Processing of aerosol particles within the Habshan pollution plume

T. A. Semeniuk¹, R. Bruintjes², V. Salazar², D. Breed², T. Jensen², and P. R. Buseck¹,³

¹Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona, USA, ²National Center for Atmospheric Research, Boulder, Colorado, USA, ³School of Earth and Space Exploration, Arizona State University, Tempe, Arizona, USA

Abstract The Habshan industrial site in the United Arab Emirates produces a regional-scale pollution plume associated with oil and gas processing, discharging high loadings of sulfates and chlorides into the atmosphere, which interact with the ambient aerosol population. Aerosol particles and trace gas chemistry at this site were studied on two flights in the summer of 2002. Measurements were collected along vertical plume profiles to show changes associated with atmospheric processing of particle and gas components. Close to the outlet stack, particle concentrations were over 10,000 cm⁻³, dropping to <2000 cm⁻³ in more dilute plume around 1500 m above the stack. Particles collected close to the stack and within the dilute plume were individually measured for size, morphology, composition, and mixing state using transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy. Close to the stack, most coarse particles consisted of mineral dust and NaCl crystals from burning oil brines, while sulfate droplets dominated the fine mode. In more dilute plume, at least 1500 m above the stack, the particle spectrum was more diverse, with a significant increase in internally mixed particle types. Dilute plume samples consisted of coarse NaCl/silicate aggregates or NaCl-rich droplets, often with a sulfate component, while fine-fraction particles were of mixed cation sulfates, also internally mixed with nanospherical soot or silicates. Thus, both chloride and sulfate components of the pollution plume rapidly reacted with ambient mineral dust to form coated and aggregate particles, enhancing particle size, hygroscopicity, and reactivity of the coarse mode. The fine-fraction sulfate-bearing particles formed in the plume contribute to regional transport of sulfates, while coarse sulfate-bearing fractions locally reduced the SO₂ loading through sedimentation. The chloride- and sulfate-bearing internally mixed particles formed in the plume markedly changed the reflectivity and scattering properties of the ambient aerosol population, as well as its hygroscopic and ice nucleation properties.

1. Introduction

Air pollutants in the United Arab Emirates (UAE) are derived from regional sources, e.g., particulate matter from dust storms or sulfate aerosols from oil fields transported in large plumes from neighboring regions, as well as specific local sources, e.g., SO₂ emissions from four oil refineries and five gas processing plants. In particular, emissions from outgassing flares in the oil fields of the Arabian Gulf, as well as gas and oil processing plants at coastal and inland sites, were associated with extremely high SO₂ concentrations, up to 500 ppb in 2002 [National Center for Atmospheric Research (NCAR), 2005]. Figure 1a shows the maximum vertical column SO₂ (in parts per billion, from 0 to 3000 m) compiled from 23 flights to monitor chemistry flown over the UAE during the summer of 2002. Highest summer concentrations of SO₂ in the UAE occurred over Das and Zirku islands in the Gulf and at the Habshan industrial area (Figure 1). In 2002, these SO₂ values were at the World Health Organization limits for health impacts (20 μg m⁻³ (7 ppb) in 24 h or 500 μg m⁻³ (174 ppb) in 10 min [Krzyzanowski and Cohen, 2008]). In addition to these massive SO₂ emissions, high loadings of chloride salts associated with processing of the oil brines are emitted in these plumes. The interaction of both these soluble pollutants with ambient particles at the Habshan industrial site was the focus of this study.

The Habshan industrial area is located in the desert, 115 km southwest of Abu Dhabi and 20 km from the coast. It is proximal to the largest onshore oil and gas fields in the UAE, so there is significant industrial activity and infrastructure associated with oil and gas processing at this site. Processing of oil and gas involves the release of H₂S, SO₂, NOₓ, CO₂, heat-stable salts, and volatile and nonvolatile organics (including carbon nanospheres—ns-soot [after Buseck et al., 2014]), forming a well-defined pollution plume [Salazar et al., 2003], referred to here as the Habshan pollution plume. At this inland location, these pollutants mainly interact with
ambient mineral dust to form internally mixed particles. Desert dust is locally lofted into the air by surface winds, but it may also be transported from considerable distances [Evans, 2004]. Sources of desert dust in the UAE include fine-mode dune sands and sabkha muds and silts, consisting of clay minerals, quartz, feldspar, carbonate, iron oxides, and gypsum particles, similar to Saharan and Arabian desert dusts [Falkovich et al., 2001; Formenti et al., 2003; Molinaroli, 1996; Pösfai et al., 2012]. In addition to desert dust, there is also a small component of ambient sea-salt particles transported inland by sea breezes. The impact of such pollution on the ambient aerosol population was studied along a vertical profile above the outlet stack at the Habshan industrial site to evaluate its effects on both aerosol-light and aerosol-cloud interactions. Given that the main component of the ambient aerosol was mineral dust, its interactions with such pollution

Figure 1. (a) Map of the United Arab Emirates showing maximum vertical column SO₂ (in ppb) compiled from 23 flights to monitor chemistry flown during the summer of 2002 [NCAR, 2005]. The maximum in column was between surface and 3000 m. These flights clearly showed that Zirku Island and Habshan industrial area had well-defined pollution plumes associated with oil flares and gas processing, respectively. Two flights specifically investigated aerosol chemistry at the Habshan industrial site. A plan view of the flight trace from Abu Dhabi Airport to Habshan industrial site for 3 September is superimposed in black. (b) Longitudinal cross section showing the flight path between Abu Dhabi Airport and Habshan industrial site for both 28 August (heavy gray trace) and 3 September 2002 (dashed gray trace). Sampling intervals for stack and plume are shown for both days, as traces where the aircraft was circling. (c) A plan view of flight path for stack and plume sampling intervals on 28 August showing circling in detail.
are certain to affect its radiative properties, as well as the formation of cloud condensation nuclei (CCN) or ice nuclei from these particles, e.g., coated dust is known to form giant CCN (GCCN). Ice nuclei or GCCN formed from mineral dust do affect aerosol-cloud interactions and precipitation, but the magnitude of this effect depends on ambient CCN concentrations, ambient atmospheric chemistry, as well as meteorological conditions [Smoydzin et al., 2012]. Thus, interactions of particles in the Habshan pollution plume can inhibit or enhance precipitation locally and regionally. In fact, given the ongoing increase in energy production related to the petroleum industry in the UAE over the last decades, “local” SO2 sources have the potential to affect climate and air pollution globally.

