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Optical, physical and chemical characteristics of Australian Desert dust aerosols: results from a field experiment

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Abstract

Mineral dust is one of the major components of the world's aerosol mix, having a number of impacts within the Earth system. However, the climate forcing impact of mineral dust is currently poorly constrained, with even its sign uncertain. As Australian deserts

- are more reddish than those in the northern hemisphere, it is important to better understand the physical, chemical and optical properties of this important aerosol. We have investigated the properties of Australian desert dust at a site in SW Queensland, which is strongly influenced by both dust and biomass burning aerosol. Three years of ground-based monitoring of spectral optical thickness has provided a statistical picture of gross aerosol properties. In November 2006 we undertook a field campaign which
- collected 4 sets of size-resolved aerosol samples for laboratory analysis both ion beam analysis and ion chromatography.

The aerosol optical depth data showed a weak seasonal cycle with an annual mean of 0.06 ± 0.03 . The Angstrom coefficient showed a stronger cycle, indicating the in-

- ¹⁵ fluence of the winter-spring burning season in Australia's north. Size distribution inversions showed a bimodal character, with the coarse mode assumed to be mineral dust, and the fine mode a mixture of biomass burning and marine biogenic material. Ion Beam Analysis was used to determine the elemental composition of all filter samples, although elemental ratios were considered the most reliable output. Scatter plots
- showed that Fe, AI and Ti were well correlated with Si, and Co reasonably well correlated, with the Fe/Si ratio higher than the crustal average, as expected. Scatter plots for Ca, Mn and K against Si showed clear evidence of a second population, which in some cases could be identified with a particular sample day or size fraction. Ion Chromatography was used to quantify water soluble ions for 2 of our sample sets, showing the importance of marine influences on both fine (biogenia) and coarse (case solt) modes.
- ²⁵ importance of marine influences on both fine (biogenic) and coarse (sea salt) modes.

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1 Introduction

The variability of the optical properties of dust particles depends in large part on the dust source region (Dubovik et al., 2002; Kubilay et al., 2003; Lafon et al., 2006). Therefore physical (size and shape) and chemical (composition and mineralogy) char-

- acterization of mineral aerosols from different source regions is important, for a number of reasons. Firstly, dust aerosol exerts a poorly understood forcing on the Earth's radiative budget (Charlson et al., 1992; Tegen et al., 1996; Sokolik et al., 2001; Forster et al., 2007), since it both scatters and absorbs solar radiation, while also absorbing and emitting some infrared radiation. Secondly, dust aerosol may change the physical and radiative properties of cloude (Demonsthen et al., 2001). Thirdly, betarageneous
- and radiative properties of clouds (Ramanathan et al., 2001). Thirdly, heterogeneous reactions on the surface of dust particles may lead to the formation of sulfate and/or nitrate layers on the surface of these particles (Prospero and Savoie, 1989; Nishikawa et al., 1991; Dentener et al., 1996; Jacob, 2000). Finally, dust particles may have an impact on human health.
- Global annual dust emission is estimated to be ~1877 Tg yr⁻¹, of which Australia contributes around 5.6% of the total emitted (Tanaka and Chiba, 2006), and is the greatest contributor of mineral aerosol in the southern hemisphere. Further, Australia's deserts are reddish, in contrast to the Sahara, for example, which is more yellow. This difference is a reflection of the mineralogy, particularly in relation to iron oxides (Sokolik and Toon, 1996). Australian mineral dust aerosol has not been well characterised to date, so that the aim of this project was to take the first key steps in filling this significant gap.

In this study we have monitored the optical properties of dust at a desert site for three years, and also conducted a field campaign which involved the collection and analysis

of size-resolved dust samples for the analysis of its chemical composition. Section 2 describes our sampling location – in the east-central part of the continent, exposed to both desert dust and biomass burning aerosol – and methods used.

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In Sect. 3 we examine the optical properties of Australian desert aerosol: optical depth, Angstrom coefficient and (seasonal average) size distribution – usually bimodal, reflecting the two major aerosol types. In Sect. 4 we present some of the field sampling results: specifically the mass size distributions and the major elemental analyses. In Sect. 6 we present an analysis of the (size-resolved) water-soluble ions, which provides valuable information on the aerosol sources. Finally Sect. 7 contains an overview of the picture these results present.

2 Study area and data sources

2.1 Field site

¹⁰ Birdsville, in south-west Queensland (25.9 S, 139.34 E, 48 m elevation), is a small outback town situated on the banks of the Diamantina River between the sands of the Simpson Desert and the gibbers of Sturt's Stony Desert (Fig. 1). Rainfall averages 167 mm per year, occurring mostly in summer, with September being the driest month. Daytime temperatures reach 38°C in summer (November–February). Annual average relative humidity is 48%, with highest values of around 67% in June. Dust devils are common. The Birdsville permanent population currently stands at approximately 120, but is augmented at times (especially winter/early spring) by tourism, peaking at around 6000 for the "Birdsville Races" in early September.

2.2 Aerosol optical depth (AOD) and Angstrom coefficient (α)

- A Cimel sun photometer at Birdsville has been monitoring aerosol optical depth (AOD) over a range of wavelengths since the spring of 2005. This instrument forms part of the CSIRO Aerosol Ground Station Network (Mitchell and Forgan, 2003), which is affiliated with NASA'a global Aerosol Robotic Network, AERONET. Instrument calibration and the generation of AOD and aerosol microphysical data (phase function, size distribution, refractive index and derived quantities such as single seattering albede and
- ²⁵ tribution, refractive index and derived quantities such as single scattering albedo and



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asymmetry factor) are performed as part of the standard AERONET processing stream (Holben et al., 1998; Dubovik and King, 2000). In this study we will use AOD at 500 nm as our measure of aerosol loading.

Another parameter which can be extracted from this data is the Angstrom coefficient, 5 α , which is obtained from a straight line fit of ln(AOD) vs. ln(λ), over the wavelength range 440 to 870 nm. As a good rule-of-thumb, small values of Angstrom coefficient are associated with larger particles, while large values are associated with smaller particles, in general.

2.3 Aerosol samples

- ¹⁰ In November 2006 we deployed a 12 stage Micro Orifice Uniform Deposition Impactor (MOUDI) (Marple et al., 1991) to collect size-segregated aerosol particles. The inlet to the MOUDI consisted of two stainless steel bowls with a 2 cm gap between them to allow air to be sampled equally from all directions, while also protecting against rain. The stage cuts are at 18.0, 10.0, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.1 and 0.056 μ m ¹⁵ aerodynamic diameters, plus an after filter (<0.056 μ m). (In the case of mineral dust particles with their relatively high density, this is likely to be an overestimate of the "true" or effective diameter by around 30%.) These stages allow for collection of samples for
- the identification of any compositional differences between particles of different size as the aerosols in many locations are known to be chemically variable, with significant differences between fine and coarse modes. For convenience we define coarse mode
- ²⁰ differences between fine and coarse modes. For convenience we define coarse mode aerosols as particles with (aerodynamic) diameters greater than $1.0 \,\mu$ m, and fine mode aerosols as those with smaller diameters: see also Fig. 6. The flow rate of the MOUDI was 30 l/min. The collection substrates used on the first 11 stages were polycarbonate Isopore filters 47 mm in diameter with 0.8 μ m pore size. The final stage substrate was a Teflon-backed Fluoropore filter 47 mm in diameter with 1 μ m pore size.

