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Aerosol Direct Radiative Impact Experiment (ADRIEX) overview

E. J. Highwood,[a]* J. M. Haywood,[b] H. Coe,[c] J. Cook,[a] S. Osborne,[b] P. Williams,[c] J. Crosier,[c] K. Bower,[c] P. Formenti,[d] J. McQuaid,[e] B. Brooks,[e] G. Thomas,[f] R. Grainger,[f] F. Barnaba,[g] G. P. Gobbi,[g] G. de Leeuw[h] and J. Hopkins[i]

[a] *University of Reading, UK*
[b] *Met Office, UK*
[c] *University of Manchester, UK*
[d] *LISA, Creteil, France*
[e] *University of Leeds, UK*
[f] *University of Oxford, UK*
[g] *ISAC–CNR, Rome, Italy*
[h] *TNO, The Netherlands*
[i] *University of York, UK*

ABSTRACT: The Aerosol Direct Radiative Experiment (ADRIEX) took place over the Adriatic and Black Seas during August and September 2004 with the aim of characterizing anthropogenic aerosol in these regions in terms of its physical and optical properties and establishing its impact on radiative balance. Eight successful flights of the UK BAE-146 Facility for Atmospheric Airborne Measurements were completed together with surface-based lidar and AERONET measurements, in conjunction with satellite overpasses. This paper outlines the motivation for the campaign, the methodology and instruments used, describes the synoptic situation and provides an overview of the key results. ADRIEX successfully measured a range of aerosol conditions across the northern Adriatic, Po Valley and Black Sea. Generally two layers of aerosol were found in the vertical: in the flights over the Black Sea and the Po Valley these showed differences in chemical and microphysical properties, whilst over the Adriatic the layers were often more similar. Nitrate aerosol was found to be important in the Po Valley region. The use of new instruments to measure the aerosol chemistry and mixing state and to use this information in determining optical properties is demonstrated. These results are described in much more detail in the subsequent papers of this special issue. Copyright © 2007 Royal Meteorological Society

1. Introduction and ADRIEX goals

Atmospheric aerosol has a substantial effect on local and regional climate, as well as being a major source of uncertainty in global climate change predictions (IPCC, 2001). Depending on their size and composition, aerosols scatter and absorb solar and terrestrial radiation (the direct effect), act as cloud condensation nuclei thereby modifying the microphysical and optical properties and lifetime of clouds (indirect effect) and alter atmospheric profiles of temperature and relative humidity (semi-direct effect) (IPCC, 2001). These aerosol-induced changes can also affect the surface energy fluxes and thus potentially the hydrological cycle. Aerosol concentrations and properties are spatially highly variable, since the sources are spatially distinct and most aerosols have a lifetime in the troposphere of only days to weeks. There

have been detailed measurement campaigns to characterize the anthropogenically influenced aerosol originating from the east coast of USA (Tropospheric Aerosol Radiative Forcing Experiment, TARFOX; Russell *et al.*, 1999), the Indian subcontinent (the Indian Ocean Experiment, INDOEX; Ramanathan *et al.*, 2000), and Asia (Aerosol Characterization Experiment, ACE-Asia; Huebert *et al.*, 2003), as well as aerosol from a mixture of sources (e.g. ACE-2; Raes *et al.*, 2000). These studies have suggested remarkable similarities between some of the bulk properties of industrially emitted aerosol from different parts of the globe, e.g. sub-micron mass scattering efficiency (Quinn and Bates, 2004). However, other properties and the radiative effect of these aerosols are still very varied, depending on chemical composition, vertical profile, aging time, relative humidity, etc.

State-of-the-art global climate models include an increasingly complex representation of atmospheric aerosol, but many assumptions are still necessary to

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* Correspondence to: E. J. Highwood, Department of Meteorology, University of Reading, Reading RG6 6BB, Berkshire, UK.
E-mail: e.j.highwood@reading.ac.uk

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determine the aerosol properties. In most cases the assumptions used concerning mixing state, size, refractive index, shape, etc., can only be some form of average. It is important to know and understand the spatial variation of aerosol characteristics in order to better predict their impact on regional climate, particularly with the steady increase in resolution of climate models, potentially allowing them to include this level of spatial variation in aerosols. Therefore it is fundamental to validate the aerosol properties used in different regions across the globe. While recent advances in satellite products and the ground-based sunphotometer Aerosol Robotic Network (AERONET) offer reasonable hope for the future, they must in turn be validated by quality *in situ* measurements of aerosol properties, paying particular attention to the variability in these properties both temporally and spatially.

The Mediterranean (Figure 1) has been described as a 'global pollution crossroads' (Lelieveld *et al.*, 2002), with air masses reaching it from a wide variety of directions. Previous campaigns in the southern Mediterranean (e.g. the Mediterranean Intensive Oxidant Study, MINOS; Traub *et al.*, 2003) have determined a possible influence of both eastern European sources, particularly biomass burning, and influence from outflow from the Asian monsoon has also been proposed (Scheeren *et al.*, 2003). It is also a region that may be particularly sensitive in terms of the hydrological cycle if surface fluxes are affected to any great extent (Markowicz *et al.*, 2002). In the summer months (June to September) the large-scale circulation over the Mediterranean is dominated by descent due to both the descending branch of the Hadley cell and the outflow of the Asian monsoon (Rodwell and Hoskins, 2000). This generally suppresses convection and

gives largely cloud-free skies unless the Asian monsoon is weaker than usual, in which case the region can be more disturbed than normal (e.g. Blackburn *et al.*, 2003, personal communication). In the more usual situation, the pollution from strong sources such as the Po Valley can accumulate in the region. The high insolation maximizes the likely direct radiative impact of the aerosol.

