mentes, B., Papaspiropoulos, G., Hansson, H.-C., Kulmala, M., Aalto, P., Väkevä, M., Berner, A., Bizjak, M., Fuzzi, S., Laj, P., Facchini, M.-C., Orsi, G., Ricci, L., Nielsen, M., Allan, B. J., Coe, H., McFiggans, G., Plane, J. M. C., Collett, J. L., Jr., Moore, K. F. and Sherman, D. E. 2000. ACE-2 Hillcloud: an overview of the ACE-2 ground based cloud experiment. *Tellus* **52B**, in press.

Church, T. M., Tramontano, J. M., Whelpdale, D. M., Andreae, M. O., Galloway, J. N., Keene, W. C., Knap, A. H. and Tokos, J. 1991. Atmospheric and precipitation chemistry over the North Atlantic Ocean: shipboard results from April–May 1984. *J. Geophys. Res.* **96**, 18,705–18,725.

Clarke, A. D., Porter, J. N., Valero, F. P. J. and Pilewskie, P. 1996. Vertical profiles, aerosol microphysics, and optical closure during the Atlantic Stratocumulus Transition Experiment: measured and modeled column optical properties. *J. Geophys. Res.* **101**, 4443–4453.

Curtius, J., Sierau, B. and Arnold, F. 1998. *Airborne measurements of aerosol sulfuric acid and aerosol precursor gases in the free troposphere during the FREETROPE/ACE 2 experiment.* IGAC Symposium, Seattle, Wash.

De Bruyn, W. J., Bates, T. S., Cainey, J. M. and Saltzman, E. S. 1998. Shipboard measurements of dimethyl sulfide and SO_2 southwest of Tasmania during the First Aerosol Characterization Experiment (ACE 1). *J. Geophys. Res.* **103**, 16703–16711.

Dore, A., Johnson, D., Osborne, S., Choularton, T., Bower, K., Andreae, M. O. and Bandy, B. 2000. Evolution of boundary layer aerosol particles due to in-cloud chemical reactions during the second Lagrangian experiment of ACE-2. *Tellus* **52B**, in press.

Draxler, R. R. and Hess, G. D. 1997. *Description of the HYSPLIT_4 modeling system.* NOAA Technical Memorandum ERL ARL-224.

Duce, R. A., Liss, P. S., Merrill, J. T., Atlas, E. L., Buat-Menard, P., Hicks, B. B., Miller, J. M., Prospero, J. M., Arimoto, R., Church, T. M., Ellis, W., Galloway, J. N., Hansen, L., Jickells, T. D., Knap, A. H. and Reinhardt, K. H. 1991. The atmospheric input of trace species to the world ocean. *Global Biogeochem. Cycles* **5**, 193–259.

Ferek, R. J., Covert, P. A. and Luke, W. 1997. Intercomparison of measurements of sulfur dioxide in ambient air by carbonate-impregnated filters and Teco pulsed-fluorescence analyzers. *J. Geophys. Res.* **102**, 16267–16272.

Formenti, P., Andreae, M. O. and Lelieveld, J., 2000. Measurements of aerosol optical depth in the North Atlantic free troposphere: results from ACE-2. *Tellus* **52B**, in press.

Ferek, R. J., Hegg, D. A., Herring, J. A. and Hobbs, P. V. 1991. An improved filter pack technique for airborne measurement of low concentrations of SO_2. *J. Geophys. Res.* **96**, 22,373–22,378.

Galloway, J. N. and Whelpdale, D. M. 1987. WATOX-86 overview and western North Atlantic Ocean S and N atmospheric budgets. *Global Biogeochem. Cycles* **1**, 261–281.

Harrison, R. M., Peak, J. D. and Kaye, A. D. 1996. Atmospheric aerosol major ion composition and cloud condensation nuclei over the northeast Atlantic. *J. Geophys. Res.* **101**, 4425–4434.

Hoell, C., O'Dowd, C., Johnson, D. W., Osborne, S. R. and Wood, R. 2000. A time scale analysis of aerosol evolution in polluted and clean Lagrangian case studies. *Tellus* **52B**, in press.

Huebert, B. J., Wylie, D. J., Zhuang, L. and Heath, J. A. 1996a. Production and loss of methanesulfonate and non-sea salt sulfate in the equatorial Pacific marine boundary layer. *Geophys. Res. Lett.* **23**, 737–740.