We weighed the substrates before and after sampling at the Institute for Environmental Research of the Australian Nuclear Science and Technology Organization (ANSTO) using a Mettler Toledo MX5 balance with repeatability 0.0008 mg at gross load. The

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temperature during the weighing process was 22±1.5°C, and the humidity was 50±5%. The sum of the masses on all MOUDI filters can be considered a good measurement of Total Suspended Particulates in the atmosphere (TSP) for one sampling period because all particles for different sizes are collected at the one time between the inlet and the after filter stages.

The substrates were analysed using accelerator-based Ion Beam Analysis (IBA) techniques (PIXE and PIGE) at ANSTO (Cohen, 1993, 1998; Cohen et al., 1996). The IBA technique uses an 8 mm diameter beam of 2.6 MeV protons with 10–15 nA target current. Cohen et al. (2002) discuss in detail the minimum detection limits and errors related to PIXE and PIGE measurements. As the spatial distribution of sample on each filter (stage) varied, and the ion beam only sampled the central 10% of the filter, we have used the IBA results primarily to obtain the ratio of elements to the most abundant element in our dust samples.

After IBA, the substrates were analysed for the concentration of soluble ions at CSIRO by suppressed ion chromatography (IC). The filters were extracted in 5 ml of MQ-grade water (MQ-grade water is $18 \text{ m}\Omega$ de-ionized water). The sample was then preserved using 1% chloroform. Anion and cation concentrations were determined by using a Dionex DX500 gradient ion chromatograph. Anions were determined using an AS11 column and an ASRS ultra-suppressor and a gradient eluent of sodium hydrox-

²⁰ ide. Cations were determined using a CS12 column and a CSRS ultra-suppressor and a methanesulfonate acid eluent.

3 Aerosol optical properties

3.1 Daily and monthly data

From plots of the daily and monthly means of AOD for the period August 2005 to June 2008, shown in Fig. 2, we see a weak seasonal variability in aerosol optical depth. Daily averages of AOD (Fig. 2a) display less variability during winter, reflecting lower

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wind speed that dominates during this season, resulting in a lack of significant local dust sources. During spring, summer and autumn, the variability in the daily average AOD is increased due to the influence of dust activity. Figure 2b shows the monthly means and standard deviations. The annual mean of AOD computed from the monthly 5 means is 0.06±0.03.

The daily and monthly means of α are presented in Fig. 3, which shows a very clear seasonal cycle, along with large variation in daily measurements, including negative values on some days – and especially during summer and early autumn – which is likely due to dust storm activity. (Inadequate cloud screening is unlikely to be a factor.) Higher values in AOD along with a wide range of α values during spring months is sug-

¹⁰ Higher values in AOD along with a wide range of α values during spring months is suggestive of a contribution from a different aerosol type such as regional biomass burning, and/or long range (intercontinental) transport (Rosen, et al., 2000; Gloudemans et al., 2006), and/or the possible influence of marine biogenic emission when the air mass is advected from the ocean. The situation is more complex during winter months, when 15 low AOD values are associated with high α values.

A scatter plot of daily average Angstrom coefficient, α , against daily average AOD at 500 nm, is presented in Fig. 4a. This figure shows a wide range of α associated with AOD less than 0.03. To isolate the low AOD measurements, we plotted the time series of all AOD<0.03 in Fig. 4b, which shows that nearly all of these measurements were during late autumn and winter. As a check, we re-plotted the time series of α excluding all data where AOD was less than 0.02: the seasonal cycle was still obvious.

20

Winter is the dry season, characterized by clear skies, along with lowest temperatures and wind speeds. It is also the burning season in the "top end" of northern of Australia, so that a biomass burning signature from that region at our Birdsville in-

strument is likely, whenever the winds are from an appropriate direction. (In addition, winter is a tourism season, when many people are camping under the stars and using firewood for cooking and heating, which produces biomass burning aerosol, although only in very small amounts).

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It should also be noted that the uncertainty in α increases significantly whenever it is computed from AOD data less than 0.02. For this reason, we did not use AOD data below 0.02 when computing α because of the high probability of unacceptable errors.

3.2 Seasonal statistics

- ⁵ The seasonal frequency distributions of daily means of AOD and *α* are presented in Fig. 5. The left panel shows that the AOD distribution was very narrow during autumn and winter, with ~60% of the data observed in the 0.03 bin in both seasons. During summer the distribution was broader and the peak was in the 0.05 bin which accounted for ~40% of the data observed, with around 20% of the data observed in each of the two adjoining bins. The spring distribution was very broad again peaking in the 0.05 bin, but with a long tail, with around 40% of the data above 0.08. Overall around 80% of daily AOD means are below 0.1. Around 80% are less than 0.06 during autumn and winter months, but only 50% fall in that range during spring and summer.
- The frequency distributions of daily means of α central panel were broad in all seasons, indicative of a range of particle sizes entering the atmosphere, or a range of atmospheric processing. This figure shows a skewed distribution during summer with approximately half the data observed in the lowest two bins, which indicates that coarse mode particles predominate. During autumn the peak was shifted to the 1.1 and 1.4 bins, and accounted for ~40% of the total daily means, while around 30% of the daily means were in the 0.2 and 0.5 bins. The winter pattern showed a normal distribution with around 65% of the data in the 0.7–1.6 range. This indicates that fine
- mode particles predominate during this season, a result of local wood burning and regional biomass burning, plus (presumably) fine dust particles. The spring distribution was approximately normal, with around 65% of the data in the 0.7–1.6 range, which
- again implies both fine mode biomass burning aerosol (plus, presumably, fine dust) and a contribution from a different aerosol type, such as coarse dust. The annual mean of α computed from the monthly means is 0.9±0.3.

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Scatter plots of daily average α vs. AOD for each season in Fig. 5 (right panel) show that during all seasons a wide range of α is associated with AOD less than 0.05. On the other hand, the α values generally decreased (including some negative values) as the value of AOD increased beyond 0.1 in all seasons, which implies that dust is the main contributor to the higher optical thickness values during those seasons. However, the spring pattern shows a second aerosol signature with larger α values contributing to the larger optical thickness measurements, indicating the influence of fine mode particles, most likely biomass burning aerosol.

3.3 Aerosol size distribution

- ¹⁰ We used the daily average (columnar) volume size distributions from the AERONET web site to calculate seasonal average volume size distributions: these are presented in Fig. 6a. This graph shows a clear bimodal pattern in all seasons, as well as some significant differences. Summer and spring have the largest aerosol loadings, with a coarse mode peak at 3.5 μ m radius, however this peak varied from day to day depend-
- ¹⁵ ing on wind speed and direction. Figure 6b shows the volume size distributions for selected days during spring 2007, and we see that the coarse mode peak shifts from day to day. The spring distribution shows the strongest fine mode, with a peak between 0.10 and 0.15 μ m radius, which is further evidence of a second aerosol contribution (most likely biomass burning) during this season. Figure 6b shows that on 8 Octo-
- ²⁰ ber 2007 the fine mode peak was dominant, and the air mass back trajectory during this day shows advection from the north, where hot spot satellite imagery confirmed that biomass burning was occurring (as expected for this time of year). The autumn and winter distributions show lower total aerosol content, with the coarse mode again dominating.
- Qin and Mitchell (2009) have performed a cluster analysis of AERONET retrievals from a number of Australian sites (3 in northern Australia subject to biomass burning, 2 desert sites, plus others), including Birdsville. This yielded 4 classes which they identify as aged smoke, fresh smoke, coarse dust, and a super-absorptive class of



undetermined origin. While all 4 classes have bimodal size distributions, it is only the coarse dust class which has a dominant course mode (and a very small fine mode).

