Investigation of the relative fine and coarse mode aerosol loadings and properties in the Southern Arabian Gulf Region

Kathleen C. Kaku^{a*}, Jeffrey S. Reid^b, Elizabeth A. Reid^b, Kristy Ross-Langerman^c, Stuart Piketh^d, Steven Cliff^e, Abdulla Al Mandoos^f, Stephen Broccardo^d, Yongjing Zhao^e, Jianglong Zhang^g, Kevin D. Perry^h

^aCSC, Naval Research Laboratory, 7 Grace Hopper Ave., Monterey, California 93943-5502 USA; kkaku@csc.com

^bNaval Research Laboratory, Aerosol and Radiation Section, Marine Meteorology Division
Naval Research Laboratory, 7 Grace Hopper Ave., Monterey, California 93943-5502 USA;
jeffrey.reid@nrlmry.navy.mil, elizabeth.reid@nrlmry.navy.mil

^cEskom, PO Box 1091, Johannesburg, South Africa; kristy.ross@eskom.co.za

^dSchool of Geo- and Spatial Science, Unit for Environmental Science and Management, North-West University, Private Bag X6001, Potchefstroom 2531, South Africa;
stuart.piketh@nwu.ac.za, sbroccardo@gmail.com

^eUniversity of California, Davis, West Village, 1605 Tilia, Suite #100, Davis, CA 95616;
sscliff@ucdavis.edu, yjzhao@ucdavis.edu

^fNational Center for Meteorology and Seismology, 29th Street, Khalifa City A, Abu Dhabi, United Arab Emirates; AMandoos@ncms.ae

^gUniversity of North Dakota, Department of Atmospheric Sciences, 4149 University Avenue Stop 9006, Grand Forks, North Dakota 58202-9006; jzhang@aero.und.edu

^hUniversity of Utah, Atmospheric Sciences, 135 S 1460 East Rm 819 (WBB), Salt Lake City, UT 84112; kevin.perry@utah.edu

*Correspondence author at: CSC, Aerosol and Radiation Section, Marine Meteorology Division, Naval Research Laboratory, 7 Grace Hopper Ave., Stop 2, Monterey, California 93943-5502, kkaku@csc.com, tel: 206.829.9443)

Abstract

The aerosol chemistry environment of the Arabian Gulf region is extraordinarily complex, with high concentrations of dust aerosols from surrounding deserts mixed with anthropogenic aerosols originating from a large petrochemical industry and pockets of highly urbanized areas. Despite the high levels of aerosols experienced by this region, little research has been done to explore the chemical composition of both the anthropogenic and mineral dust portion of the aerosol burden. The intensive portion of the United Arab Emirates Unified Aerosol Experiment (UAE²), conducted during August and September 2004 was designed in part to resolve the aerosol chemistry through the use of multiple size-segregated aerosol samplers. The coarse mode mass (derived by subtracting the PM_{2.5} aerosol mass from the PM₁₀ mass) is largely dust at 76% ± 7% of the total coarse mode mass, but is significantly impacted by anthropogenic pollution, primarily sulfate and nitrate. The PM_{2.5} aerosol mass also contains a large dust burden, at 38% ± 26%, but the anthropogenic component dominates. The total aerosol burden has significant impact not only on the atmosphere, but also the local population, as the air quality levels for both the PM₁₀ and PM_{2.5} aerosol masses reached unhealthy levels for 24% of the days sampled.

Keywords: Arabian Gulf; dust aerosols; PM_{2.5}; trace metals; positive matrix factorization

1. Introduction

The large aerosol burden in the Arabian Gulf (also known as Persian Gulf) region is well recognized. Significant dust events result in the region being classified as the world's third largest dust source (Prospero et al., 2002). Comprehensive analyses of this region are rare, but literature suggests consistently high Aerosol Optical Thickness (AOT) levels are typical. Aerosol Robotic Network (AERONET) based studies throughout the Arabian Gulf region suggest mean 500 nm AOTs on the order of 0.4 to 0.5 (e.g., Smirnov et al. 2002; Eck et al., 2008; Kim et al., 2011; Alam et al., 2014). Similarly, Arabian Gulf level 3 AOT calculated from the MODIS data set from 2002 to 2014 suggest mean total 550 nm AOT ranges from 0.3 to 0.5 punctuated by frequent significant aerosol events produced by perennial dust storms creating maxima as high as 0.8 depending on location and satellite (e.g., Zhang and Reid, 2010; Hsu et al., 2012; Peyridieu et al., 2013).