Figure 2 shows an analysis of 5-day back trajectories for air arriving at 3 km altitude at several AERONET sites across the region of interest during August over several recent years, calculated using National Center for Environmental Prediction (NCEP) re-analyses and the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model. It suggests that the AERONET site at Crete does indeed fit the description of a 'global pollution crossroads', receiving trajectories in approximately equal amounts from the different areas, including the Sahara and the Mediterranean itself. This is consistent with observations from the MINOS campaign (Traub *et al.*, 2003). However, Figure 2 also suggests that the aerosol composition found during MINOS may not be representative of the eastern Mediterranean overall. AERONET sites in central northern Italy (Rome, Venice and Ispra) receive air masses preferentially from the Atlantic and western European sectors. Due to different source types and strengths affecting the trajectories from different directions, the aerosol properties are likely to vary substantially. Examination of the European Monitoring and Evaluation Programme emission estimates (not shown) suggests that the Po Valley has high values of NO_x and NH_3 emissions compared to more eastern regions, whilst sulphur emissions are strong across the eastern region between the Adriatic and the Black Seas. Differences in
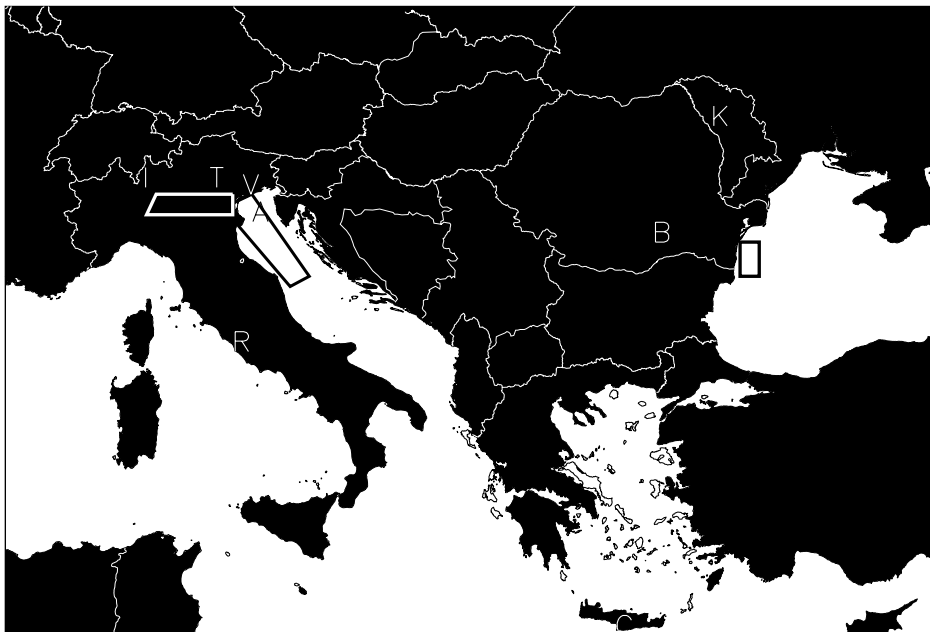

Figure 1. Map of the Mediterranean and Black Sea regions. Rectangles denote the approximate operating areas for ADRIEX flights; letters indicate Treviso (T), the ocean tower (A), and the AERONET stations (B = Bucharest, K = Kishinev, I = Ispra, V = Venice, R = Rome, C = Crete).
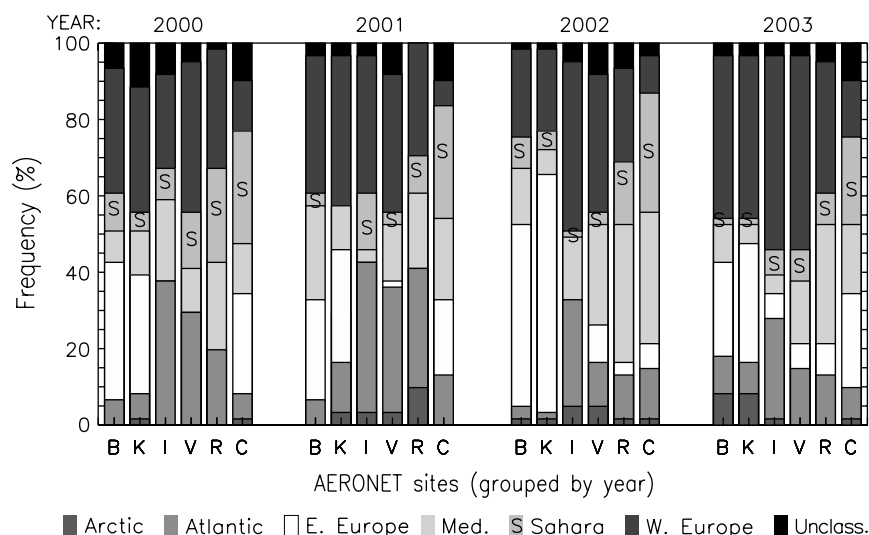
Figure 2. Frequency distribution of the origin of 5-day back trajectories arriving at 3 km altitude over each of six AERONET stations during August 2000 to 2003 (B = Bucharest, K = Kishinev, I = Ispra, V = Venice, R = Rome, C = Crete). Back trajectories were calculated using HYSPLIT with NCEP analyses. Stacked bars begin with the Arctic at the base of the stack, and then subsequent sectors build in the order shown in the legend.

some properties may be significant for changing optical properties and radiative effects; others may be more significant for cloud activation.

The eastern Mediterranean region therefore makes a good base for an aircraft-based measurement campaign concerning *in situ* measurements of aerosol physical and optical properties, and estimations of its radiative impact. The interpretation of some of these measurements is simplified if they are made over water which has a relatively well-characterized albedo, hence the use of the northern Adriatic. There is also a good network of AERONET sites for surface-based measurements of aerosol in this region. A base in the Northern Adriatic also allows the exploration of aerosol properties in eastern Europe source regions, which may potentially affect the eastern Mediterranean. AERONET stations at Bucharest and Kishinev (Figure 2) show substantially different air mass influences, including possible biomass burning influences. The western area of the Black Sea provides a good region in which to make contrasting measurements of aerosol properties and radiative impact.

The potential for variability in aerosol properties over this relatively small region, together with advances in resolution in regional climate models, suggest that it will be important to understand the significance of any such variations for climate models. This motivated the Aerosol Direct Radiative Experiment (ADRIEX) which was conducted as a joint campaign between the UK Met Office and the UK university community, part-funded by NERC and led by the University of Reading. The campaign benefited from the new Facility for Airborne Atmospheric Measurements (FAAM) BAE-146 aircraft, and the participation of groups from the University of Manchester, the University of Leeds, the University of Oxford, LISA (Laboratoire Inter-universitaire des Systèmes Atmosphériques, Paris), TNO (The Netherlands

Institute of Applied Geoscience), ISAC–CNR (Istituto di Scienze dell'Atmosfera e del Clima–Consiglio Nazionale delle Ricerche, Italy) and the University of York.

The ADRIEX campaign had the following objectives:

(1) To characterize aerosol composition, radiative properties and vertical profile, and their variability across the northern Adriatic and Po Valley region;
(2) To compare the radiative and chemical properties of aerosol from eastern and western European sources;
(3) To develop methodologies for combining new aerosol chemistry information with microphysical and radiative observations;
(4) To validate the use of remote-sensing methods for industrial aerosol; and
(5) To estimate the magnitude of the likely radiative impact of industrial aerosol in the Adriatic and Black Sea regions.

2. ADRIEX approach

The ADRIEX campaign took place between 26 August and 6 September 2004. The BAE-146 aircraft was based at Treviso Airport, Italy (45.6 °N, 12.1 °E), close to Venice.

2.1. Flight overview

Eight flights of approximately 4.5 hours duration were performed over the northern Adriatic, the Po Valley, and over the Black Sea. A summary of the flights performed is given in Table I. An important waypoint for the Adriatic flights was the ocean tower (point A on Figure 1), at which there is an AERONET site (Venice–ocean tower). Typical flight manœuvres included profiles from ∼15 m above sea level to 5000 m in order to detect the vertical

Table I. Summary of flights during ADRIEX.