In this study, we used aerosol data collected in a regional study of atmospheric pollutants over the UAE by the National Center for Atmospheric Research (NCAR) from June to September 2002 during the Phase 1 of a rainfall enhancement project. Airborne measurements of trace gases and aerosol particles were conducted specifically at the Habshan industrial site to characterize the pollution emissions as a source for CCN in local convection zones. Pollution-related aerosol particles were sampled close to the source (stack sample) and in higher, more dilute regions of the pollution plume (plume sample) to compare individual particle characteristics along natural transport lines. Collection of individual particles provided material to study atmospheric processing within the plume with transmission electron microscopy (TEM) coupled with energy-dispersive X-ray (EDX) spectrometry. Both our airborne and TEM measurements are presented here. How transport and activation of these pollution-related particles affected cloud seeding experiments in the Oman mountain region was discussed in an earlier paper [Semeniuk et al., 2014].

### 2. Materials and Methods

Although 23 missions were carried out to study aerosol chemistry in the UAE during summer 2002, only two flights specifically investigated the Habshan industrial site (Figure 1a). Aerosol sampling took place within the Habshan pollution plume between 10:00 and 12:00 UTC (early afternoon) on 28 August and 3 September 2002 using a Beechcraft King Air 200 twin-engine turboprop. Boundaries to the plume were visually defined. Both flights tracked the plume, either spiraling from the stack upward or descending to the stack, recording data between 430 and 3500 m altitudes. Onboard instruments for determining aerosol particle sizes and concentrations included a Droplet Measurement Technologies, Inc.-modified Forward Scattering Spectrometer Probe (FSSP) for particles between 2 and 47 μm in size, a Particle Measuring Systems, Inc. Passive Cavity Aerosol Spectrometer Probe (PCASP) for particles between 0.1 and 3 μm in size, a TSI Incorporated-type condensation nuclei (CN) counter (model 3010), and a University of Wyoming cloud condensation nuclei (CCN) counter. Trace gas analyzers measured SO2, NO/NO2/NOx, and O3 (Thermo Fisher Scientific Inc., MA, USA; model 43i-HL SO2 analyzer, model 42i NO-NO2-NOx analyzer, and model 49i Ozone analyzer). Relative humidity (RH) and temperature were measured with a Vaisala temperature/RH sensor. In-flight data were recorded at per second intervals, and provided ambient contextual data (Table 1).

In addition, we accessed the global model data for the southwest Asian composite region from the Navy Aerosol Analysis and Prediction System (NAAPS), showing global dust and sulfate maps for both dates at midday (http://www.nrlmry.navy.mil/aerosol/globaer/ops_01/swasia_composite/200208/2002082812_swasia_composite.gif; http://www.nrlmry.navy.mil/aerosol/globaer/ops_01/swasia_composite/200209/2002090312_swasia_composite.gif), as well as radiosonde data recorded at Abu Dhabi airport for both dates at midday, available as skew-T diagrams from the University of Wyoming (http://weather.uwyo.edu/upperair/sounding.html), both provided a regional context to measurements.

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<td>Time (UTC)</td>
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<td>Temperature (°C)</td>
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Aerosol particles were sampled over 5 min intervals close to the outlet stack at 430 m altitude and at 1600 and 1760 m altitude above the stack in more dilute plume (Table 1). Sampling directly above the stack allowed us to compare changes in time and with altitude. The contexts of these sampling intervals on the flight path are shown in Figure 1, while Figure 2 provides a record of atmospheric conditions, including altitude, temperature, and relative humidity between sampling intervals. Specific conditions during sampling are listed in Table 1. Particles were directly collected onto TEM grids using two three-stage microanalysis figures.

Figure 2. Air and aerosol parameters measured on flights on 28 August and 3 September 2002. Stack and plume sampling intervals (5 min) are marked on each panel. Measurements between these intervals represent a vertical profile through the plume. Altitude (left axis), temperature, and relative humidity (RH) (shared right axis) for (a) 28 August and (b) 3 September. CCN measurements for (c) 28 August and (d) 3 September. PCASP measurements for (e) 28 August and (f) 3 September. SO$_2$ concentration (left axis) and O$_3$ concentration for (g) 28 August and (h) 3 September. No O$_3$ data were recorded for 3 September 2002. Peaks on background represent denser plume penetrations by the aircraft while circling.
particle samplers (California Measurements, Inc.) with isokinetic sample inlets, operated at flow rates around 1.75 L/min. Samplers collected particles on lacey carbon (LC) on 28 August or film carbon (FC) on 3 September, as well as Ca-coated formvar (Ca-C) Cu-mesh TEM grids, simultaneously. Each sampler fractionated samples onto three stages, with 50% particle size cutoffs at 2 μm, 0.3 μm, and 0.05 μm. Particles up to 20 μm in diameter occurred in the coarsest fraction, suggesting that particles on the first stage (coarse grid fraction) provided a representative population of particle sizes documented by the FSSP. Data from both PCASP and FSSP channels were normalized for Figure 3, which show particle size distributions of ambient aerosols for each sampling interval. The gray shading indicates the range of particles collected on each of the TEM grid fractions: light gray for the fine fraction (0.05–0.3 μm), medium gray for the intermediate fraction (0.3–2 μm), and dark gray for the coarse fraction (2–20 μm).