The aerosol size distribution over Birdsville is clearly bimodal: a fine mode which we believe is primarily biomass burning, and a coarse mode which we believe is mineral

⁵ dust. The contributions of each vary seasonally in ways which are quite predictable. The fine mode occurs mainly in spring, the peak of the biomass burning season in northern Australia. The coarse mode strength is primarily dictated by wind speeds, which are stronger in spring and summer.

4 Aerosol samples: gravimetric mass distributions

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In November 2006 we deployed a 12 stage Micro Orifice Uniform Deposition Impactor (MOUDI) to collect size-segregated aerosol particles. During this field campaign we collected 5 sets of samples – denoted A, B, C, D and E. Sample A was used for equipment testing only, and has not been included in the analysis. Table 1 gives the start and finish times of our sampling periods. Note that collection times varied, depending on dust activity conditions.

The size-resolved mass concentrations for different data sets are presented in Fig. 7, which shows that the size spectrum was quite variable during our field campaign. Total suspended particulates (TSP) during the sampling period are in order C>B>E>D: see Table 2. The mass concentration was significantly higher during periods B and C due to the influence of moderate to high wind speeds and local dust storm activity on those days.

During sampling period B there was significant raised dust, although not associated with a dust storm. (A dust devil may have contributed to this.) The mass size distribution during this period was multi-modal, but without a definable "structure".

²⁵ During period C, a weak local dust storm occurred (but for few a moments only). The resulting size distribution was tri-modal with peaks at 0.18, $0.56 \mu m$ diameter, and a broad coarse mode peak. During the other sampling periods the distributions



were relatively flat.

We applied a smoothing/inversion procedure to these 4 data sets (Keywood et al., 1999), and the results are presented in Fig. 7b. From these retrievals we are able to extract the masses in key size ranges (see below). AERONET retrievals were available on two of these days, and particularly sampling period C, which gave the most clearly defined modal distribution. In Fig. 7c we replot our inverted distribution for this period, along with the AERONET retrieval. Several factors may explain the differences, particularly for sizes above $10 \,\mu$ m. Firstly our results are for the surface only while AERONET is a column retrieval (hence the different scales): the larger particles are likely to be found only in the lowest atmospheric layers. Secondly our results are based on a 24 h sampling period. Finally, a number of authors have questioned the reliability of AERONET retrievals in this size range, given that the longest measurement wavelength is only 1.02 μ m. In particular, the comparison shown in Fig. 7c suggests

that the AERONET inversion leads to an artificially steep decline on the large particle
 side of the coarse mode peak, an issue discussed by Qin and Mitchell (2009). Given these caveats, we consider the agreement to be excellent.

Table 2 shows the ratios between PM₁₀, PM_{2.5}, PM₁ and TSP; PM_{2.5}, PM₁ and PM₁₀; and PM_{2.5} and PM₁. ("PM_n" is "particulate matter with diameters less than n μm".) On average the PM₁₀, PM_{2.5} and PM₁ components make up 76%, 46% and 31% of TSP
respectively. PM_{2.5} and PM₁ comprise 61% and 41% of PM₁₀ respectively, and PM₁ makes up 68% of PM_{2.5}. From the above analysis we can conclude that the PM_{2.5} component (sometimes taken as the fine mode for air quality purposes) accounts for approximately 50% of all particulate mass in the Birdsville atmosphere at this time of year. The coarse particles are, of course, more rapidly removed by gravitation.

25 5 Elemental composition and source apportionment

Ion Beam Analysis showed that, as expected, Si is an abundant element in all size fractions, and is used in this study as a dust "indicator" for Australian desert aerosol.



We used the elemental concentrations determined through the IBA to calculate the mass ratio of elements to Si: these ratios are summarised in Table 3, along with the mass ratios of these elements in the Earth's crust from CRC Handbook (Lide, 1997). Size-resolved mass ratios for selected elements are presented in Fig. 8. Scatter plots

for some of these elements, based on all 48 data values, are presented in Fig. 9. We classified the elements to two groups: crustal elements (e.g. Al, Fe, Ca, K, Mn and Ti); and Na and Cl.

5.1 Crustal elements

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The TSP Fe/Si ratios are in the range 0.215–0.232, which is moderately higher than the value in the Earth's crust: this most probably reflects the high amount of Fe which occurs naturally in Australian desert soil. The Fe/Si mass ratios for all samples are shown in Fig. 8, which shows a complex structure, reasonably consistent across all four samples. The scatter plot of Fe versus Si in Fig. 9a shows an excellent linear relationship with R^2 =0.98, indicating that soil is the source of Fe in our samples. This ratio of Fe to Si may be used to build a signature for Australian soil.

The TSP Al/Si mass ratios are in the range 0.271–0.292, close to the value in the Earth's crust, and the scatter plot of Al against Si in Fig. 9a again shows an excellent linear relationship with R^2 =0.99. The TSP Ti/Si mass ratios were between 0.018 and 0.026, which is in good agreement with the crustal value. The scatter plot of Ti against Si again shows an excellent linear relationship with R^2 =0.97. Both of these ratios can be incorporated in our soil signature.

The Ca/Si TSP mass ratios are lower than the value in the Earth's crust by ~60–80% for all samples. The scatter plot of Ca against Si appears to show two populations, indicative of two sources. The primary population displays an excellent linear relationship with R^2 =0.97, so that this population can be assumed to be associated with Si in Australian soil. The second population comprised particles between 1.8 to 10.0 μ m, and from samples D and E only. This population also shows a reasonable correlation

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trajectories suggest the air mass reaching the sampling site had travelled over gypsum mines during sampling periods D and E (see Fig. 10).

The TSP mass ratios of Mn to Si are greater than the Earth's crustal values by 33– 66 %, and Fig. 8 shows that the higher mass ratios occurred mainly in the size range $50.32 \,\mu$ m and below. Moreover the scatter plot of Mn against Si appears to show two populations: the dominant population, showing an excellent linear relationship with R^2 =0.94, can be assumed to be associated with Si in Australian soil. The second population shows a poor relationship with Si, and all points were from the size range below 1.8 μ m, and from all samples.

¹⁰ The scatter plot of K against Si again shows two populations, indicative of two sources. The dominant population shows an excellent linear relationship with R^2 =0.98, and is again clearly associated with Si in Australian soil. The second population points are in the fine range 0.32 μ m and smaller, and from the B and C samples only. They showed no correlation with Si, indicating an unrelated source: most likely biomass burning/smoke, or similar.

Figure 9b shows scatter plots of Co, Cu and Zn against silicon: these plots show less correlation. For these elements, possible statistical variability of the low values obtained may be masking a modest relationship to Si.

5.2 Na and Cl

- ²⁰ The TSP mass ratios of Na/Si are in good agreement with the values in the Earth's crust during sampling periods B and C, but are high during sampling periods D and E, suggesting the contribution of other aerosol sources such as sea spray. Back-trajectories for the 4 days, shown in Fig. 10, show that during periods D and E the air was advected from the ocean. Furthermore, the size-resolved mass ratios in Fig. 8
- ²⁵ show that the Na/Si mass ratio is very high in most sizes during periods D and E, however this ratio is larger in the fine fraction during periods B and C. Table 3 shows that the ratio of CI to Si is very high during all events, with the coarse fraction ratio at $3.2 \,\mu$ m diameter (Fig. 8) being especially high during period D. As a result, the Cl/Na ratio was



0.65, 0.38, 0.98 and 0.84 during sample periods B, C, D and E respectively, which is very much higher than the value of 0.006 in the Earth's crust, but closer to (though still lower than) the value of 1.8 in seawater.