Flight No.	Date	Time (UTC)	Region	Flight type; pollution level	Satellite instruments
B043	27 Aug 2004	07:57–12:57	Northern Adriatic/ Po Valley	*In situ*; light	MODIS, MISR
B044	28 Aug 2004	08:15–13:10	Northern Adriatic	Radiometric and *In situ*; light	MODIS
B045	29 Aug 2004	08:00–13:00	Po Valley	*In situ* measurements; moderate	MODIS, MISR, AATSR
B046	30 Aug 2004	10:00–14:50	Northern and mid-Adriatic	Radiometric and *In situ*; aged moderate	
B047	02 Sep 2004	08:15–13:15	Northern Adriatic	Radiometric and *In situ*; moderate	MODIS
B048	03 Sep 2004	06:07–10.59 12:57–16:40	Black Sea (refuel Constanta)	Radiometric and *In situ*; heavy east European	MODIS, AATSR
B049	05 Sep 2004	09:42–14:33	Northern Adriatic	Radiometric and *In situ*; moderate	MODIS, MISR
B050	06 Sep 2004	08:00–12:50	Northern Adriatic/ Po Valley	Radiometric and *In situ*; heavy pollution	MODIS

structure of the aerosol, and straight and level runs within, above and below the aerosol layers for *in situ* sampling or radiative measurements. In particular we performed repeated 'zig-zag' patterns up the Po Valley towards Milan on days with light, moderate and heavy pollution. To our knowledge, this is the first occasion upon which such extensive airborne measurements have been performed in the Po Valley. Flight patterns are shown in detail in Crosier *et al.* (2007) and Osborne *et al.* (2007).

2.2. Aircraft instrumentation

FAAM is the result of a collaboration between the Met Office and the Natural Environmental Research Council (NERC) and has been established as part of the NERC Centres for Atmospheric Science (NCAS) to provide an aircraft measurement platform for use by all the UK/European atmospheric research community on campaigns throughout the world. The modified BAE-146 aircraft is owned by BAE Systems and operated by DirectFlight. During ADRIEX, the aircraft was fitted with a range of aerosol microphysics and radiative flux instruments, which are listed in Table II. Of particular note is the novel combination of aerosol chemistry (Volatile Aerosol Chemistry and Composition (VACC; Brooks *et al.*, 2002) and Aerodyne Aerosol Mass Spectrometer (AMS; Crosier *et al.*, 2007)) measurements with those of aerosol microphysics and radiative measurements. More details of particular instruments are included in the papers which use their measurements in the analysis (particularly Osborne *et al.*, 2007 and Crosier *et al.*, 2007).

2.3. Ground-based instrumentation

The ADRIEX campaign both made use of existing ground-based measurements pertaining to aerosols and

their radiative effect, and provided additional measurements during the campaign.

2.3.1. Sunphotometer data

The northern Adriatic region is well served with AERONET sites at the ocean tower (45.3 °N, 12.5 °E), and in the centre of Venice (ISDGM-CNR; 45.4 °N, 12.3 °E). TNO provided an additional CIMEL sunphotometer at Nicelli airport (Venice Lido; 45.4 °N, 12.4 °E), the results of which have been incorporated into the main AERONET dataset. The level 2.0 retrievals (quality assured, cloud screened) have been used for aerosol optical depth at a range of visible wavelengths and for Ångström exponent. In addition to these AERONET instruments, a hand-held Microtops sunphotometer, on loan from the NERC Field Spectroscopy Facility (FSF) was used at Treviso airport. This instrument must be manually pointed at the sun. Under clear-sky (no cloud) conditions, it can provide aerosol optical depth at a number of wavelengths, Ångström exponent, and total precipitable water. Observations were made approximately every half hour at the airport when other activities allowed. As such, the representivity of the data must be carefully considered. Similar Microtops observations were also made at Nicelli airport.

2.3.2. Lidar

The Vehicle-mounted Lidar Station (VELIS) was provided by ISAC-CNR and consisted of a an elastic depolarization lidar and a Kipp and Zonen CM-11 broadband pyranometer (0.3–3 µm). This was stationed at Nicelli airport throughout the ADRIEX campaign (see Barnaba *et al.*, 2007). The Venice Lido closes the Venice Lagoon to the southeast and is around 5 km from Venice and 10 km from the mainland. The lidar provided a more continuous view of the vertical profile of aerosol than

Table II. Instrumentation on the FAAM BAE-146 aircraft during ADRIEX.

Name	Instrument	Quantity measured
AVAPS	Airborne Vertical Atmospheric Profiler System (dropsonde)	Profiles of pressure, temperature, RH, wind speed and direction
PCASP[a,b]	Aerosol Size Spectrum optical probe	Aerosol particle concentration, mean volume radius, size spectrum (0.1–3 μm)
CO	Air samples	Carbon monoxide
Filters (LISA)[b,c]	Two-stage 47 mm filter units Nucleopore and quartz	Water-soluble ions Carbonaceous aerosols
Nephelometer[a,b]	Rosemount pair inlet	Total scattering and hemispheric backscattering coefficient at 450, 550 and 700 nm
PSAP[a,b]	Particle Soot Absorption Photometer	Aerosol absorption coefficient
SID[a,b]	Small ice detector	Size distribution
OZONE	TECO 49 UV photometric instrument	Ozone
Rosemount	Temperature sensors	De-iced and non de-iced temperatures
AMS (Manchester)[b,c]	Aerosol Mass Spectrometer	Mass distribution of volatile and semi-volatile components of aerosols as a function of particle size (50–500 nm)
CCN (Met Office)	Cloud condensation nuclei	Cloud condensation nuclei
CVI (Met Office)	Counter flow Virtual Impactor	
VACC (Leeds)[d]	Volatile aerosol concentration and composition temperatures 300–70 °C	Volatile aerosol components Mixing state
WAS (York)	Whole air sample bottles	Sample collection only

[a] Osborne *et al.* (2007); [b] Cook *et al.* (2007); [c] Crosier *et al.* (2007); [d] Brooks *et al.* (2007)

could be achieved by dropsondes from the aircraft, or indeed even surface-launched radiosondes. Daily profiles of extinction coefficient at 532 nm and depolarization were retrieved regularly from the lidar between approximately 0800 and 1600 UTC.

2.4. Satellite data

As suggested in Table I, flights were timed to coincide as often as possible with overpasses of satellites with instruments dedicated to observing aerosol properties. In particular, 'golden days' with multiple intercomparison opportunies were identified in both the Adriatic and Black Sea regions. These were taken into account in planning flights, although cloud-free skies and likely aerosol loading were the primary motivations for flying. The satellite instruments of particular interest to ADRIEX in terms of validating possible satellite retrievals include the Moderate-resolution Imaging Spectroradiometer (MODIS) on board the Earth Observing System (EOS) Terra (am) and Aqua (pm) satellites, the Multi-Angle Imaging Spectroradiometer (MISR) on board EOS Terra, the Advanced Along-Track Scanning Radiometer (AATSR) on board ENVISAT, and the Spinning Enhanced Visible and InfraRed Imager (SEVIRI) on board METEOSAT-8. The interest for ADRIEX is to use *in situ* measurements in comparison with satellite aerosol optical depth both for validation of existing products (Osborne *et al.*, 2007) and for development and validation of new retrievals of aerosol optical depth from AATSR and SEVIRI (Thomas *et al.*, 2007).