Typically, LC provided a better substrate to view and analyze particles, and there are less systematic errors introduced in EDX analysis associated with this type of carbon support. However, given that organic compounds were not investigated in this study, these advantages only contributed to easier and more rapid classification of particle on LC grids. Since these grids only support dry particles, wet particles and droplets fluoresce under ambient conditions, forming residues. In contrast, our special in-house-produced Ca-C grids have an oxide film [Kojima et al., 2006; Yamato and Ono, 1989; Yamato and Tanaka, 1994] with which wet particles and droplets react to form stable Ca salts on impact. These crystallized salts, e.g., mainly CaSO₄ or CaCl₂, preserve evidence of their fluid state at the time of collection (see detailed description in Semeniuk et al. [2014]). Using different grid types, complementary information on chemistry and physical state for different particle types can be determined simultaneously for ambient particle populations. In this way, we could readily distinguish between primary gypsum particles formed in evaporate deposits, and secondary CaSO₄ formed through interaction of carbonates or sea salt with SO₂ gas, using a combination of context (single crystal, core grain with coating, or residue), EDX spectra (pure or impure CaSO₄), crystal morphology (robust or lath shape), and physical state within the atmosphere (solid or droplet).

TEM samples were stored in a desiccator prior to analysis for up to 36 months. Under dry, vacuum conditions, there are negligible changes to particles on TEM grids [Pósfai et al., 1995]. An analysis of individual aerosol particles was carried out using a Phillips CM-200 FEG transmission electron microscope operated at 200 kV during 2004–2005. TEM analyses provided structural and chemical information on individual particles through conventional and high-resolution imaging in bright-field mode, electron diffraction, and chemical analysis using EDX spectra. Particles with sizes 0.02 to 20 μm were analyzed within representative grid-mesh squares near the centers of the grids. Quantitative information on size, shape, composition, speciation, mixing state, and surface coatings was collected for up to 22 different particle types on each grid and whenever particle type was unclear from visual inspection. For representative particle types, EDX spectra for each distinct component within the particle were collected, which assisted identification and classification of other particles of this type on the same grid. For some beam-sensitive compounds, such as K₂SO₄ and H₂SO₄, only qualitative EDX spectra were measured; such spectra were usually sufficient to facilitate...
Volatile components, especially organics, but also ammonium sulfate are typically lost on exposure to the electron beam; hence, these components cannot be measured reliably or reproducibly. Furthermore, organic compounds cannot always be differentiated from the background measurements of LC or FC grids.

Using data for our reference set of 22 particle types (see Table 3 of Semeniuk et al. [2014]) as a baseline, compositional data were compiled using both morphology and some additional EDX spectra to classify 100 to 150 particles per grid, resulting in the classification of 300–400 particles per sample. For example, sulfate-rich droplets or particles were classified as mixed cation sulfates (MCS; pollution derived) when they did not show Cl peaks in their spectra; otherwise, they were classified as NaCl/MCS (derived from processed sea salt or brine components). Spectra for MCS typically comprise various cation peaks (Na, Ca, and Mg) with a strong S peak. While size and crystal morphologies of CaSO₄ components were used to distinguish between gypsum (larger size, robust crystal shape, and distinct diffraction pattern) and recrystallized MCS droplets (lath crystal shape). Table 3 of Semeniuk et al. [2014] also shows the correspondence of particle types for different grid types; e.g., NaCl-rich droplets on Ca-C grids are equivalent to NaCl or NaCl/MCS on LC grids. Errors associated with classifying particles into types are difficult to assess for such a labor-intensive manual task. Our empirical experience indicates that such errors are very low (<1%) for both grid types, given that multiple criteria are used to classify each particle, and any particles not easily classified are analyzed with EDX spectrometry. Types with frequencies less than 1% are not shown, e.g., Fe oxides, NaNO₃, silicate/carbonate aggregates, etc. Types encountered only on Ca-C grids are marked with an asterisk. Percentages for two important chloride-bearing types (NaCl/silicate aggregates and NaCl-rich droplets) are indicated adjacent to the columns.

3. Results
3.1. Regional and Airborne Measurements
NAAPS global model data showed a low-intensity plume of dust and sulfate over this region on 28 August and a low-sulfate loading for 3 September [Navy Aerosol Analysis and Prediction System (NAAPS), 2002a, 2002b]. A small temperature inversion occurred at around 2000 m in the radiosonde sounding taken 150 km away at Abu Dhabi at midday on both sampling dates. These conditions contributed to elevated particle identification.
concentrations below the inversion layers on both dates, as shown by the elevated PCASP particle concentrations at around 1500 m (Figures 2e and 2f).

All measurements shown in Figure 2 are between TEM sampling intervals; as such, they are all “within the plume.” Peaks on background represent denser plume penetrations by the aircraft while circling. Peaks coincident with sampling times represent particle concentrations at the stack and within higher dilute plume (Figures 2c–2h).