The contribution of mineral dust to the regional aerosol burden is well-known and has been explored in depth in the literature. Kunte and Aswini (2015) deduced that super sandstorms are often the result of the convergence of two separate sandstorms. Reid et al. (2008a) found a mean dust concentration of $125 \mu\text{g}/\text{m}^3$ at one site in the United Arab Emirates (UAE), and was able to identify six distinct dust sources based on mineral dust chemical composition and size distributions. Engelbrecht et al. (2009a&b) explored the chemical composition of the mineral dust in multiple sites throughout the Arabian Peninsula as well as the ramifications of the high regional dust concentration on human health. Modaihsh (1996) measured the mineral composition and trace element contamination of urban dust in Riyadh city, Saudi Arabia and Rashed (2008) measured the trace metal contamination of road dust resulting from urban traffic in Aswan City, Egypt.

While Southwest Asia has considerable dust loadings, there is also substantial contribution from anthropogenic fine mode particles to the high AOTs experienced by the region. Anthropogenic aerosol particles sources result from large oil production centers and refineries, as well as mobile sources and local industries. AOT levels are further elevated by mid-tropospheric transport from Eastern Europe, the Indian Subcontinent, and potentially Africa (Reid et al., 2008b). Eck et al. (2008) and O'Neill et al. (2008) examined the fine mode contribution to the total AERONET-derived 500-nm AOT over a two month period in the UAE and found

significant anthropogenic influence in the aerosol burden, with pollution aerosols predominant some days, and the 500 nm fine mode fraction (FMF) ranging from below 0.2 to higher than 0.8. While the importance of these anthropogenic aerosols for both regional health issues and their contribution to the total global aerosol burden is known, little research has been done on the Arabian Gulf fine mode aerosols' climatology and chemical composition. Past studies have focused on the unique aerosols associated with post-Gulf War oil fires (Hobbs and Radke, 1992; Cahill et al., 1992). More recent studies published have examined filters collected in three urban centers in Saudi Arabia and analyzed via X-ray fluorescence (XRF; Khodeir et al., 2012; Rushdi et al., 2013; Shaltout et al., 2013) and examined soluble aerosols deposited by dry deposition in Bahrain via ion chromatography (IC; Ali-Mohamed and Ali, 2001). While it is known that air quality parameters are measured by individual agencies throughout the region (e.g., Habeebullah, 2014a), such data and important metadata are not generally available to the scientific community. While these studies have provided us with some information on the high PM₁₀ levels at isolated urban Arabian Peninsula receptors, there has yet to be a study of any site that could be considered regionally representative and the use of single technologies for chemical analyses in past studies has limited the possible conclusions. In situ fine mode size distributions are also yet to be published, and the shoulder of the coarse mode particle size distribution from species such as dust can swamp PM_{2.5} measurements thus masking anthropogenic components (Atwood et al., 2013).

We hypothesize that both anthropogenic and mineral dust aerosol concentration behavior frequently result in fine and coarse mode aerosol concentrations exceeding the air quality guidelines set by the US-based Environmental Protection Agency (EPA) and the World Health Organization (WHO) to prevent health effects linked to high concentrations in either of these aerosol size populations. With the goal of better understanding the regional aerosol burden, a research consortium implemented the United Arab Emirates Unified Aerosol Experiment (UAE²) in the southern Arabian Gulf region (Figure 1). The intensive phase of the field campaign took place August - September 2004 and was designed to provide a comprehensive data set to study the sources, concentrations, and also the radiative impacts of regional aerosol particles. This period was selected to observe the peak of the boreal summertime northwest monsoon and start of the transitional period to winter. The research consortium included collaboration among over 20 laboratories from global entities including the US Naval Research Laboratory (NRL), NASA

Goddard Space Flight Center (GSFC), the South African University of the Witwatersrand and the UAE Department of Water Resources, contributing to a network of resources including a research aircraft (South African Aerocommander 690) and 15 Aerosol Robotic Network (AERONET) sun photometers. The ground mission was anchored by an interior desert NASA Surface Based Mobile Atmospheric Research & Testbed Laboratories (SMART; Hansell et al., 2008) and the coastal NRL Mobile Atmospheric Aerosol and Radiation Characterization Observatory (MAARCO). This combination of resources allowed for collection of critical aerosol property information on a scale never before achieved in the Arabian Gulf region (Reid et al., 2008b).