Figure 9c shows scatter plots of Na and Cl against Si, and also a scatter plot of Cl against Na. No trend line is presented in the plots against Si. The scatter plot of Cl against Na shows a reasonable linear relationship with R^2 =0.81. High Cl/Na ratios during periods D and E are clearly due to some combination of influences of sea spray aerosols from the ocean (see Fig. 10) and salt from Australia's dry lakes (southwest of Birdsville). The high value of Cl may relate to the high amount of dry salt (halite, NaCl) from dry lakes in the Australian arid region, mixed with desert aerosol.

6 Water-soluble ions

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The concentration of total, and coarse $(1.0-18 \,\mu\text{m} \text{ range})$ ion species found in sample periods C and E are presented in Table 4. The size distributions of important ions are presented in Fig. 11.

 SO_4^{2-} , Ca^{2+} and K^+ ions are found in sea spray aerosol and also in soil, and fine mode K^+ may be found in biomass burning aerosol. We removed the sea spray component from the concentration of these ions by using the following definitions:

$$nssSO_{4}^{2-} = SO_{4}^{2-} - Na^{+} (SO_{4}^{2-} / Na^{+})_{seawater}$$
(R1)

$$nssCa^{2+} = Ca^{2+} - Na^{+} (Ca^{2+} / Na^{+})_{seawater}$$
(R2)

where $(SO_4^{2^-}/Na^+)_{seawater}$, $(Ca^{2^+}/Na^+)_{seawater}$ and $(K^+/Na^+)_{seawater}$ are the mass ratios of $SO_4^{2^-}$, Ca^{2^+} and K^+ in seawater, and we used values from Millero and Sohn (1992).

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(R3)

6.1 Na⁺, Cl⁻ and Mg²⁺

Figure 11 shows that Na⁺ is predominantly in the coarse mode during period C, with a broad peak in the 1.0–3.2 μ m range, while during period E this peak shifted to the 3.2–5.6 μ m range. A secondary peak is found in the ultra-fine range during both periods.

- ⁵ The total concentration of this ion was 0.314 and $0.225 \,\mu g/m^3$ for periods C and E, respectively, with the coarse fraction predominating with 78% and 58% respectively. The size distribution of Cl⁻ ion was bimodal for both periods, the first peak occurring in the coarse mode in the 3.2–5.6 μ m range for both samples, and a secondary peak in the ultra-fine range. The total concentration of Cl⁻ was 0.137 and 0.122 μ g/m³, with
- 61% and 68% in the coarse fraction, for periods C and E, respectively. The Cl⁻/Na⁺ mass ratios were 0.44 and 0.54, which is lower than the value in seawater, although greater than the value in the Earth's crust. Sodium chloride may react with nitric acid gas (see Reaction R4 below) to deplete the chlorine concentration, and thus reduce the Cl⁻/Na⁺ mass ratio.
- ¹⁵ We see from Fig. 11 that Mg^{2+} was found predominantly in the coarse mode for both periods C and E. The size distribution of this ion has a broad peak centred at $3.2 \,\mu$ m for period C and at $3.2-5.6 \,\mu$ m during period E. The total concentration of Mg^{2+} was 0.042 and 0.014 μ g/m³ during periods C and E, respectively, with the coarse fraction containing 78% and 61% respectively (Table 4). Mg^{2+} is present in mineral dust and sea salt. However, the mass ratios of Mg^{2+}/Na^+ are in good agreement with the seawater ratio in all size fractions during period C, indicating the primary influence of sea spray on this ion. However, this ratio was significantly reduced during period E, a consequence of the longer time spent over land as seen in Fig. 10.

6.2 Ca²⁺

²⁵ We see from Fig. 11 that Ca^{2+} was found primarily in the coarse mode, with a predominant peak in the 3.2–5.6 μ m range for period C, and at 5.6 μ m for period E. (This shift in peak may be a reflection of the second population identified in Sect. 5.1; Fig. 9a.) The

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total concentration of Ca²⁺ was $0.16 \mu g/m^3$ during period C, but this reduced sharply during period E to only $0.05 \mu g/m^3$, with 77% and 72%, respectively, in the coarse mode. (These results are consistent with the overall higher mass concentrations during period C – see Fig. 7 – resulting from the local dust storm.)

The TSP mass ratios of Ca²⁺/Na⁺ were much higher than the ratio in sea water (Table 4) during those periods, which indicates that most of the calcium originated from dust particles. Calcium is found in sea salt and in mineral dust, as calcite (CaCO₃) and/or in gypsum (CaSO₄). We removed the seawater component from total Ca²⁺ using Reaction (R2), and found that 92% and 83% of the total Ca²⁺ was nssCa²⁺ during periods C and E, respectively. The size distributions of nssCa²⁺ are very similar to the Ca²⁺ patterns for both samples.

6.3 NO₃⁻

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It is clear from Fig. 11 that the NO_3^- in the atmosphere was concentrated in the lower coarse mode region, with a distribution similar to the Na⁺, Ca²⁺ and Mg²⁺ distributions. The concentrations of NO_3^- are found to be 91% and 72% in the coarse fraction during periods C and E, respectively. When NaCl particles are present in the atmosphere, coarse mode NO_3^- may be produced as a result of the reaction of HNO₃ with NaCl to produce NaNO₃ and HCl (Wall et al., 1988; Zhuang et al., 1999):

 $HNO_3 + NaCI \rightarrow NaNO_3 + HCI$

- ²⁰ Consequently, studies by Savoie and Prospero (1982), Harrison and Pio (1983) and John et al. (1990) report that coarse mode nitrate is dominant in coastal regions, whereas the fine mode is dominant in rural areas. We note from Fig. 11 that the CI^{-}/Na^{+} mass ratio is especially low in the 1.8 μ m bin in period C, which corresponds to the nitrate peak.
- ²⁵ HNO₃ can also react with Ca and Mg carbonates on soil particles to generate coarse mode nitrate via the reaction (Wolf, 1984; Dasch and Cadle, 1990;



(R4)

Mamane and Gottlieb, 1992; Pakkanen et al., 1996):

 $2HNO_3(g) + CaCO_3(s) \rightarrow Ca(NO_3)_2(s) + H_2O + CO_2(g)$

In summary, we have found that Australian desert dust is well mixed with NaCl as a result of salt-rich dry lakes in the Australian arid zone (see Sects. 6 and 6.1). The reaction of HNO₃ on dust particles and/or dry NaCl leads to the formation of nitrate particles in the coarse ranges seen in Fig. 11.

6.4 K⁺

The sources of K⁺ may be soil, sea spray or biomass burning aerosol. The size distribution of K⁺ was multi-modal, but without an easily definable "structure" for both periods. However, the additional peak at 0.18–0.32 μ m in period C is fully consistent with the second population noted in Sect. 5.1. The total concentrations of K⁺ were 0.083 and 0.021 μ g/m³, with 52% and 53% present in the fine mode of the C and E samples, respectively.