On 28 August, the plume penetrated to higher altitudes (Figure 2a). RH was relatively low and quite stable, resulting in stable CCN counts around 500 cm$^{-3}$ (Figure 2c). Close to the stack, PCASP counts were over 10,000 cm$^{-3}$, dropping to less than 1000 cm$^{-3}$ in more dilute plume above the stack (Figure 2e). High concentrations of SO$_2$ (up to 300 ppb; Figure 2g), NO$_x$ (up to 200 ppb), and O$_3$ (up to 40 ppb; Figure 2g) were recorded close to the stack, while at higher altitude, all these trace gas concentrations were <30 ppb. Background concentrations of these gases are typically 3 ppb SO$_2$, 0 ppb NO$_x$, and up to 20 ppb O$_3$ (measured at 700 m altitude on same flight, closer to Abu Dhabi Airport).

On 3 September, RH was much higher and less stable (Figure 2b). Close to the stack, CCN concentrations were over 3000 cm$^{-3}$ (Figure 2d), dropping to around 1300 cm$^{-3}$ in more dilute plume. Both CCN and CN counters experienced count saturation close to the stack, providing only intermittent data (CN data not shown). PCASP particle concentrations near the stack were over 10,000 cm$^{-3}$ (Figure 2f) but dropped to below 7000 cm$^{-3}$ in more dilute plume. On 3 September, two visually well-defined pollution bands were recognizable at 1500 m and 2500 m, with relatively higher particle (>4000 cm$^{-3}$) and moderate trace gas concentrations compared with background levels (e.g., SO$_2$ concentrations were ~50 ppb compared with ~8 ppb background levels) (Figures 2f and 2h). Perhaps these bands were related to the regional plume detected in the NAAPS model data.

Combined FSSP and PCASP particle-size spectra are shown in Figure 3. FSSP spectra are distinct for stack and plume intervals; spectra close to the stack were characterized by larger particles (>1 μm), with a notable fraction >10 μm in size (~30% of FSSP counts were recorded by channels for particles sizes >10 μm). PCASP data for stack and plume were almost coincident, indicating that the size distribution of finer-fraction particles was more consistent throughout the plume. However, higher numbers of particles <0.3 μm were present in more dilute plume at higher altitude on 3 September related to the pollution band present at around 1500 m (Figure 3b).

3.2. TEM Measurements

3.2.1. Particle Types

Although some single-phase mineral grains (e.g., sheet silicates, gypsum, and NaCl) and soot were common, all other single-phase types were rare, rather forming components of internally mixed particles. Thus, most individual particles had components that included mineral dust, inorganic salts, and/or carbonaceous material. This contrasts with TEM samples from outside the plume, which comprised up to 40% single-phase mineral grains (T. A. Semeniuk, unpublished data, 2004), as well as with mostly unreacted “rock fragments” sampled in dust storms in Saudi Arabia (Pósfai et al., 2012).

Despite the fact that most particles were internally mixed, it is worth discussing the compositions of their components in more detail. The most common dust mineral components were sheet silicates (clays, 40%), other Al-bearing silicates (12%), quartz (6%), gypsum (28%), carbonates (14%), and iron oxides (<1%), as also described in other studies in the Arabian, Sahara, and Negev deserts [Pósfai et al., 2012; Formenti et al., 2001; Molinaroli, 1996]. Salt components were chlorides and sulfates, with rare nitrates. NaCl was the most abundant chloride, although MgCl and CaCl$_2$ also were recorded. Sulfate components included CaSO$_4$, K$_2$SO$_4$, Na$_2$SO$_4$, and sulfuric acid. These components were often internally mixed to form MCS droplets. The main nitrate component was NaNO$_3$. Although most of these inorganic salts are typical of maritime regions [Li et al., 2003a, 2003b; McInnes et al., 1997], they are also components of the brines associated with oil and gas processing in the UAE. The variable intensities of C peaks associated with sulfate droplets suggested that an organic component was present on many particles.

Most internally mixed particles in the plume (both close to the stack and in more dilute regions) were chloride bearing or sulfate bearing, making up over 85% of the total number of particles per sample. This can clearly be seen in Figure 4, where different types of chloride-bearing or sulfate-bearing aggregates are shown in
black or white patterned swatches, respectively. Figure 5 presents the TEM bright-field images that show the diversity of individual NaCl-containing particles, while images in Figure 6 show the MSC- or soot-containing particles. Given their numerical abundance, these two main particle categories, covering a number of particle types (e.g., NaCl/silicate aggregates, NaCl/gypsum, and NaCl/MCS), became the focus of this study.

Figure 5. Chloride-bearing aggregate particle types resulting from the interaction between ambient mineral particles and the salt component of the pollution plume. (a) Euhedral NaCl crystal together with silicate dust particle (NaCl/silicate aggregate; Figure 4). (b) Two distinct sizes of euhedral NaCl attached to silicate particle surface (NaCl/ silicate aggregate; Figure 4). (c) Rounded NaCl aggregated with and partly coating a silicate dust particle (NaCl/ silicate aggregate; Figure 4). (d) NaCl engulfing a silicate dust particle (NaCl/ silicate aggregate; Figure 4). (e) NaCl grains cemented by gypsum (NaCl/gypsum; Figure 4). (f) NaCl together with gypsum (NaCl/gypsum; Figure 4).
The chloride-bearing aggregates, mainly NaCl/silicate and NaCl/gypsum particle types, dominated the coarse (up to 73%) and intermediate fractions (up to 55%) (Figure 4). These aggregates consisted of two to nine grains per cluster. Their chloride component was typically NaCl. Much NaCl was euhedral, often located between silicate grains or attached to silicate surfaces (Figures 5a and 5b), whereas others were subhedral.