In this paper, we reprocess previously unpublished aerosol chemistry data collected during the UAE² mission at the MAARCO coastal site. This site on the Arabian Gulf coast north-east of Abu Dhabi was selected as a regionally representative receptor for background conditions in the southern Arabian Gulf. The aerosol meteorology discussions within Reid et al., (2008b) suggest the site was frequently impacted by local and regional dust sources and regional anthropogenic pollution including petrochemical emissions and emissions from mobile sources. The most severe pollution events were a result of the development of convergence zones over the Arabian Gulf (Reid et al., 2008b). While the UAE² study period is too short to ascertain climatological loadings, it nevertheless provides one of the first, and arguably the most thorough reported regional aerosol composition dataset. While the Arabian Gulf region is well known for its frequent coarse mode dust events, clearly fine mode anthropogenic pollutants are also important air pollutants and climate forcers. Based on trajectories to the MAARCO site reported by Reid et al., (2008b) the intensive chemical properties of aerosol particles presented here appear to be regionally representative over the Arabian Gulf and surrounding coastal areas.

We will first provide the basic aerosol chemistry of regional aerosol particles sampled during the UAE² campaign. Second, we will break our data into size segregated categories, examining the chemistry of coarse mode (CM) particulate matter (defined here as aerosols with a diameter between 2.5 μm and 10 μm), sub-2.5 μm particulate matter (PM_{2.5}) and higher size and time resolution aerosol chemistry derived from an eight stage impactor. Third, we will hypothesize on the sources of the aerosol populations using positive matrix factorization (PMF) analysis. Finally, we will discuss implications of our study for regional air quality.

149 2. Methodology

150 The intensive phase of the UAE² campaign was conducted in the southern Arabian Gulf/Persian
151 Gulf region during August through September 2004. In situ sampling discussed in this paper will
152 focus on the MAARCO site, located at a remote coastal site in Al Taweela (24.70°N; 54.65°E,
153 elevation: 480 m) about 50 km NE the urban core of Abu Dhabi and 80 km SW of Dubai, where
154 multiple sets of filters were collected to allow for chemical analyses at different aerosol sizes.
155 The location just outside of Abu Dhabi allowed for collection of samples indicative of regional
156 values as well as samples representative of nearby urban cores. An inlet 7 m above surface level
157 with an approximate diameter cut point of 10 µm pulled at a rate of ~80 lpm at ambient RH
158 (approximately 61% ± 14%). The first set of Teflon filters collected a total of 51 PM₁₀ aerosol
159 samples (aerosols with a diameter less than 10 µm). In parallel to the PM₁₀ Teflon filter impactor
160 and downstream from the inlet an impactor with a 50% diameter cut point of 2.5 µm was in
161 place, allowing for collection of 52 total PM_{2.5} aerosol samples on both Teflon filters and
162 quartz filters. While it is well documented that the minimum diameter of the lognormal
163 distribution between the fine and CM aerosols frequently lies below the 2.5 µm aerosol diameter
164 cut point, this cut point was chosen to be in agreement with cut points set by the EPA and the
165 WHO to study the impact of aerosols on human health (c.f. Kampa and Castanas, 2008). These
166 three sets of filters (two sets of Teflon filters and one set of quartz filters) were used to
167 characterize the inorganic chemistry of the 24-hour PM_{2.5} and PM₁₀ aerosol burden, as well as
168 the PM_{2.5} total carbon (TC; the sum of organic carbon and black carbon) concentration during
169 the UAE² campaign from 9 August to 1 October, 2004. Sampling was over a 24-hour period
170 (starting approximately 09:00 local time/05:00 UTC). The two sets of Teflon filters underwent
171 analysis at the Desert Research Institute (e.g. Engelbrecht et al., 2009a) for gravimetry,
172 inorganic anion and cation ion chromatography analysis (IC), and x-ray fluorescence (XRF). The
173 quartz filters underwent thermal optical transmittance analysis to determine the concentration of
174 organic and black carbon (OC and BC, respectively) present in the PM_{2.5} aerosol population.
175 Filter sampling and analysis, including the use of blanks, calibration, and the establishment of a
176 limit of detection followed DRI protocol, have been documented by Reid et al., 2008a and can be
177 accessed on-line at DRI EAF capabilities (<http://www.dri.edu/eaf-capabilities?showall=1>, last
178 accessed Aug. 2015). While the Teflon filters were stored and shipped cold to prevent

179 evaporative loss of volatile particulate matter, literature suggests that some nitrate loss is
180 expected. While it is difficult to accurately estimate the amount of nitrate volatilization without
181 a complex thermodynamic model, it is expected that the nitrate concentrations presented here
182 could be underestimated by as much as 44% by mass (e.g. Chow et al., 2005; Hering and Cass,
183 1999).