Air mass back trajectories in Fig. 10 show that during both sampling periods the air ¹⁵ was advected from the ocean: we therefore removed the sea spray component from the total concentration of K⁺ by using Reaction (R3), and found that 86% and 61% of the total K⁺ was nssK⁺ during periods C and E, respectively. We may note that the coarse mode of nssK⁺ was strongly depleted in the 1.0-5.6 μ m range relative to total K⁺ peak during period C, but that depletion was in the 0.56–5.6 μ m range (and also at <0.056 μ m) for period E. This is consistent with the size distributions of Na⁺, Mg²⁺, etc.

The K⁺/Na⁺ mass ratio was 0.27 during period C, greater than the sea water value. However, since the contribution of seasalt K⁺ was 39% to total concentration of K⁺ during period E, the mass ratio K⁺/Na⁺ during this period was reduced to 0.09, which ²⁵ is close to the seawater value. While there is no direct evidence of K⁺ from biomass burning sources, we can speculate that on some occasions dust devils may pass over old biomass burning vegetation ash, and thus some of this ash will be mixed with

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(R5)



dust particles. Overall we can conclude that the total potassium found in the Birdsville atmosphere has contributions from a number of sources, including biomass burning, crustal and sea spray.

6.5 SO_4^{2-} , NH_4^+ and Methanesulfonate (MSA)

- ⁵ Sulfate exists in the coarse fraction as gypsum in soil dust particles, and as Na₂SO₄ in sea salt. The source of fine mode SO_4^{2-} over land is industrial pollution and motor vehicle emissions, while marine biogenic emission is the dominant source of fine nssSO₄²⁻ over the ocean. The strong similarity in the SO₄²⁻ and MSA size distributions suggests that the marine contribution was significant at our site.
- ¹⁰ The total concentrations of $SO_4^{2^-}$ were 0.66 and $0.53 \mu g/m^3$ during periods C and E, respectively, which is the highest (mass) concentration found among the watersoluble ions in our samples. 85% and 90% of those concentrations, respectively, was associated with the fine fraction (Table 4 and Fig. 11). 88% and 89% of total $SO_4^{2^-}$ was found to be $nssSO_4^{2^-}$ for periods C and E, respectively. The $nssSO_4^{2^-}$ size pattern followed the $SO_4^{2^-}$ pattern in the entire region $\leq 0.56 \mu m$, but in the coarse mode the $nssSO_4^{2^-}$ is depleted. It has been reported (Saltzman et al., 1983; Huebert et al., 1993; Quinn et al., 1993; Gao et al., 1996) that the majority of $nssSO_4^{2^-}$ aerosol particles collected near coastal regions have a size range $0.35-0.7 \mu m$ in diameter. This fine mode $nssSO_4^{2^-}$ is a feature of gas-to-particle conversion (Fitzgerald, 1991).
- The total concentrations of NH_4^+ measured during these sampling periods were 0.22 and 0.73 μ g/m³, with 85% and 95% of those concentrations in the fine fraction for periods C and E, respectively. The NH_4^+ size distribution is similar to the SO_4^{2-} and MSA size distributions. Ammonia gas reacts with sulphuric acid, and reactive sulphates, to form species in the ammonium sulphate family: NH_4HSO_4 ; $(NH_4)_2SO_4$; and metal ammonium sulphates. For a remote, non-industrial location such as our sampling site, sulphuric acid concentrations are likely to be minuscule, so that $(NH_4)_2SO_4$ is the most



likely of these species.

Kadowaki (1976) showed that if the size distribution of sulfate follows the size distribution of NH_4^+ then this indicates the presence of $(NH_4)_2SO_4$ in the air: studies by Kulshrestha et al. (1998), Zhuang et al. (1999) and Parmar et al. (2001) support this argument. Overall, the similarity of the size distributions of NH_4^+ and SO_4^{2-} indicates that $(NH_4)_2SO_4$ was present in the fine fraction in the Birdsville atmosphere during the sampling period. (The mass ratios support this conclusion.)

The oxidation of dimethylsulfide is believed to be the source of methanesulfonate (MSA) and nssSO₄²⁻ over the ocean (Bates et al., 1987; Leck and Rodhe, 1991). ¹⁰ The total atmospheric concentrations of MSA during both sampling periods was $0.015 \,\mu$ g/m³, which is quite close to the value of $0.017 \,\mu$ g/m³ found at Cape Grim in Tasmania (Ayers et al., 1986). 88% and 90% of this amount was in the fine mode for periods C and E, respectively. The size distribution of MSA is dominated by the fine fraction, in the range <0.32 μ m in diameter for both samples (Fig. 11). This distribution ¹⁵ is quite similar to that of nssSO₄²⁻.

Results from cascade impactors at a coastal area of the China Sea have shown that $nssSO_4^{2-}$ and MSA have similar size distributions in the fine mode (particles $\leq 0.5 \,\mu$ m) (Gao et al., 1996). In addition, the size distribution of MSA in this study is consistent with that observed in the atmosphere of US coastal regions (Saltzman et al., 1983, Ovince at al., 1902). The mass ratios of the $nas2O_4^{2-}$ to MSA during the compliant

Quinn et al., 1993). The mass ratios of the nssSO₄²⁻ to MSA during the sampling periods were 39.5 and 31, which is greater by factor of 2 than the values observed at American Samoa of 18.1±0.9 (Savoie et al., 1994) and over the North Atlantic Ocean islands 19.6±2.1 (Savoie et al., 2002). On the other hand, those ratios are much lower than that obtained over the China Sea, which ranged from 60 to 870, as a result of nssSO₄²⁻ input from anthropogenic sources (Gao et al., 1996), and over coastal regions in Asia (480 for Hong Kong, and 580 for Taiwan) (Arimoto et al., 1996).

We calculated the concentration of $nssSO_4^{2-}$ from nonbiogenic sources by using the following reaction (Arimoto et al., 1996)

nonbiogenic nssSO₄²⁻=total nssSO₄²⁻-(MSA*16)





(R6)

The constant 16 represents the ratio of biogenic $nssSO_4^{2-}$ to MSA found at Cape Grim, Australia by Ayers et al. (1986). This showed that 60% and 48% of the $nssSO_4^{2-}$ was found to be nonbiogenic during periods C and E, respectively. Overall our results suggest that of the total $nssSO_4^{2-}$ found in this study, continental emissions and marine biogenic activity made equal contributions.

7 Discussion and conclusions

Birdsville is an ideal location for the study of Australian continental aerosol, and especially mineral dust, as it is often downwind of both mineral dust source regions, and biomass burning regions. We have found clear signatures of both aerosol types in our analysis, as well as clear evidence of the advection of marine aerosol including not only salts, but MSA and related biogenic oxidation products.

Our analysis of AERONET data has shown that around 80% of the daily mean AOD are below 0.1 for the measurements collected over 3 years, with a weak annual cycle and a mean of 0.06 ± 0.03 . On other hand, there is a clearer seasonal cycle in the Angstrom coefficient, with 77% of daily means in the 0.4-1.6 range and an annual

- ¹⁵ Angstrom coefficient, with 77% of daily means in the 0.4–1.6 range and an annual mean of 0.9±0.3. Seasonal average volume size distributions show that summer and spring have maximum aerosol content with coarse mode volume peaking at $3.85 \,\mu$ m radius for both seasons, while during spring there was a fine mode peak with radius range between 0.11 and $0.15 \,\mu$ m, which is evidence of a second aerosol source: almost certainly biomass burning. Analysis of the mass distributions shows that the fine
- $_{20}$ most certainly biomass burning. Analysis of the mass distributions shows that the r mode (PM_{2.5}) is the dominant fraction in the Birdsville atmosphere.