Figure 6. Sulfate-bearing aggregate particle types resulting from the interaction between mineral, salt, ns-soot, and sulfate components of the pollution plume. (a) Gypsum particle coated with mixed cation sulfates (MCS) (MCS/gypsum category; Figure 4) and coated ns-soot particles (MCS/ns-soot; Figure 4). (b) NaCl particle coated with MCS (MCS/NaCl category; Figure 4). (c) Silicate with attached MCS droplet (MCS/silicate category; Figure 4). (d) NaCl particle coated with MCS and with attached sodium sulfate crystals (MCS/NaCl category; Figure 4). (e) Carbonate with attached MCS droplet (rare category, not shown in Figure 4). (f) Silicate coated with MCS and with attached ns-soot (MCS/ns-soot/silicate category; Figure 4).
chloride-bearing aggregates in detail to establish their origins and properties. This involved measuring individual particle components, as well as documenting the location and coordination of NaCl crystals within each individual aggregate. Figure 7 presents the frequencies for NaCl-containing aggregate size versus their internally mixed NaCl crystal size (Figure 7a), the location of NaCl grains within these particles (Figure 7b), and the coordination of NaCl grains to mineral grains within these aggregates. Using the grain size information and coordination information presented in Figure 7, and assuming cubic crystal habit, we estimated the volume of the NaCl component in 54 effloresced NaCl/silicate aggregates to range from 0.0027 to 224 μm⁻³, with an average volume of 21.7 μm⁻³. The average mass of NaCl in such coarse aggregates can also be estimated using this average NaCl volume and the average material density for NaCl (2.16 g cm⁻³) to be ~4.68 × 10⁻¹¹ g. Clearly, when one or more NaCl crystals are aggregated with other particles, they constitute a sizable soluble fraction, capable of engulfing the entire aerosol particle as it undergoes hygroscopic growth and producing GCCN from these aggregates [Osada, 2013].

The sulfate-bearing aggregates that dominated the fine and intermediate fractions typically consisted of silicate, gypsum (Figures 6a, 6c, and 6d), inorganic salts (Figures 6b and 6e), or ns-soot (Figure 6f) with MCS droplets or microcrystalline calcium sulfate adhering to their surfaces. Aside from MCS droplets, the most common sulfate-bearing particles were MCS/ns-soot (up to 60% of fine fraction; stack sample, 3 September), MCS/ns-soot/silicate aggregates (up to 23% of intermediate fraction; stack sample, 28 August), MCS/NaCl (up to 21% of intermediate fraction; plume sample, 3 September), and MCS/silicate (up to 11% of coarse fraction; plume sample; 28 August) (Figure 4). Effloresced MCS particles are typically 0.3 μm in size, with an estimated mass of around 4 × 10⁻¹⁴ g (assuming simple spherical shape and potassium or magnesium sulfate composition). Some single-phase dust and NaCl grains were entirely coated with MCS (<10% of all particles). These coatings vaporized under the electron beam and were likely a mixture of sulfuric acid and organics. Although we mostly observed discrete sulfate particles on the surface of larger particles, we surmise that these soluble sulfate components form coatings as they age in the atmosphere, i.e., as they undergo hygroscopic growth, as more sulfate particles are agglomerated during transport, and as these internally mixed particles continue to react with gas species in the plume.

### 3.2.2. Differences Between Stack and Plume Samples

Particle populations close to the stack had higher concentrations of single-phase particles (>30%): NaCl (stack sample, 28 August), silicates (stack sample, 3 September), and ns-soot (stack sample, 3 September) (Figure 4). In contrast, at greater altitude, the plume had significantly fewer single-phase particles (<10%) but higher concentrations of chloride- and sulfate-bearing aggregates. Figure 8 depicts the proportion of sulfate- and/or chloride-bearing particles in each size fraction for stack and plume samples based on the dry particle compositions on FC or LC grids shown in Figure 4. The particles shown in Figure 4 were categorized as chloride-bearing type, sulfate-bearing type, both, or other. On 28 August, there is noticeable increase in sulfate-bearing types in the coarse fraction and chloride-bearing types in the fine fraction along the plume, while on 3 September, there were more sulfate- and chloride-bearing types in all fractions at higher elevations. This change in distribution suggests that most internally mixed particles formed within the plume.

Ca-C grids showed enhanced numbers of wet particles in the plume relative to the stack (Figure 4), with >70% of the coarse fraction activated in plume samples at the time of collection on both sampling dates. Our results are consistent with hygroscopic changes associated with chloride-bearing particles (and possible organic-bearing particles), as RH increases with altitude.

In addition to the changes in overall aerosol populations, changes to specific particle types occurred along the plume length. In particular, chloride-bearing aggregates (e.g., silicate/NaCl aggregates) increased in size along the plume length on 28 August from 6.0 ± 2.8 μm to 6.3 ± 3.3 μm (a Wilcoxon signed rank test on the two samples shows that the median is significantly greater than the test median (0) at a 95% confidence level; \( P = 5.5 \times 10^{-17} \)). The internally mixed NaCl crystals within these aggregates also increased in size, from 1.6 ± 1.2 μm to 1.7 ± 0.9 μm (a Wilcoxon signed rank test on the NaCl in the same two samples shows that the median is significantly greater than the test median (0) at a 95% confidence level; \( P = 5.4 \times 10^{-22} \)) (Figure 7a).