184 Supplementing filter samples and corresponding to the airborne component of the campaign of
185 27 August -5 October, 2004, a ground-based eight-stage Davis Rotating-drum Uniform size-cut
186 Monitoring (DRUM) impactor was deployed. The DRUM sampler allowed for a three hour
187 resolution of aerosol particle elemental chemistry on stages 1-8 with a 50% aerodynamic
188 diameter cut size, respectively, of: inlet to 5 μm , 2.5 μm , 1.1 μm , 0.74 μm , 0.56 μm , 0.34 μm ,
189 0.24 μm , and 0.07 μm , with each stage collecting 251 samples. The DRUM samples were
190 analyzed using Synchrotron XRF at the Advanced Light Source-Lawrence Berkeley Laboratory
191 (Berkeley, CA), identifying 17 elements with atomic weights between aluminum and zinc (Reid
192 et al., 2008a; Atwood et al., 2013). DRUM impactors are prone to several sampling artifacts,
193 including peak broadening, matrix effects, and mis-sizing of the sample due to humidification
194 (Atwood et al., 2013). To minimize these errors, Na is not analyzed within the DRUM data, and
195 for the smaller size ranges, stages 5 and 6 as well as 7 and 8 are combined after the laboratory
196 analysis. Additionally, the DRUM filter measurements of sulfur appear compromised due to the
197 high sulfur loadings experienced by the region, so are not included in this study.

198 As dry fine mode size distribution data were not collected at the MAARCO station,
199 measurements from the Passive Cavity Aerosol Spectrometer Probe (PCASP) mounted aboard
200 the South African Weather Service Aerocommander 690A were utilized in this study. Flybys
201 above the MAARCO station at an altitude of 160 m or less (54 m on average) were compiled and
202 revealed a snapshot of data of the fine mode aerosol (diameter 0.1 -3 μm) at a dry RH (~35-
203 40%). Calibrations were performed before and after deployment using polystyrene spheres with
204 a refractive index of 1.59, establishing median bin diameters within 0.02 μm . Further
205 information about the PCASP can be found in Reid et al. (2008b) and Reid et al. (2003).

206 The chemistry of the dust encountered during the UAE² study is clearly complex. The literature
207 survey for the region by Hansel et al., (2008) suggested the dust is composed primarily of
208 silicates (largely quartz: SiO_2) and clays (largely kaolinite: $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) with internal

209 mixtures of hematite and calcite (Fe_2O_3 and CaCO_3 , respectively). However, Engelbrecht et al.
210 (2009a) suggested that the dust composition contained K feldspar, Ca feldspar (KAlSi_3O_8 ,
211 $\text{CaAl}_2\text{Si}_2\text{O}_8$) and Ca-Mg dolomite (CaMgCO_3)₂, based on secondary-electron images. Reid et al.,
212 (2008a) found that specific sources were identifiable based on clear differences in particle
213 chemistry and size. Such diversity in the literature likely reflects significant variability in dust
214 sources throughout Southwest Asia. For our purposes we will assume the dust metals occur in
215 their simplest oxide form, and the complications resulting from this assumption will be discussed
216 in the text.

217 Positive Matrix Factorization (PMF; US EPA PMF version 5.0) (Paatero and Tapper, 1994)
218 receptor modeling was applied to the chemical analysis results. PMF is one of the most
219 commonly used receptor models and has been applied successfully in situations spanning
220 multiple continents (e.g. Pandolfi et al., 2011; Kim et al., 2003). The PMF algorithm searches
221 for a solution of chemical mass balance between the matrices of factor contributions and factor
222 profiles by minimizing an object function, Q , based on the uncertainties associated with each
223 observation (Norris et al., 2014). For our methodology, instrumental uncertainties were used in
224 the PMF solution, with a minimum of 5% assumed based on handling uncertainties in the field.
225 To prevent double counting, sodium results from the IC analysis were chosen over sodium from
226 the XRF analysis due to lower levels of instrumental uncertainty and magnesium, and calcium
227 and potassium from XRF were used so that insoluble dusts could be included in the analyses.
228 Filter samples with missing values were excluded from analysis. To determine the number of
229 sources, PMF was run multiple times with different seeds and a different number of assumed
230 sources to find the most stable solution. To confirm some of the results, back trajectory analyses
231 were computed for each filter collection time using the Air Resources Laboratory HYSPLIT
232 model (Draxler and Hess, 1998).