Huebert, B. J., Zhuang, L., Howell, S., Noone, K. and Noone, B. 1996b. Sulfate, nitrate, methanesulfonate, chloride, ammonium, and sodium measurements from ship, island, and aircraft during the Atlantic Stratocumulus Transition Experiment/Marine Aerosol Gas Exhange. *J. Geophys. Res.* **101**, 4413–4423.

Huebert, B. J., Howell, S. G., Zhuang, L., Heath, J. A., Litchy, M. R., Wylie, D. J., Kreidler-Moss, J. L., Coppicus, S. and Pfeiffer, J. E. 1998. Filter and impactor measurements of anions and cations during the First Aerosol Characterization Experiment (ACE 1). *J. Geophys. Res.* **103**, 16493–16509.

John, W., Hering, S., Reischl, G., Sasaki, G. and Goren, S. 1983. Characteristics of Nuclepore filters with large pore size (II). Filtration properties. *Atmos. Environ.* **17**, 373–382.

Johnson, D. W., Osborne, S., Wood, R., Suhre, K., Johnson, R., Businger, S., Quinn, P. K., Wiedensohler, A., Durkee, P., Russell, L. M., Andreae, M. O., O'Dowd, C., Noone, K., Bandy, B., Rudolph, J. and Rapsomanikis, S. 2000a. An overview of the Lagrangian experiments undertaken during the North Atlantic regional Aerosol Characterization Experiment (ACE-2). *Tellus* **52B**, in press.

Johnson, D. W., Osborne, S. R., Wood, R., Suhre, K., Quinn, P. K., Bates, T., Andreae, M. O., Noone, K., Glantz, P., Bandy, B., Rudolph, J. and O'Dowd, C. 2000b. Observations of the evolution of the aerosol, cloud and boundary layer characteristics during the first ACE-2 Lagrangian experiment. *Tellus* **52B**, in press.

Lawrence, M. G. and Crutzen, P. J. 1999. Influence of NO_x emissions from ships on tropospheric photochemistry and climate. *Nature* **402**, 167–170.

Meij, R. 1994. Trace element behavior in coal-fired power plants. *Fuel Processing Technology* **39**, 199–217.

Neusüß, C., Weise, D., Birmili, W., Wiedensohler, A. and Covert, D. 2000. Size-segregated chemical, gravimetrical and number-distribution derived mass closure of the marine aerosol in Sagres (Portugal) during ACE-2. *Tellus* **52B**, in press.

Ockelmann, G., Bürgermeister, S., Ciompa, R. and Georgii, H.-W. 1987. Aircraft measurements of various sulfur compounds in a marine and continental environment. In: G. Angeletti and G. Restelli (eds.). *Physico-chemical behaviour of atmospheric pollutants.* Reidel, Dordrecht, pp. 596–603.

Osborne, S. R., Johnson, D. W., Wood, R., Bandy, B. J., Andreae, M. O., O'Dowd, C. D., Glantz, P., Noone, K., Rudolph, J., Bates, T. and Quinn, P. 2000. Evolution of the aerosol, cloud, and boundary layer dynamic and thermodynamic characteristics during the second Lagrangian experiment of ACE-2. *Tellus* **52B**, in press.

Pio, C. A., Cerqueira, M. A., Castro, L. M. and Salgueiro, M. L. 1996. Sulfur and nitrogen compounds in variable marine/continental air masses at the southwest European coast. *Atmos. Environ.* **30**, 3115–3127.

Prospero, J. M. and Savoie, D. L. 1989. Effect of continental sources on nitrate concentrations over the Pacific Ocean. *Nature* **339**, 687–689.

Putaud, J. P., van Dingenen, R., Mangoni, M., Virkkula, A., Raes, F., Maring, H., Prospero, J. M., Swietlicki, E., Berg, O. H., Hillamo, H. and Mäkelä, T. 2000. Chemical mass closure and origin assessment of the submicron aerosol in the marine boundary layer and the free troposphere at Tenerife during ACE-2. *Tellus* **52B**, in press.

Quinn, P. K., T. S. Bates, Coffman, D. J., Miller, T. L., Johnson, J. E. and Covert, D. S. 2000. A comparison of aerosol chemical and optical properties from the First and Second Aerosol Characterization Experiments. *Tellus* **52B**, in press.