3. ADRIEX synoptic situation

The most striking synoptic evolution during ADRIEX was a change in dominant airflow from westerlies to easterlies during the last three days of the campaign period. A back-trajectory analysis (not shown) shows a change in the likely source region for aerosol from western Europe and the Atlantic to central and eastern Europe. The geopotential height of the 850 mb surface is shown in Figure 3 at 12 UTC for each day of the campaign. At the start of the period (26 August), a small trough extended from a low pressure system further north in Europe. This brought with it significant rainfall associated with the passage of the cold front. During subsequent days, the mid-tropospheric flow was predominantly westerly, the Adriatic region being influenced by another small trough on 31 August. Although this did not have much rain associated with it, cloud cover was more extensive and prevented flying activity that day. Towards the end of the period, high pressure began to build across the central Mediterranean, and as a result the mid-tropospheric flow in the ADRIEX region becomes more easterly, certainly being so on 3–5 September. A low pressure system affected the western end of the Black Sea on 27–28 August, but towards the end of the ADRIEX period this region also was influenced by the high pressure.

4. Results overview

4.1. General aerosol conditions

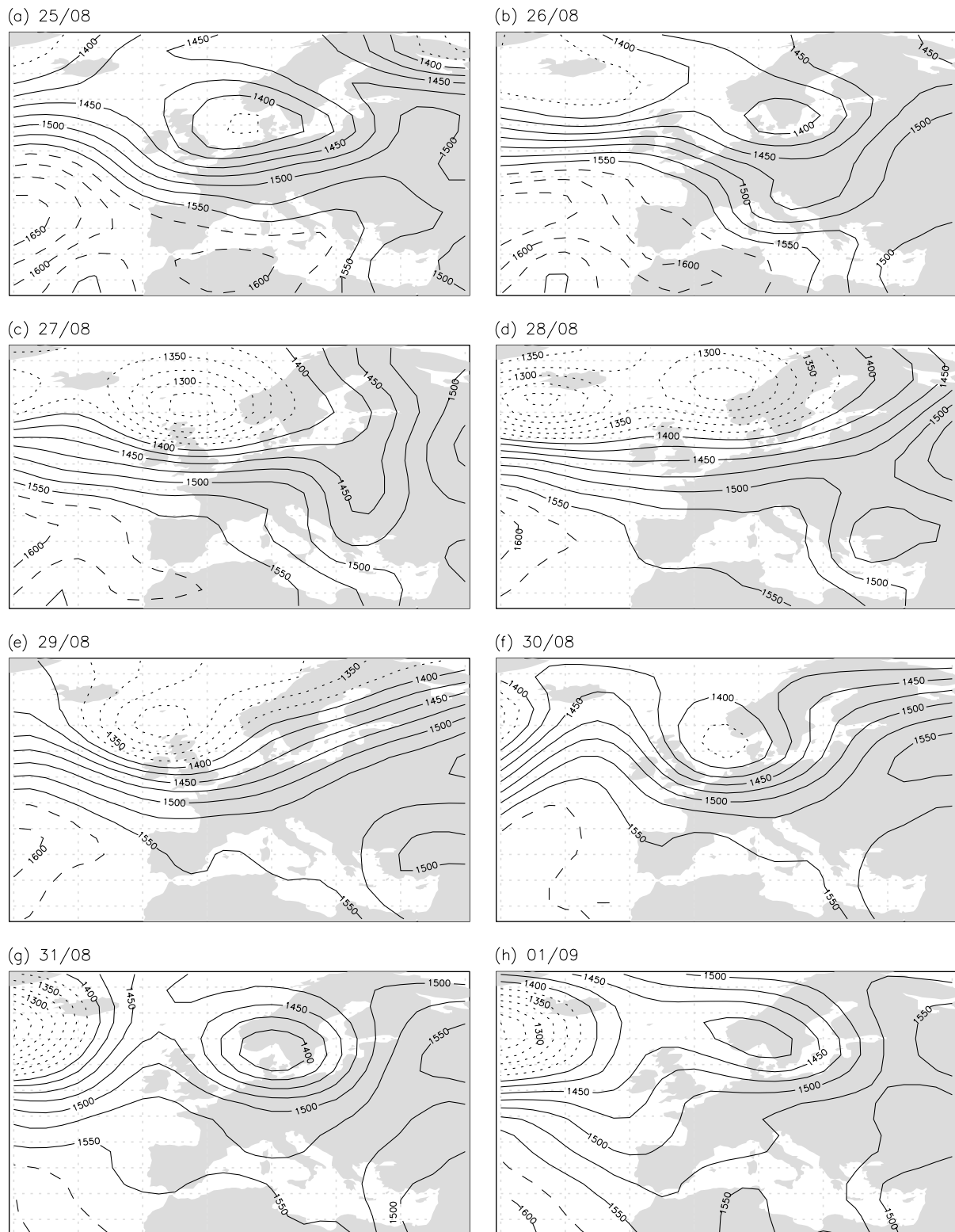The time evolution of aerosol amount in the ADRIEX region during the campaign is shown in Figure 4(a), using

Figure 3. NCEP re-analysis 850 mb geopotential height at 12 UTC during the ADRIEX campaign from (a) 25 August to (n) 7 September 2004. The contour interval is 25 m; contours below 1400 m are dotted, 1400–1550 m are solid, and 1500 m and above are dashed.