In addition to size change, these internally mixed NaCl crystals also showed a shift from euhedral to subhedral with altitude, tending to coat or engulf other particles with time (Figure 7b). Subhedral NaCl grains also had
Figure 7. Changes to physical and chemical aspects of NaCl/silicate and other NaCl/mineral grain aggregate particles along the plume length on 28 August 2002. (a) Histograms showing size distribution of internally mixed NaCl crystals within silicate aggregates, compared with overall aggregate size in stack and plume samples (N = number of particles). (b) Pie charts showing types of NaCl-bearing aggregate particles in stack and plume samples. These different types (1–9) are categorized based on the locations of NaCl crystals within the aggregate, which are indicative of their formation process, in soil or sabkha (e.g., types 4 and 5) versus within the plume (e.g., types 1–3 and 6–9). Some (types 2, 3, 4, 6, and 7) are illustrated in Figure 5. (c) Ratios of internally mixed NaCl grains to other grains within 54 or 48 distinct NaCl/silicate aggregates from stack and plume samples collected on 28 August 2002. The frequency of occurrence of these ratios is indicated by the color of the symbol on both graphs: black (>10 aggregates), dark gray (5–10 aggregates), and light gray (<5 aggregates).
elevated S, C, O, Mg, and K peaks in their EDX spectra, suggesting that NaCl grains reacted with sulfates and organics (Figure 7b). Finally, aggregates close to the stack had higher numbers of NaCl grains coordinated with fewer mineral grains, while a higher ratio of other grains to NaCl occurred in plume samples, suggesting that NaCl played a role in aggregating particles within the plume (Figure 7c). This is consistent with their increase in size (Figure 7a) and the increase in NaCl-bearing aggregates (especially types 8 and 9 shown in Figure 7b) in all size fractions with altitude.

3.2.3. Differences in Particles Between Dates

Skew-T diagrams, NAAPS global model data, and in-flight measurements show that despite their similar summer synoptic conditions (temperature and wind profiles), a number of factors varied between sampling days, including local SO$_2$ levels, regional dust and SO$_2$ loadings, and RH stability. In addition, the source emissions appeared to vary, since stack sample compositions on each date were quite different. On 28 August, there were more NaCl single-phase particles in the coarse fraction and more MCS droplets in intermediate and fine fractions, while on 3 September, there was a higher single-phase mineral component and much higher soot fractions. Thus, source and meteorological differences clearly affected the makeup of particle populations (LC and FC grids; Figure 4). Higher SO$_2$ levels on 28 August resulted in a high fraction (>30%) of MCS particles in the intermediate fraction of both stack and plume samples compared with those from 3 September, suggesting that these were nucleated from SO$_2$, perhaps enhanced by O$_3$ oxidation. In contrast, under higher RH and lower SO$_2$ levels on 3 September, a greater diversity of sulfate-bearing aggregate particles was recorded at the stack, suggesting that gas-to-particle conversions on mineral or ns-soot surfaces played a greater role in forming sulfates under these conditions; e.g., MCS/ns-soot fractions are high in the finer fractions. Changes to particle compositions with altitude were also distinct on each date. On 28 August, the chloride-bearing component of the fine fraction increased, while on 3 September, markedly more sulfate-bearing types were present in the coarse fraction over time (Figure 8). Finally, higher particle concentrations in the fine mode occurred on 3 September (Figure 3) that were possibly related to regional pollution (NAAPS global model data). Differences in RH resulted in different droplet fractions on Ca-C grids, with more wet particles present on 3 September (Figure 4). This is consistent with the higher numbers of CCN recorded on this date.

4. Discussion

One of the most interesting aspects of this study is the range of particle types in our TEM samples. This diversity reflects the interaction of ambient mineral particles with chloride and sulfate pollution components and is further enhanced by aging within the plume.

Chloride-bearing particles had distinct morphologies (Figures 5 and 7b), reflecting their different formation processes. Some particles were clearly primary, formed in soils or sabkhas (e.g., cemented grains; Figure 5e). However, the majority formed in the plume either through aggregation (e.g., NaCl between, attached to, or engulfing silicate particles; Figures 5a–5d) or through absorption onto mineral surfaces with subsequent crystallization (e.g., microhalite crystals on silicate surfaces; Figure 5b). The initially smaller sizes, euhedral
shapes, and greater abundances of single-phase NaCl crystals in stack samples suggest that their main source was from burning oil brines rather than from soil particles or a maritime source. Large fractions of NaCl were also reported in oil-fire emissions in Kuwait, where dark plumes typically comprised up to 30% NaCl and white plumes up to 80% NaCl from oil brines [Ferek et al., 1992]. Despite their different morphologies, all types of chloride-bearing particles showed changes in concentration, chemistry, and size related to aging of their internally mixed NaCl components along the plume length (Figures 7a–7c). Specifically, the morphological and chemical changes in NaCl were similar to those described for sea salt due to oxidation by SO₂ [Mclnnes et al., 1994; Pósfai et al., 1995]; these particles also were likely formed by SO₂ oxidation in the plume. Changes in aggregate size and the coordination of internally mixed NaCl with other grains suggest that NaCl enhanced aggregation of coarse mode particles in the plume.

Sulfates occurred as both crystalline solids and MCS droplets, depending upon their soil or plume origin. We infer that aggregates containing euhedral gypsum were lofted soil particles, whereas NaCl particles with acicular microcrystals of CaSO₄ likely formed through coagulation of MCS droplets in the plume. MCS droplets also adhered to or coated other particle types, formed due to heterogeneous uptake and oxidation of SO₂ [Usher et al., 2002] or to direct uptake of H₂SO₄ vapor, depending on RH conditions [Manktelow et al., 2010]. Heterogeneous reactions that produce coatings on mineral surfaces are well documented for SO₂ [Balkanski et al., 2003] and occur in many regions with high sulfate loadings [Levin et al., 1996].