Ion beam analysis was used primarily to study the mass ratios of crustal (and some other) elements to silicon. These results show that the Australian arid region is rich in Fe and Ca, as the ratios of these elements to Si were higher than the values in the Forth? a grupt A number of elements were well correlated with Si over all size fractions.

Earth's crust. A number of elements were well correlated with Si over all size fractions, especially Fe, AI and Ti. Ca and Mn show two populations, with one clearly correlated

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with Si. Other elements show a weaker correlation. Potassium also showed clear evidence of two populations, one well correlated with Si, and hence presumably crustal, and one not, and almost certainly of biomass burning origin. For those elements which are well correlated with Si – including some with more than one population – the slope of the scatter plot (Fig. 9) may be included as part of an Australian desert dust signa-

ture.

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The Na/CI mass ratio of 0.38 is greater than the values in Earth's crust, which is a reflection of the dry lakes which are widespread in the Australian arid region, so that dry salt is well mixed with mineral dust. On the other hand, the analysis of water-soluble ions found that the Na⁺/Cl⁻ mass ratio was 0.44 (for sample period C), which is close to the values found in the IBA results, supporting our conclusion that dry salt is well mixed with mineral aerosols in the Australian arid region.

Analysis of soluble ions showed that Na⁺, Cl⁻, Mg²⁺, Ca²⁺ and NO₃⁻ have similar size distributions, peaking in the lower coarse mode. For most, if not all of these ions, a ¹⁵ common source, such as sea spray, can be reasonably assumed. (Mineral dust Ca is, we presume, non-soluble.) The chemical reactions discussed in Sect. 6.4 would help to link these distributions. We also note that the sea salt fraction of potassium is largely found in the same size range as the sea water ions.

Water-soluble analysis (ion chromatography) shows that ~85% of sulfate was associated with particles $\leq 0.56 \,\mu$ m in diameter, and 88% of total sulfate was found to be nss sulfate, and depletion occurred only in the coarse fraction. In addition, the size distribution of MSA follows that of nss sulfate, with maximum concentration (88%) again allied with particles $\leq 0.56 \,\mu$ m in diameter. In addition, the mass ratio of nssSO₄²⁻ to MSA, which were in the 39.4–31 range, suggests a large input of marine biogenic emission

to atmospheric nss sulfate over the Australian arid region. The ammonium concentration was dominated by particles with diameter $\leq 0.56 \,\mu$ m, with the size distribution again following the nss sulfate pattern, which strongly suggests that ammonium sulfate is present in the fine fraction in this region.

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From our analyses, the following picture of aerosol in the Birdsville area emerges. The size distribution can be considered bimodal for our purposes. The fine mode is strongly influenced by biomass burning in spring, but also has a significant contribution of marine biogenic origin whenever the airmass has recently passed over the ocean.

5 The coarse mode is dominated by crustal elements (which also contribute to the fine mode), with a higher than average iron content. There is also an important contribution from saline elements, either from dry lakes or the sea – most likely both.

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10 **References**

15

Arimoto, R., Duce, R. A., Savoie, D. L., Prospero, J. M., Talbot, R., Cullen. J. D., Tomza, U., Lewis, N. F., and Ray, B. J.: Relationships among aerosol constituents from Asia and the North Pacific during PEMWest A, J. Geophys. Res., 101, 2011–2023, 1996.

Ayers, G. P., Ivey, J. P., and Goodman, H. S.: Sulfate and Methanesulfonate in the maritime aerosol at Cape Grim, Tasmania, J. Atmos. Chem., 4, 173–185, 1986.

Bates, T. S., Cline, J. D., Gammon, R. H., and Kelly-Hansen, S. R.: Regional and seasonal variations in the flux of oceanic dimethylsulfide to the atmosphere, J. Geophys. Res., 92, 2930–2938, 1987.

Charlson, R. J., Schwartz, S. E., Hales, J. M., Cess, R. D., Coakley, J. A., Hansen, J. E., and

 Hofmann, D. J.: Climate forcing by anthropogenic aerosols, Science, 255, 423–430, 1992.
 Cohen, D. D.: Applications of simultaneous IBA techniques to aerosol analysis, Nucl. Instrum. Meth. B, 79, 385–388, 1993.

Cohen, D. D.: Characterisation of atmospheric fine particles using IBA techniques, Nucl. Instrum. Meth. B, 136, 14–22, 1998.

²⁵ Cohen, D. D., Graham, M. B., and Kondepudi, R.: Elemental analysis by PIXE and other IBA techniques and their application to source fingerprinting of atmospheric fine particle pollution, Nucl. Instrum. Meth. B, 109–110, 218–226, 1996.

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Characteristics of Australian Desert dust aerosols





Cohen, D. D., Siegele, R., Ivo, O., and Stelcer, E.: Long-term accuracy and precision of PIXE and PIGE measurements for thin and thick sample analyses, Nucl. Instrum. Meth. B, 189, 81–85, 2002.

Dasch, J. M. and Cadle, S. H.: The removal of nitrate acid to atmospheric particles during a wintertime field study, Atmos. Environ., 24A, 2557–2562, 1990.

5

25

Dentener, F. J., Carmichael, G. R., Zhang, Y., Lelieveld, J., and Crutzen, P. J.: Role of mineral aerosol as a reactive surface in the global troposphere, J. Geophys. Res., 101, 22869–22889, 1996.

Dubovik, O., Holben, B., Eck, T. F., Smirnov, A., Kaufman, Y. J., King, M. D., Tanré, D., and

- ¹⁰ Slutsker, I.: Variability of absorption and optical properties of key aerosol types observed in worldwide locations, J. Atmos. Sci., 59, 590–608, 2002.
 - Dubovik, O. and King, M. D.: A flexible inversion algorithm for retrieval of aerosol optical properties from Sun and sky radiance measurements, J. Geophys. Res., 105, 20673–20696, 2000.
- Fitzgerald, J. W.: Marine aerosols: A review, Atmos. Environ., 25, 533–545, 1991. Forster, P., Ramaswamy, V., Atraxo, P., Bernsten, T., Betts, R., Fahey, D., Haywood, J., Lean, J., Lowe, D., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., and Dorland, R. V.: Changes in Atmospheric Constituents and in Radiative Forcing, in: Climate Change 2007: The Physical Science Basis, Contribution of Working Group I to the Fourth Assessment
- Report of the Intergovernmental Panel on Climate Change, edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2007.
 - Gao, Y., Arimoto, R., Duce, R. A., Chen, L. Q., Zhou, M. Y., and Gu, D. Y.: Atmospheric non-sea-salt sulfate, nitrate and methanesulfonate over the China Sea, J. Geophys. Res., 101(D7), 12601–12611, 1996.
 - Gloudemans, A. M. S., Krol, M. C., Meirink, J. F., de Laat, A. T. J., van der Werf, G. R., Schrijver, H., van den Broek, M. M. P., and Aben, I.: Evidence for long-range transport of carbon monoxide in the Southern Hemisphere from Sciamachy observations, Geophys. Res. Lett., 33, L16807, 2006.
- ³⁰ Harrison, R. M. and Pio, C. A.: Size-differentiated composition of inorganic atmospheric aerosols of both marine and polluted continental origin, Atmos. Environ., 17, 1733–1783, 1983.