Raes, F., Bates, T. F., McGovern, F. M. and Van Liedekerke, M. 2000. The second Aerosol Characterization Experiment: General overview and main results. *Tellus* **52B**, in press.

Rocklin, R. D., Pohl, C. A. and Schibler, J. A. 1987. Gradient elution in ion chromatography. *J. Chrom.* **411**, 107–119.

Savoie, D. L. and Prospero, J. M. 1982. Particle size distribution of nitrate and sulfate in the marine atmosphere. *Geophys. Res. Lett.* **9**, 1207–1210.

Savoie, D. L. and Prospero, J. M. 1989. Comparison of oceanic and continental sources of non-seasalt sulphate over the Pacific Ocean. *Nature* **339**, 685–687.

Savoie, D. L., Prospero, J. M. and Saltzman, E. S. 1989. Non-seasalt sulfate and nitrate in trade wind aerosols at Barbados: evidence for long-range transport. *J. Geophys. Res.* **94**, 5069–5080.

Schmeling, M., Russell, L. M., Erlick, C., Collins, D. R., Jonsson, H., Wang, Q., Kregsamer, P. and Streli, C. 2000. Chemical composition and characterization of aerosol particles from Pelican flights in clean, anthropogenically-influenced and dust-containing air masses during ACE-2. *Tellus* **52B**, in press.

Slanina, J., Ten Brink, H. M. and Khlystov, A. 1999. Fate of products of degradation processes: consequences for climatic change. *Chemosphere* **38**, 1429–1444.

Talbot, R. W., Andreae, M. O., Berresheim, H., Artaxo, P., Garstang, M., Harriss, R. C., Beecher, K. M. and Li, S. M. 1990. Aerosol chemistry during the wet season in Central Amazonia: the influence of long-range transport. *J. Geophys. Res.* **95**, 16,955–16,969.

Tarrasón, L. and Iversen, T. 1992. The influence of north American anthropogenic sulfur emissions over western Europe. *Tellus* **44B**, 114–132.

Tegen, I., Hollrig, P., Chin, M., Fung, I., Jacob, D. and Penner, J. 1997. Contribution of different aerosol species to the global aerosol extinction optical thickness: estimates from model results. *J. Geophys. Res.* **102**, 23,895–23,915.

Ten Brink, H. M., Veefkind, J. P., Waijers-Ijpelaan, A. and van der Hage, J. C. 1996. Aerosol light-scattering in the Netherlands. *Atmos. Environ.* **30**, 4251–4261.

Thornton, D. C. and Bandy, A. R. 1993. Sulfur dioxide and dimethyl sulfide in the Central Pacific troposphere. *J. Atmos. Chem.* **17**, 1–13.

Tomza, U., Maenhaut, W. and Cafmeyer, J. 1982. Trace elements in atmospheric aerosols at Katowice, Poland. In: D. D. Hemphill (ed.), *Trace substances in environmental health* (XVI). Univ. of Missouri Press, Columbia, MS, pp. 105–115.

UK Government Statistical Service, 1998. *UK Energy in Brief*. UK Stationery Office, London.

Verver, G., Raes, F., Vogelenzang, D. and Johnson, D. 2000. The second Aerosol Characterization Experiment: meteorological and chemical overview. *Tellus* **52B**, in press.

Warneck, P. 1988. *Chemistry of the natural atmosphere.* Academic Press, Inc., San Diego, 757 pp.

Whelpdale, D. M., Keene, W. C., Hansen, A. D. A. and Boatman, J. 1987. Aircraft measurements of sulfur, nitrogen and carbon species during WATOX-86. *Global Biogeochem. Cycles* **1**, 357–368.

Wolff, G. T. 1984. On the nature of nitrate in coarse continental aerosols. *Atmos. Environ.* **18**, 977–981.

Wood, R., Johnson, D., Osborne, S., Andreae, M. O., Bandy, B., Bates, T., O'Dowd, C., Glantz, P., Noone, K., Quinn, P., Rudolph, J. and Suhre, K. 2000. Boundary layer and aerosol evolution during the third Lagrangian experiment of ACE-2. *Tellus* **52B**, in press.