The presence of many particles with the entire or partial MCS coatings (up to 10% of coarse fractions or up to 50% of fine fractions) in our samples suggests that such reactions were efficient within the Habshan pollution plume. We surmise that these reactions were enhanced by the inorganic salts from the burning oil brines on mineral dust surfaces, given that the fraction of internally mixed particles with both a chloride and sulfate component was enhanced in all size fractions on both sampling days in plume samples (Figure 8). This interaction between NaCl particles and SO₂ gas (or H₂SO₄) resulted in sulfate coatings that changed the NaCl surface chemistry [Li et al., 2003b; Mclnnes et al., 1997, 1994] and surface morphology (this study). Thus, NaCl in both aggregates and as single particle underwent similar changes along the plume trajectory, resulting either in sulfate coatings or attached acicular sulfate crystals. It is likely that SO₂ reacted with carbonate grains and CaCl₂ to form the Ca-rich sulfate droplets (rare particle type, with frequency <1%; not shown in Figure 4) and tabular CaSO₄ components documented in plume samples. Hwang and Ro [Hwang and Ro, 2006] described similar particles from an Asian dust storm event produced by heterogeneous reactions of carbonate with SO₂ and NOₓ pollutants. The abundance of sulfate-bearing particles in all size fractions was significantly higher in dilute plume than in stack samples (Figure 4); some types only occurred within the plume. The changes in the proportion of sulfate-bearing aggregates, especially the coarse and intermediate fractions, as time and RH increased along the plume, was consistent with laboratory experiments on the uptake of sulfates on mineral dust [e.g., Adams et al., 2005; Ullerstam et al., 2002; Usher et al., 2002].

In Figure 8, we showed that there was an increase in both chloride- and sulfate-bearing particles between the sampling points by grouping particle types present in Figure 4 into chloride- and/or sulfate-bearing categories for each size fraction. Size fractions are differentiated in the figure because they have different initial percentages of these types. Although, the percentage of chloride-only-bearing particles appears to decrease in the coarser fractions, there is an overall increase in the percentage of particles with a Cl component in these fractions. Notably, aggregation and adsorption of sulfates onto “other particle types” and “chloride-bearing types” convert them into sulfate-bearing ones over time. Importantly, the chloride-bearing and sulfate-bearing particles recorded in this study were larger, more hygroscopic, and more reactive with SO₂ and other gases in the plume than their equivalent-sized single-phase dust particles, markedly changing the properties of the ambient mineral dust-dominated aerosol population.

5. Implications

5.1. Changes to Chemical Components of the Plume in Time and Space

The Habshan pollution plume, rich in NaCl, SO₂, and O₃, incorporates dust with a high silicate content rather than a high carbonate content described for many Asian plumes. The TEM samples showed that the industrial component quickly interacted with ambient aerosols to form many internally mixed aerosol types, mainly chloride- and sulfate-bearing particles close to the outlet stack. In addition, we could record some particles with organic and ns-soot components. The formation of these particles likely occurred through different
increasing altitude is consistent with observations of aerosol particles in the Kuwait oil-
domesticated. Thus, some of the internally mixed particles recorded in the Habshan industrial plume are
documented. The increase in concentration of both MCS droplets and sulfate-bearing aggregates within the plume with
analogous to those formed in pollution plumes in other arid regions, although the diversity of internally
increase in particle size and enhanced numbers of silicate/NaCl aggregates also occurred in dust storms in Asia and over the
Mediterranean Sea [Levin et al., 2005; Zhang et al., 2003], suggesting a high propensity for these species to
aggregate. Internally mixed ammonium sulfate and dust, similar to the MCS/silicate or MCS/gypsum
aggregates in the fine fractions of plume samples in this study, were recorded in the fine fractions of Asian
Dust outflows [Martin et al., 2003], the Saharan Dust Experiment, and the Mediterranean Israeli Dust
Experiment [Formenti et al., 2003; Levin et al., 2005]. Hence, sulfates on mineral dust surfaces are also well
documented. Thus, some of the internally mixed particles recorded in the Habshan industrial plume are
analogous to those formed in pollution plumes in other arid regions, although the diversity of internally
mixed particles recorded in this study has not previously been reported.

The increase in concentration of both MCS droplets and sulfate-bearing aggregates within the plume with
increasing altitude is consistent with observations of aerosol particles in the Kuwait oil-fire plumes [Parungo
et al., 1992]. In our study, there was a positive correlation between high SO$_2$ level and high CCN counts.
There is a negative association between SO$_2$ and sulfate not derived from sea salt, suggesting that the
conversion of SO$_2$ into a particulate phase was efficient at forming CCN. This negative association contrasts
with physical and chemical changes in aerosol particles over the Negev desert [Formenti et al., 2001],
although in that study, long-range transported pollutants may have obscured local reactions of SO$_2$ to
sulfate. The enhancement of the sulfate fraction with increasing altitude in the Habshan pollution plume occurs through rapid sedimentation of the coarser chloride-bearing fraction and preferential lofting of the
finer, more sulfate-rich fraction, as well as ongoing uptake of SO$_2$ on particle surfaces. These small-sized,
internally mixed sulfates have longer lifetimes in the plume and greater potential for regional transport
compared with other aggregate types in this study. The lifetime of similar types of sulfates in an Asian
pollution plume with heavy SO$_2$ loading was in the range of 1–4 days [Li et al., 2010]. Thus, the sulfate-bearing
particles formed in this pollution plume are dispersed throughout and beyond the UAE, enhancing regional
transport of sulfates [Li-Jones and Prospero, 1998; Matsumoto et al., 2006].