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- Holben, B. N., Eck, T. F., Slutsker, I., Tanre, D., Buis, J. P., Setzer, A., Vermote, E., Reagan, J. A., Kaufman, Y. J., Nakajima, T., Lavenu, F., Jankowiak, I., and Smirnov, A.: AERONET A federated instrument network and data archive for aerosol characterization, Remote Sens. Environ., 66, 1–16, 1998.
- ⁵ Huebert, B. J., Howell, S., Laj, P., Johnson, J. E., Bates, T. S., Quinn, P. K., Yegorov, V., Clarke A. D., and Porter, J. N.: Observations of the atmospheric sulfur cycle on SAGA 3, J. Geophys. Res., 98, 16985–16995, 1993.
 - Jacob, D. J.: Heterogeneous chemistry and tropospheric ozone, Atmos. Environ., 34, 2131–2159, 2000.
- ¹⁰ John, W., Wall, S. M., Ondo, J. L., and Winklmayr, W.; Modes in the size distributions of atmospheric inorganic aerosol, Atmos. Environ., 24A, 2349–2359, 1990.
 - Kadowaki, S.: Size distribution of atmospheric total aerosols, sulfate, ammonium and nitrate particulate in the Nagoya area, Atmos. Environ., 10, 39–43, 1976.
 - Keywood M. D., Ayers G. P., Gras J. L., Gillett R. W., and Cohen D. D.: Relationships between
- size segregated mass concentration data and ultrafine particle number concentrations in urban areas, Atmos. Environ., 33, 2907–2913, 1999.
 - Kubilay, N., Cokacar, T., and Oguz, T.: Optical properties of mineral dust outbreaks over the northeastern Mediterranean, J. Geophys. Res., 108(D21), 4666, doi:10.1029/2003JD003798, 2003.
- Kulshrestha, U. C., Saxena, A., Kumar, N., Kumari, K. M., and Srivastava, S. S.: Chemical composition and association of size-differentiated aerosols at a suburban site in a semi-arid tract of India, J. Atmos. Chem., 29, 109–118, 1998.
 - Lafon, S., Sokolik, I. N., Rajot, J. L., Caquineau, S., and Gaudichet, A.: Characterization of iron oxides in mineral dust aerosols: Implications for light absorption, J. Geophys. Res., 111, D21207, doi:10.1029/2005JD007016, 2006.
 - Leck, C. and Rodhe, H.: Emissions of marine biogenic sulfur to the atmosphere of northern Europe, J. Atmos. Chem., 12, 63–86, 1991.

25

- Lide, D. R.: CRC Handbook of Chemistry and Physics, 78th edition, CRC Press, Boca Raton, Fl., 1997.
- Mamane, Y. and Gottlieb, J.: Nitrate formation on sea-salt and mineral particles a single particle approach, Atmos. Environ., 26A, 1763–1769, 1992.
 - Marple, V. A., Rubow, K. L., and Behm, S. M.: A Microorifice Uniform Deposit Impactor (MOUDI): Description, calibration and use, Aerosol Sci, Tech., 14, 434–446, 1991.

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- Mitchell, R. M. and Forgan, B. W.: Aerosol Measurement in the Australian Outback: Intercomparison of Sun Photometers, J. Atmos. Oceanic Tech., 20, 54–66, 2003.
 Millero, F. J. and Sohn, M. L.: Chemical Oceanography, CRC Press, Boca Raton, Fla., 1992.
 Nishikawa, M., Kanamori, S., Kanamori, N., and Mizoguchi, T.: Kosa aerosol as eolian carrier
- of anthropogenic material, Sci. Total Environ., 107, 13–27, 1991.
- Pakkanen, T. A., Kerminen, V. M., Hillamo, R. E., Makinen, M., Makela, T., and Virkkula, A.: Distribution of nitrate over sea-salt and soil derived particles – implications from a field study, J. Atmos. Chem., 24, 189–205, 1996.

Parmar, R. S., Satsangi, G. S., Kumari, M., Lakhani, A., Srivastava, S. S., and Prakash, S.:

- ¹⁰ Study of size distribution of atmospheric aerosol at Agra, Atmos. Environ., 35, 693–702, 2001.
 - Prospero, J. M. and Savoie, D. L.: Effect of continental sources of nitrate concentrations over the Pacific Ocean, Nature, 33, 687–689, 1989.

Qin, Y. and Mitchell, R. M.: Characterisation of episodic aerosol types over the Australian continent. Atmos. Chem. Phys., 9, 1943–1956, 2009.

http://www.atmos-chem-phys.net/9/1943/2009/.

15

20

25

- Quinn, P. K., Covert, D. S., Bates, T. S., Kapustin, V. N., Ramsey-Bell, D. C., and McInnes, L. M.: Dimethylsulfide/cloud condensation nuclei/climate system: Relevant size-resolved measurements of the chemical and physical properties of atmospheric aerosol particles, J. Geophy. Res., 98, 10411–10427, 1993.
- Ramanathan, V., Crutzen, P. J., Kiehl, J. T., and Rosenfeld, D.: Aerosols, climate, and the hydrological cycle, Science, 294, 2119–2124, 2001.
- Rosen, J. M., Young, S. A., Laby, J., Kjome, N., and Gras, J.: Springtime aerosol layers in the free troposphere over Australia: Mildura Aerosol Tropospheric Experiment (MATE 98), J. Geophys. Res., 105, 17833–17842, 2000.
- Saltzman, E. S., Savoie, D. L., Zika, R. G., and Prospero, J. M.: Methanesulphonic acid in the marine atmosphere, J. Geophys. Res., 88, 10897–10902, 1983.
- Savoie, D. L. and Prospero, J. M.: Particle size distribution of nitrate and sulfate in the marine atmosphere, Geophys. Res. Lett., 9, 1207–1210, 1982.
- ³⁰ Savoie, D. L., Prospero, J. M., Arimoto, R., and Duce, R. A.: Non-seasalt sulfate and methanesulfonate at American Samoa, J. Geophys. Res., 99, 3587–3596, 1994.

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- Savoie, D. L., Arimoto, R., Keene, W. C., Prospero, J. M., Duce, R. A., and Galloway, J. N.: Marine biogenic and anthropogenic contributions to non-sea-salt-sulfate in the marine boundary layer over the North Atlantic Ocean, J. Geophys. Res., 107(D18), 4356, doi:10.1029/2001JD000970, 2002.
- ⁵ Sokolik, I. N. and Toon, O. B.: Direct radiative forcing by anthropogenic airborne mineral aerosols, Nature, 381, 681–683, 1996.
 - Sokolik, I. N., Winker, D. M., Bergametti, G., Gillette, D. A., Carmichael, G., Kaufman, Y. J., Gomes, L., Schuetz, L., and Penner, J. E.: Introduction to special section: outstanding problems in quantifying the radiative impacts of mineral dust, J. Geophys. Res., 106, 18015–18027, 2001.
 - Tanaka, T. Y. and Chiba, M.: A numerical study of the contributions of dust source regions to the global dust budget, Glob. Planet. Change, 52, 88–104 2006.

10

Tegen, I., Lacis, A. A., and Fung, I.: The influence on climate forcing of mineral aerosols from disturbed soils, Nature, 380, 419–422, 1996.