data from the regional AERONET sites and a hand-held sunphotometer at Treviso airport. Daily averaged aerosol optical depth (at 440 nm) shows relatively large values at the very start of the campaign followed by a dramatic decrease on 26 August (the first possible day for flying). This was due to extensive thunderstorms and rainfall in the region which cleaned out the aerosol. Subsequently, aerosol optical depth increased, reaching a peak of 0.5 on 31 August and 3 September. All three AERONET sites agree well with the observations taken at Treviso airport, however it is worth noting that, within any one flight, the aircraft may have experienced higher optical
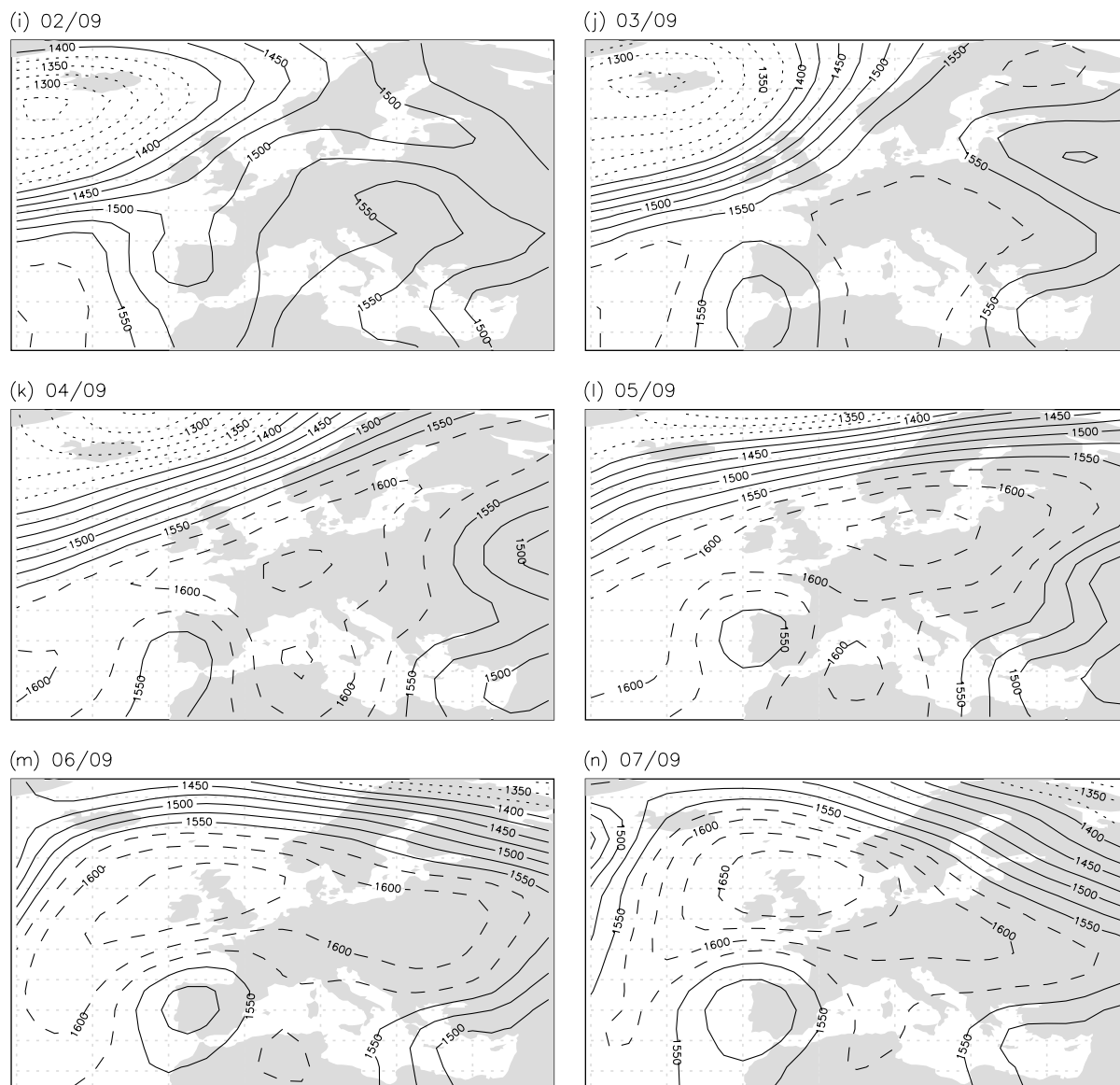
Figure 3. (*Continued*).

depths if close to a strong local source. In addition, the daily mean values for Treviso are less meaningful since measurements were taken at irregular times and generally only in the morning or the middle of the day which will skew the averages in the case of a diurnal cycle, tending to underestimate the actual daily mean in the former and overestimate it in the latter case. The Constanta airport data point is not a daily average, since it was only available from the Microtops sunphotometer at midday during refuelling at the airport and may therefore be an overestimate of the true daily average. Figure 4(b) shows the Ångström exponent which can be taken as an indication of particle size (larger particles tending to have smaller Ångström exponent). Again there is good agreement in general between the AERONET sites, although the hand-held sunphotometer estimates from Treviso tend to underestimate the Ångström exponent compared to the AERONET sites. All show an increase in Ångström exponent, suggesting a decrease in particle size throughout the campaign.

4.2. Objective 1: Characteristics of aerosol in the northern Adriatic and Po Valley

4.2.1. Vertical structure of aerosol

The most obvious characteristic of aerosol across the northern Adriatic is the distinctive layered structure which can be separated into a marine boundary layer (MBL) and an elevated pollution layer (EPL), often with a very distinct clean slot between them. Over the Po Valley there is also vertical structure in the aerosol showing generally two or more distinct layers. Table III shows the main layers of aerosol found during the campaign, the second column showing their altitudes as indicated by the aircraft data, and the fourth column showing the altitudes of layers detected by the lidar for the same date. For the Adriatic and Po Valley regions, Osborne *et al.* (2007), Crosier *et al.* (2007) and Barnaba *et al.* (2007) describe two layers that are readily defined in terms of aerosol number concentration, aerosol scattering, and aerosol chemistry. Associated with aerosol

differences are similar demarcations in relative humidity and temperature, as well as changes in carbon monoxide (CO). This structure could perhaps be understood in terms of the evolution of the well-mixed boundary layer. Aerosol, or aerosol precursors emitted during the day, are mixed up to increasing heights as the surface heating increases convection. During the night, with surface heating shut off (and some aerosol emissions reduced), the height of the boundary layer collapses, leaving a residual elevated pollution layer to be sampled early the next day. This was evident to some extent in changes in cloud-top heights, for example on the Po Valley flight B045 when the zig-zag was repeated twice, when the top of the boundary layer was as much as 2000 ft higher on the second run later in the morning. However, this is not particularly evident from aircraft profiles of aerosol scattering or the (five per hour) lidar profiles (Barnaba *et al.*, 2007). An alternative explanation is that the elevated layer of pollution is due to long-range pollutant transport whilst the lower layer is due to local sources. The lidar depolarization suggests Saharan dust on 29 August between 4 and 6 km. In the case of the Po Valley, considerable information can be gleaned from the measurments of chemical composition of the aerosol (Crosier *et al.*, 2007). Two distinct layers are described, one warm and moist layer being rich in nitrate aerosol, suggesting that it has recently been lifted from the boundary layer. Other pollutants (e.g. ozone) suggest that the pollution in this layer is relatively fresh. These layers were found mostly on either the north or south side of the Po Valley and not in the central part, their location being consistent with wind direction in that katabatically driven flows appear to drive convection and therefore pollutant uplift in the region. The other layer tends to be less nitrate rich and suggests a background aged aerosol with higher sulphate and organics.

These chemical composition and single-scattering albedo (SSA) differences between the layers, suggest that there might be a difficulty in interpreting column-average optical properties from remote sensing.