The rate of uptake of gaseous pollutants on dust surfaces relative to dust deposition affects the efficiency of
the formation of internally mixed dust particles, the amount of pollution removed from the atmosphere
to deposition, and the amount that undergoes regional transport; e.g., Asian plumes exhibited
decreases in SO$_2$ loading through dust loss during transport [Li et al., 2010]. Our study covers only a short
time and space range, but it clearly shows that under the atmospheric conditions in the UAE, the uptake of
chlorides and sulfates (and probably organics) on dust is fast and efficient, producing CCN, as well as
removing a component of this pollution through dust lost. The influence of organic coatings is not clear,
since organic films can change the uptake of pollutants on dust, dependent on their solubility, molecular
weight, surface tension, reactivity, and reaction products with gas species [Smoydzin and von Glasow, 2006].
Other regional- to global-scale studies of pollutant partitioning on dust particles found that uptake is
slow compared with deposition rates and that volatilization of ammonium sulfate transfers red nitrates to
dust [e.g., Fairlie et al., 2010]. Such reactions may be important during the regional transport of the fine-fraction
MCS-bearing particles and droplets recorded in this study.

5.2. Changes to Radiative Properties of Dust and Pollution Aerosol

At the individual particle scale, the newly formed chloride- and sulfate-bearing aggregates have significantly
different radiative behavior than their precursor dust particles [Adachi et al., 2011]. The internally mixed
components will have a direct effect on scattering and adsorption, with changes to optical depth and
other radiative properties consistent with the presence of chloride, sulfate, ns-soot, and organic
components [Li et al., 2010]. The effect of internally mixed ns-soot on optical properties is well documented, resulting in greater absorption of light [Adachi and Buseck, 2008]. While at the local to regional scale, coagulation of MCS droplets with dust particles shifts some fine-mode sulfate into the coarse mode [Manketlow et al., 2010], leading to a decrease in its climate-cooling effect linked to lower sulfate concentrations [Dentener, 1996]. The scattering and adsorption properties of the primary pollutant aerosols are also affected by the formation of internally mixed particles in the plume. The effects on scattering of the uptake of gas components on dust were measured during Aerosol Characterization Experiments-ASIA, where the uptake of these components on the dust reduced the mass scattering of the pollution aerosol by 50%, also suppressing changes in scattering due to RH [Howell et al., 2006]. Similar effects are likely to occur in the Habshan pollution plume.

5.3. Changes to Hygroscopic Properties of Dust and Ambient Aerosol Populations

The hygroscopic behavior of internally mixed particles is more complex than single-phase particles [Freney et al., 2010]; typically, a higher proportion of particles are activated, with activation occurring over a range of RH values. Such behavior was observed in deliquescence experiments carried out on individual chloride-bearing dust particles from the UAE inside an environmental cell chamber of a TEM [Semeniuk et al., 2007; Wise et al., 2007], which showed that large droplets formed when RH was >70–75%. Sulfate-bearing particles undergo rapid hygroscopic growth above RH > 80%. While in particles with multiple aqueous components, hygroscopic growth occurs in multiple stages. Given the high volume ratio (up to 60%) of chloride components in many of the internally mixed particles in the plume, they have great potential to act as GCCN [Osada, 2013; Teller and Levin, 2006; Yin et al., 2000]. Clearly, the soluble components in these aggregates have sufficient mass to engulf all insoluble materials in their core. In plume samples, Ca-C grids indicated that more than 70% of the aerosol particles were activated in the coarse fraction, most relevant to CCN formation, even at relatively low RH. Given that the deliquescence points for common inorganic phases documented in this study are all well above 25%, we believe this behavior to be the effect of organics on particle solubility, as described in an atomic field microscopy study on ammonium sulfate particles [Pósai et al., 1998]. Such a large fraction of activated particles constitutes a major change to the original activation potential of the ambient aerosol population.

Pollution plumes related to oil and gas processing are associated with high numbers of CCN in the UAE, e.g., Habshan industrial site, Das and Zirku Islands [NCAR, 2005; this study]. In addition, our previous TEM work on the activation of individual particles below cloud base in natural convection zones in the Oman mountain region highlighted the role that these pollution-related particles play in enhancing CCN formation. Specifically, we found that industrially derived chloride-bearing particles significantly affected artificial rainfall enhancement practices in updrafts by forming GCCN. While industrially derived sulfate-bearing particles formed smaller CCN close to cloud base [Semeniuk et al., 2014]. Similar enhancement of CCN was recorded during the Kuwait oil-fires [Hudson and Clarke, 1992] and in clouds forming above dust storms in the Arabian Desert [Pósai et al., 2012]. Thus, the internally mixed aerosol particles formed in the plume have the potential to affect cloud-aerosol interactions throughout the UAE.

6. Conclusions

A wide range of internally mixed particles within the Habshan pollution plume was collected on two flights in summer 2002. Diverse types of chloride- and sulfate-bearing aggregates formed through aggregation, adsorption, and coagulation of mineral dust with pollution components in the plume. These secondary particles continued to undergo morphological and chemical changes along the plume length, enhancing the sulfate component in all particle-size fractions.

The uptake of non–sea salts derived from burning oil brines on up to 70% of mineral dust particles significantly changes the hygroscopic properties of the ambient aerosol population and increases the number of GCCN locally and regionally in convection zones associated with the Oman mountains [Semeniuk et al., 2014]. These salts appear to enhance the uptake of SO2 on internally mixed particles in the plume. In plume samples, more than 50% of the fine and intermediate fractions contain sulfates (Figure 8), contributing to regional transport of sulfates in regional dust plumes. In addition, coagulation and oxidation reactions shift this fine-mode sulfate into the intermediate and coarse size particle fractions, further increasing the number of GCCN, as well as reducing the atmospheric SO2 load through dust sedimentation. The high
fraction of internally mixed aerosol particles generated in the Habshan pollution plume by its chloride and sulfate components will affect regional climate by decreasing the reflectivity of dust in the atmosphere, changing the scattering effects of the pollution aerosol, as well as altering hygroscopic and ice nucleation properties of the precursor mineral particles.

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