- ¹⁵ Wolf, G. T.: On the nature of nitrate in coarse continental aerosols, Atmos. Environ., 18, 977– 981, 1984.
 - Wall, S. M., John, W., and Ondo, J. L.: Measurement of aerosol size distributions for nitrate and major ionic species, Atmos. Environ., 22, 1649–1656, 1988.

Zhuang, H., Chan, C. K., Fang, M., and Wexler, A. S.: Size distributions of particulate sulfate,

nitrate, and ammonium at a coastal site in Hong Kong, Atmos. Environ., 33, 843–853, 1999.

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Table 1. Times of the samples.

Collection	Start		End	Total hours	
Concolion	date	time	date	time	
В	1 November 2006	09:10 a.m.	2 November 2006	09:10 a.m.	24
С	2 November 2006	04:00 p.m.	3 November 2006	04:00 p.m.	24
D	3 November 2006	05:00 p.m.	5 November 2006	05:00 p.m.	48
E	5 November 2006	06:00 p.m.	7 November 2006	06:00 a.m.	36

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Table 2. Mass fractions.

	В	С	D	Е	Average
TSP μ g/m ³	57.2	107.5	17.5	28.8	
PM ₁₀ /TSP	73%	78%	80%	72%	76%±4
PM _{2.5} /TSP	42%	44%	53%	47%	46%±5
PM ₁ /TSP	32%	27%	32%	34%	31%±3
PM _{2.5} /PM ₁₀	58%	57%	66%	65%	61%±5
PM_1/PM_{10}	44%	35%	40%	47%	41%±5
$PM_1/PM_{2.5}$	76%	62%	60%	73%	68%±8





Flement	Ratio/Si					
Liement	В	С	D	Е	Crust*	
Na	8.63E-02	7.14E-02	3.80E-01	1.77E-01	8.37E-02	
Al	2.71E-01	2.92E-01	2.73E-01	2.71E-01	2.92E-01	
Р	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	
CI	1.18E-02	4.36E-03	2.03E-02	3.56E-2	3.72E-03	
K	5.54E-02	2.69E-02	3.70E-01	1.48E-01	5.14E-04	
Ca	6.18E-02	5.49E-02	5.24E-02	4.75E-02	7.41E-02	
Ti	3.06E-02	3.20E-02	5.91E-02	4.39E-02	1.47E-01	
Cr	2.23E-02	2.55E-02	1.81E-02	1.87E-02	2.00E-02	
Mn	7.36E-03	3.37E-03	1.25E-02	1.27E-02	3.62E-04	
Fe	3.77E-03	3.68E-03	4.77E-03	4.61E-03	3.37E-03	
Со	2.15E-01	2.25E-01	2.32E-01	2.28E-01	2.00E-01	
Ni	1.42E-03	1.30E-03	1.22E-03	1.54E-03	8.87E-05	
Cu	9.71E-03	4.17E-03	1.75E-02	1.98E-02	2.98E-04	
Zn	1.92E-03	9.89E-04	1.66E-03	1.54E-03	2.13E-04	
Br	1.30E-03	8.96E-04	1.55E-03	1.82E-03	2.48E-04	
Pb	3.09E-03	1.45E-03	6.88E-03	4.89E-03	8.51E-06	

Table 3. Ratio of elements to Si.

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* Crust ratio computed from Lide (1997)

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Table 4. Ionic species concentrations of all ions detected in Ion Chromatographic analysis, with the mass ratios of these ions to Na⁺. (Coarse fraction is the sum of species concentration that found at the stage $1.0 \,\mu$ m and above).

		C Sample		E Sample			E Sample		lon/Na ⁺
	Concentration, μ g/m ³		TSP lon/Na ⁺	μ_{a^+} Concentration, $\mu g/m^3$ TSP lon/Na ⁺		in sea water			
	TSP	Coarse	i oli ioli/ita	TSP	Coarse	i oli ioli, i da			
Na ⁺	3.14E-01	2.24E-01	1.00E+00	2.25E-01	1.30E-01	1.00E+00	1.00E+00		
NH_4^+	2.22E-01	3.22E-02	7.08E-01	1.64E-01	7.45E-03	7.31E-01	_		
K ^{+'}	8.30E-02	3.94E-02	2.65E-01	2.13E-02	1.01E-02	9.48E-02	3.71E-02		
Mg ²⁺	4.16E-02	3.24E-02	1.33E-01	1.38E-02	8.46E-03	6.16E-02	1.20E-01		
Ca ²⁺	1.59E-01	1.23E-01	5.07E-01	5.02E-02	3.63E-02	2.23E-01	3.82E-02		
CI⁻	1.37E-01	8.36E-02	4.37E-01	1.22E-01	8.35E-02	5.43E-01	1.80E+00		
NO_2^-	1.13E-02	6.04E-03	3.59E-02	7.57E-03	5.67E-03	3.37E-02	_		
NO [±]	4.45E-01	4.04E-01	1.42E+00	1.51E-01	1.09E-01	6.70E-01	_		
SO_4^{2-}	6.59E-01	9.98E-02	2.10E+00	5.34E-01	5.28E-02	2.37E+00	2.52E-01		
$C_2 O_4^{2-}$	7.91E-02	4.71E-02	2.52E-01	5.30E-02	2.27E-02	2.36E-01	_		
PO₄ ^{3−}	2.53E-02	2.00E-02	8.08E-02	4.13E-03	1.48E-03	1.84E-02	_		
F	1.80E-02	8.20E-03	5.75E-02	1.11E-03	8.08E-04	4.93E-03	1.21E-04		
Acetate	3.33E-01	1.57E-01	1.06E+00	5.36E-02	2.81E-02	2.38E-01	-		
Formate	1.10E-01	5.82E-02	3.51E-01	7.18E-02	3.67E-02	3.20E-01	-		
MSA	1.47E-02	1.77E-03	4.68E-02	1.54E-02	1.47E-03	6.85E-02	-		
nssCa ²⁺	1.47E-01	1.14E-01	4.68E-01	4.16E-02	3.13E-02	1.85E-01	_		
nssK ⁺	7.14E-02	3.11E-02	2.28E-01	1.30E-02	5.28E-03	5.78E-02	_		
$nssSO_4^{2-}$	5.80E-01	4.32E-02	1.85E+00	4.77E-01	2.01E-02	2.12E+00	-		

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Fig. 1. Map of Australia showing Birdsville location.





Fig. 2. (a) Daily means of AOD from August 2005–June 2008. (b) Monthly means and standard deviations of AOD for same period.

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Fig. 5. Left panel: Seasonal frequency distributions of daily mean AOD. Central panel: Seasonal frequency distributions of daily mean α . Right panel: Seasonal scatter plots of daily mean α vs. daily mean AOD.

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Fig. 6. (a) Seasonal average volume size distributions. (b) Daily average volume size distribution for selected days.



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Fig. 7. (a) Size resolved mass concentrations for all 4 samples. (b) Smoothed size distributions. (c) Comparison of MOUDI size distribution with AERONET retrieval for sample C.



Fig. 8. Size-resolved mass ratios of some elements to Si for all samples.

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Fig. 9. (a) Scatter plots of Fe, Ti, Al, Ca, Mn and K against Si. (b) Scatter plots of Co, Cu and Zn against Si. (c) Scatter plots of Na and Cl against Si, and Cl against Na.

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Fig. 10. Back-trajectories during aerosol sampling days.









Interactive Discussion

Fig. 11. Size-resolved concentrations of major water-soluble ionic species during sampling periods C and E.