4.2.2. *Size distribution*

Whilst the vertical profile of aerosol number and properties varied considerably from day to day and substantially between the locations, the size distribution appeared to vary somewhat less throughout ADRIEX. Fitting log-normal modes to the number distribution suggested that three modes fit the data best in most cases, with average geometric mean radii for the number distributions of 0.099, 0.188 and 0.957 μm respectively for the Adriatic region (Osborne *et al.*, 2007). Sunphotometer data from the Nicelli measurements also suggested fine mode aerosol (Barnaba *et al.*, 2007) as dominating the light extinction, this being around 90% of the total for the Adriatic under moderate aerosol loading, and slightly higher during the days when an easterly flow was experienced. A slightly lower fine mode fraction on 27–29 August may have been due to refractory super-micron aerosol observed
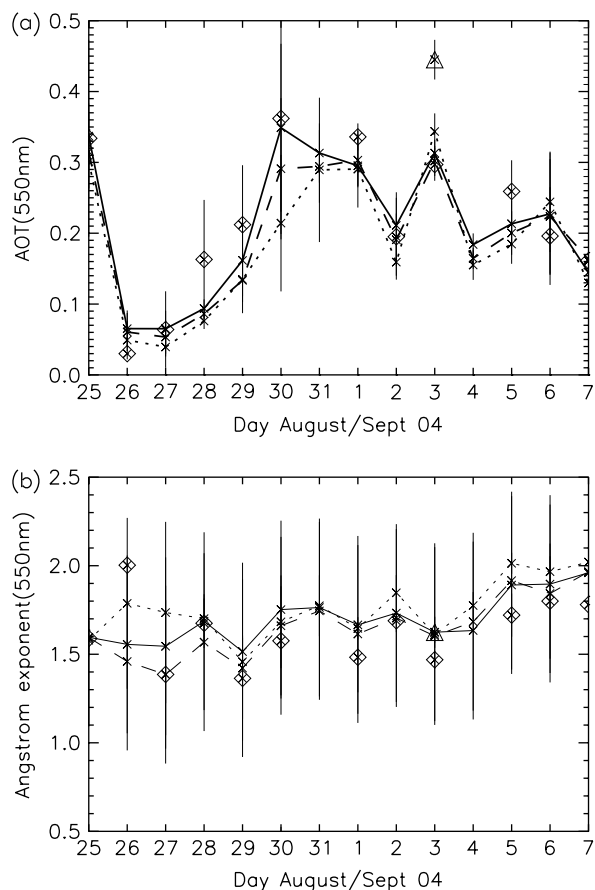

Figure 4. (a) Aerosol optical depth (AOD) at 550 nm and (b) 440–870 nm Ångström exponent at three AERONET stations (ISDGM-CNR, solid; Nicelli airport, dashed; Venice–ocean tower, dotted) and from the hand-held sunphotometer measurements at Treviso (diamonds) and Constanta (triangles) airports.

aloft during this time. The size distribution of aerosol over the northern Adriatic varied little, and also resembled that found in previous campaigns such as TARFOX, etc. (Osborne *et al.*, 2007). Where industrial aerosol is of similar age and has not undergone cloud processing, it could be deduced that one size distribution could be used universally. However, it is important to note that, even if the size distribution appears similar, the chemical composition and mixing state of the aerosol may be dramatically different, leading to potentially very different radiative impacts.

4.2.3. *Aerosol optical properties*

The specific (mass) extinction, SSA and asymmetry parameter typical of each flight are given in detail in Osborne *et al.* (2007). Campaign-mean optical properties at 0.55 μm are given in Table IV. It is unfortunate that *in situ* measurements of scattering and absorption were only available from flight BO46 onwards, and therefore values from earlier flights were determined using the *in situ* size distribution and Mie scattering calculations. For Adriatic flights where both methods are used, the SSA calculated in this manner tends to be within a few percent of the *in situ* value, the difference being

Table III. Summary of the location of aerosol layers identified during ADRIEX flights.

Flight number and date	Height of pollution layer detected from aircraft profiles	Location	Pollution layers detected by lidar
B043 27 Aug	900 m + low level?	Po Valley	1–3 km
B044 28 Aug	1) 1700 m; 2) 760 m; 3) 30 m	Starting at ocean tower	0–1 km; 1–2.5 km; 2.5–4 km
B045 29 Aug	1) 1200–2100 m; 2) 900 m; 3) 2700 m	1) Eastern end of Po Valley; 2) Eastern end of Po Valley; 3) Closer to Milan	0–0.7 km; 1–2.8 km; 4–6 km
B046 30 Aug	1) 300–800 m; 2) Surface to 1200 m; 3) 3800 m	Near ocean tower	0–0.7 km; 0.8–2.8 km; 3–4 km
B047 02 Sep	1) 1200–2100 m; 2) 30 m	Adriatic	0–0.8 km; 1–3 km
B048 03 Sep	1) Surface–600 m; 2) 1500–3000 m	Black Sea	–
B049 05 Sep	1) MBL; 2) 1200–2100 m; 3) Ocean tower	Northern Adriatic	0–1 km; 1–4 km
B050 06 Sep	1) Surface–180 m; 2) 300–3000 m; 3) 4500 m	Adriatic	–

Table IV. Campaign representative aerosol optical properties at 0.55 μm.

Quantity		Adriatic EPL	Adriatic MBL	Po Valley	Black Sea EPL	Black Sea MBL
Single-scattering albedo	(Mie)	0.92	0.91	0.90	–	–
	(in situ)	0.92	0.91	0.92	0.95	0.91
Specific (mass) extinction (m^2g^{-1})	(Mie)	1.96	1.75	1.41	2.41	3.87
Asymmetry parameter		0.55	0.56	0.56	0.55	0.55

slightly larger in the EPL than the MBL case. SSA values from the Nicelli CIMEL instrument are in good agreement with those from the *in situ* measurements, additionally showing a reduced SSA on 27–28 August which increases on 3–5 September. Barnaba *et al.* (2007) suggest that this is due to the presence of super-micron refractory aerosol aloft during the earlier period. The range of SSA values encountered are close to the so-called 'critical SSA' where the global mean surface temperature response changes sign from negative to positive (Haywood and Shine, 1995) and in particular close to the region of SSAs where the relationship between radiative forcing and climate response breaks down (e.g. Cook and Highwood, 2004). Although not a measure of local response, this suggests that the sign of temperature response of the surface to an increase in aerosol of this type may not be as expected from estimation of the radiative forcing. The difference in specific extinction from IPCC values highlights the importance of characterizing the full size distribution of aerosol. Optical depth estimates from the aircraft

measurements are biased low compared to AERONET and lidar estimates (Osborne *et al.*, 2007; Cook *et al.*, 2007). Although some of this difference can be explained through very local differences in aerosol column and through the undersampling of total aerosol number by aircraft instrumentation, this is obviously a cause for concern as the optical depth is one of the most important quantities for comparison with remote sensing and model output. The apparent undersampling by the PCASP in aerosol optical depth closure studies has been noted to a lesser extent when the PCASP was fitted to the C-130 aircraft (Haywood *et al.*, 2003), where the detected particle concentration was found to be sensitive to the pitch of the aircraft. There may be a potential problem with the PCASP concentration measurements due to the location of the instrument on the inboard side of the wing-mounted cloud physics pylon; flow distortion may be caused by proximity to the aircraft engines. Further flights are proposed where two nominally identical PCASP instruments are flown on the inboard and outboard pylon positions to investigate this effect.

4.3. Objective 2: comparison of properties of eastern and western European aerosol sources

An extensive and categorical comparison is precluded here since weather conditions favoured only one ADRIEX excursion to the Black Sea and eastern European sources (B048). As in the Adriatic, two distinct layers of aerosol were observed over the Black Sea region, with the distinction between the two being more significant than over the Adriatic. Table IV shows the lower layer having a SSA of 0.91 compared to 0.95 in the upper layer. A full comparison of B048 with flights over the Adriatic is presented in Cook *et al.* (2007) with additional information in Osborne *et al.* (2007). Trajectory analysis suggested that the two well-defined layers over the Black Sea had different sources, the EPL originating from central and western Europe whilst the MBL had more signal from eastern European sources. The more strongly scattering EPL was also consistent with a different chemical composition, that of the EPL containing more sulphates whilst the MBL contained more organic species (Cook *et al.*, 2007; Crosier *et al.*, 2007), and this may reflect much stronger organic sources in eastern Europe than in the northern Adriatic and western European regions. It was anticipated that more black carbon (BC) might be seen in the eastern European aerosol due to weaker regulation on sources and potential biomass burning. However, the filter analysis for all flights, including the Black Sea, showed very little BC in any of the samples, consistently at the limits of detection. This suggests that attempts to distinguish between east and west aerosol on these grounds, or to establish whether BC is responsible for the observed SSAs in either case, will be problematical given the limits of current instrumentation. Observational evidence suggests that some organic aerosol compounds from fossil fuels are relatively weakly absorbing but do absorb solar radiation at some ultraviolet and visible wavelengths (e.g. Jacobson, 1999; Bond *et al.*, 1999; Bond, 2001) although organic aerosol from high-temperature combustion such as fossil-fuel burning (Dubovik *et al.*, 1998) appears less absorbing than from low-temperature combustion such as open biomass burning.

4.4. Objective 3: methodologies for combining aerosol chemical and microphysical information to inform radiative properties

Core chemistry information such as CO and ozone concentrations have routinely been used in conjunction with aerosol scattering as indicators of air-mass origin and age. The ranges of key chemical constituents are given flight by flight in Table V. Peaks were reached during B046, with peroxyacetyl nitrate (PAN) being considerably less during the Black Sea flight and in the later Adriatic flights likely to have been influenced by easterly flow.

The ADRIEX campaign carried two new instruments on the BAE-146 concerning chemical composition of the aerosol. The Quadrupole Aerodyne Aerosol Mass Spectrometer (AMS) provided quantitative information concerning the composition of non-refractory sub-micron aerosol. Crosier *et al.* (2007) show that a highly significant amount of nitrate aerosol was present over the northern Adriatic, being the major component during westerly and southwesterly flow regimes. Correlation with other pollutants and equivalent potential temperature suggest that air masses with high nitrate concentration have been recently lifted from the surface and carry the emissions from the sources in the Po Valley. Sulphates and organics dominated during easterly flow, perhaps due to the source regions in this case being a long way upstream and the aerosol ageing substantially. The Black Sea measurements gave a striking constrast between layers, with the EPL having aged sulphates and organics similar to background Adriatic measurements, whilst the MBL showed higher masses of organics. The mass size distributions from the AMS also suggest an internal mixture of aerosol given that there is similar modal behaviour for the different components. Additionally, in the nitrate-rich air masses, there is some evidence that the nitrate is correlated with the sulphate and organic aerosol, implying that they are secondary and produced together, the nitrate perhaps condensing onto pre-existing acidified sulphate or organic material.

In addition to these valuable measurements of chemical composition, the comparison of Black Sea and Adriatic aerosol by Cook *et al.* (2007) illustrates how information from the AMS can be used to infer refractive indices for

Table V. Flight by flight ranges of concentrations of key gaseous chemistry species.

Flight	Date	CO (ppbv)		O$_3$ (ppbv)		PAN (pptv)
		Max	Min	Max	Min	Max
B043	27 Aug	155	80	103	21	1490
B044	28 Aug	175	65	106	58	1630
B045	29 Aug	180	70	106	41	1320
B046	30 Aug	225	85	101	55	2285
B047	02 Sep	135	70	89	38	825
B048	03 Sep	145	70	104	48	650
B049	05 Sep	160	65	96	45	730
B050	06 Sep	170	65	94	59	1105

the aerosol, for subsequent use in calculations of optical properties not measured *in situ* and in the estimation of radiative effect. Taking the measured size distribution and mass size distributions for each of the main chemical groups, and considering that a single size peak suggests an internal mixture, a refractive index can be found using volume-weighted mixing. The AMS is unable to measure BC or other refractory aerosol components such as dust, but BC is the most likely such component of ADRIEX aerosol. Thus an iterative technique adjusting BC to match the *in situ* SSA suggested amounts of BC of only a few percent, consistent with the filter measurements. This supports the hypothesis from previous sections that the SSA can be explained by a small amount of BC, but that our current measurement techniques cannot directly measure it at these low abundances. Throughout this process, it is apparent that the amount of water in the aerosol plays an important role and it is imperative to have good estimations of this. In ADRIEX, growth rates had to be assumed from literature. However, in the future, the development of a wet nephelometer by the UK Met Office to measure *in situ* growth factors will be of huge significance in this type of methodology. An additional source of uncertainty that was revealed during the analysis of ADRIEX data is the unknown degree of drying of samples by the PCASP instrument.

Information concerning the mixing state of aerosol can also be obtained from the VACC instrument on the aircraft. Brooks *et al.* (2007) report the relative mass loadings of sulphate, ammonium and nitrates from this new aircraft instrument, and these were found to be in good agreement with estimates from the AMS, despite the types of instrument and measurement being very different. The VACC was uniquely able to indicate the mixing state of the aerosol species as a function of size. Results for flight B050 over the Adriatic suggest that there is an external mixture of two types of internally mixed aerosol. One of the internal mixtures contains long-chain hydrocarbons, ammonium hydrogen sulphate, ammonium sulphate and ammonium nitrate, whilst the other is an internal mixture of these with the non-volatile core. Proportions of the volatile species within each internally mixed 'type' vary.

4.5. Objective 4: validation of remote-sensing methods for industrial aerosol

Three methods of remote sensing of aerosol have been considered during ADRIEX: ground-based lidar, AERONET and various satellite instruments. AERONET and satellite instruments describe the bulk properties of the aerosol column, whilst lidar, along with the profiles from *in situ* aircraft flights, provide the important vertical profile information of aerosol; they are therefore complementary methods. However, the representiveness of bulk column measurements is called into question by the variability in aerosol properties in the different layers observed throughout ADRIEX. The most appropriate comparison is therefore with aerosol optical depth

(AOD). As mentioned earlier and discussed by Osborne *et al.* (2007), Cook *et al.* (2007) and Banarba *et al.* (2007), the aircraft-estimated AOD consistently underestimates both the AERONET observations and those derived by radiometric measurements from the lidar. In many cases, much of the extinction in the lidar profiles comes from a very localized and low-altitude aerosol layer that is not evident in the aircraft samples. The lidar tends to slightly overestimate AOD compared to AERONET, even when collocated. Cook *et al.* (2007) ruled out the underestimation of coarse particles causing the difference between aircraft and AERONET but suggests that uncertainties in aerosol growth factor may play a role. There is also the possibility that some semi-volatile components of the aerosol are not measured in the aircraft instrumentation due to heating of air during sampling. Retrievals of AOD from MODIS agree reasonably well with AERONET and aircraft data over the Adriatic regions, although this may be partly because the MODIS retrievals have been tuned to match AERONET, although not necessarily at this location and to this extent. ADRIEX provided a case-study for new retrievals of AOD from AATSR (two retrievals) and SEVIRI. The new retrievals generally give a larger value of AOD than that reported by AERONET. Over land, the TNO algorithm produces a smoothly varying field that exceeds the AERONET value by about 50% at 550 nm. The Oxford/Rutherford Appleton Laboratory Aerosol and Cloud (ORAC) optimal estimation retrieval scheme shows much greater variability and difference from AERONET; the use of the AATSR dual view by TNO clearly results in less bias here. Over the sea, the situation is reversed, with the ORAC algorithm showing a smaller difference (37%) from AERONET than the TNO algorithm. In general the comparison between AERONET and the satellite-retrieved values do not agree within the one sigma uncertainties, suggesting that systematic errors (e.g. assumptions made in the radiative forward model) are dominating the error budget.

4.6. Objective 5: estimation of likely radiative impact of industrial aerosol in the Adriatic and Black Sea regions

Pyranometer measurements at Nicelli reported in Barnaba *et al.* (2007) suggest a decrease in maximum daily flux recorded through the duration of the campaign due to the build-up of aerosol loading. Simulations with a discrete ordinate model reported in the same paper, using aerosol SSA and asymmetry parameters from the sunphotometer data, showed good agreement with the measured fluxes. Due to the relatively high SSA of the aerosol, the fluxes were insensitive to the details of the vertical profile of aerosol. The aerosol radiative effect – defined as the net flux (aerosols) minus net flux (no aerosol) – was calculated at the surface as being between $-10(\pm 5)$ W m^{-2} to $-14(\pm 7)$ W m^{-2} depending on the surface characteristics assumed. The instantaneous top of the atmosphere aerosol forcing would be $-4(\pm 2)$ W m^{-2} over

vegetation, and $-8(\pm4)$ W m^{-2} over ocean. The atmospheric absorption is therefore around 7 W m^{-2} and the aerosol forcing efficiency at the surface -75 W m^{-2} over sea water and -55 W m^{-2} over vegetation. This is in good agreement with MINOS results in the summertime southern Mediterranean (-71 W m^{-2}; Markowicz *et al.*, 2002). However, the observed aerosol properties and profiles were used with the Edwards and Slingo (1996) radiation code for B049 and B048. For the Adriatic (B049), the optical depth used was that of the Venice AERONET site (0.18) due to concerns regarding the *in situ* measurement of number concentration as discussed above. The radiative effect in this case was calculated as -28 W m^{-2} at the top of the atmosphere and -59 W m^{-2} at the surface, giving an atmospheric absorption of 31 W m^{-2}. For B048 over the Black Sea, the radiative effect was calculated using the optical depth derived from nephelometer and PSAP instruments as -23 W m^{-2} at the top of the atmosphere and -40 W m^{-2} at the surface. The atmospheric absorption in this case was somewhat less than over the Adriatic, i.e. 18 W m^{-2}. These values are considerably higher than those calculated from the pyranometer. This could be due to different assumptions concerning the optical depth and optical properties of the aerosol, and these estimates should be treated with caution, especially since direct measurements of the radiative effect of aerosol for consistent comparison were not possible from the aircraft due to instrument issues.

5. Conclusions and implications

ADRIEX successfully measured a variety of aerosol conditions across the northern Adriatic, the Po Valley and the Black Sea. Although substantial variation in vertical profile and loading were found, in general two well-defined aerosol layers were generally visible. Over the Adriatic these tended to have similar properties and origins, whilst over the Black Sea different chemistry and radiative properties were evident in the different layers. Of particular note from ADRIEX are:

- The importance of nitrate species for the Po Valley (and northern Adriatic depending on flow regime), as revealed by the AMS. This suggests that nitrate aerosol is indeed becoming increasingly important for industrial regions following reduction in sulphate emissions. It also suggests that future *in situ* measurements of ammonia might be crucial to close the aerosol mass budget; this requires substantial technological and theoretical development.
- The somewhat surprising lack of black carbon in all regions, although absorption by some component of aerosol reduced the SSA to the region of critical SSA for the breakdown of radiative forcing and response relationships. Estimates of the BC content obtained by iterations to match SSA are broadly consistent with low levels measured by the filter techniques. There are two interpretations of this finding. Firstly, BC is

responsible for most of the absorption occurring but we are not able to measure it sufficiently accurately at these low levels to prove this hypothesis. Secondly, some of the absorption is due to 'brown' organic carbon compounds. Direct measurements of particle BC content *in situ* are highly desirable.

- The consistent underestimation of AOD by *in situ* measurements, particularly when using the number concentrations from the PCASP compared to the lidar and AERONET. The inability to measure total aerosol number during profiles introduces substantial uncertainty into AOD estimates from aircraft data. The existence of an apparent very local and low-altitude aerosol plume only visible by the lidar highlights the importance of extremely local sources.
- A surprising lack of variation in the size distribution, and a general agreement with anthropogenic aerosol from previous campaigns suggests that models may not need to represent many aerosol size distributions when no cloud processing has been involved. However, radiative properties can still differ due to differing chemical composition.
- Both the AMS and VACC offer substantial new insights into aerosol chemistry and mixing state and, with the development of techniques for modelling radiative properties, should be considered as core instruments for aerosol microphysics investigations. The addition of an instrument to measure directly black carbon *in situ*, an improvement in the ability to size both the coarse mode of aerosol and very small aerosol sizes, the ability to measure gaseous ammonia, and the development of the wet nephelometer to measure growth factor explicitly *in situ* would complete a world-leading aerosol microphysics instrument suite.

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