233 Errors can be introduced into PMF model results through three possible avenues: errors in the
234 data values; rotational ambiguity within the PMF model solution; and modeling errors. A more
235 thorough discussion can be found elsewhere (e.g. Paatero et al., 2014, Brown et al., 2015), but
236 briefly, three tools exist within PMF version 5.0.12 that allow the user to estimate the errors in
237 the model results associated with each of these error sources. Bootstrap analysis (BS) estimates
238 error in the original data through perturbation of the data, and displacement analysis (DISP)
239 repeatedly fits the model after each variable is separately displaced from its original fitted value,

thus capturing the uncertainty caused by data errors as well as errors caused by rotational ambiguity. These two methods are sometimes combined, resulting in bootstrapping enhanced with DISP (BS-DISP), with the results representing both the random uncertainty and the rotational uncertainty. Unfortunately none of these processes do an adequate job of representing modelling errors. In order to be transparent about errors associated with our PMF results, we followed the PMF reporting recommendations suggested by Brown et al. (2015) and our results are shown in Table 2. All analyses were run in robust mode with a random seed value. The number of bootstraps in BS was 100 with a minimum r^2 of 0.6 for all cases.

3. Results

3.1 Aerosol Chemical Composition

We begin our results with the time series representation of the chemical composition of the PM_{2.5} aerosols and CM aerosols (derived from subtracting the PM_{2.5} aerosol concentrations from the PM₁₀ aerosol concentrations), normalized by the CM aerosol gravimetric mass. Dust was assumed to be in its common oxide form (K₂O, CaO, Fe₂O₃, SiO₂, TiO₂, MgO, Al₂O₃), sea salt was calculated using $\text{Cl}^- + 1.47 \cdot \text{Na}^+$, and TC was not adjusted. In general, reconstructed mass is within 15% of gravimetry for both modes. There are several instances of the presumed filter chemical composition exceeding the measured gravimetric mass, while in other instances a residual of unknown composition is present. This can be due to errors in either the gravimetry (weight or flow) or the chemistry, and will be discussed in further detail in Section 3.2. Figure 2(c) shows a reproduction of the Reid et al., (2008b) total gravimetric mass concentrations for the UAE² study period.

The large influence of multiple dust events is immediately evident, coincident with the high mass percentage of dust oxides in both the CM and PM_{2.5} mode mass fractions. Dust mineral concentrations are highly correlated to CM filter mass variability ($R^2 = 0.76$ and 0.85 for silicon and calcium, respectively) and influence PM_{2.5} mass variability ($R^2 = 0.27$ for both silicon and calcium). These seven dust mineral oxides also dominate the aerosol mass, comprising 38% and 76% on average of the total PM_{2.5} and CM aerosol mass, respectively; and dominate even the PM_{2.5} aerosol mass during dust events, exceeding 74% of the mass loadings during the dust event 29 September 2004.

Also evident in Figure 2 are several pollution events. While not associated with as large a jump in the $PM_{2.5}$ mass as observed in the dust events, in part because of the constant presence of dust in the $PM_{2.5}$ filter mass, there are peaks in the $PM_{2.5}$ filter mass that correspond to high loadings of ammonium sulfate on the filter. On average, the sum of the inorganic ions of ammonium, nitrate, and sulfate comprises 47% of the total $PM_{2.5}$ mass, and pollution is most responsible for the variability in the $PM_{2.5}$ aerosol mass, with sulfate concentrations being correlated to the $PM_{2.5}$ aerosol filter mass ($R^2=0.56$). Organic carbon and black carbon are also present at significant levels, comprising 15% on average of the total $PM_{2.5}$ mass, but are not highly correlated to mass variability ($R^2(TC)=0.23$). Figure 2(d) also shows an approximation of the fine mode (FM) mass derived by subtracting the $PM_{2.5}$ dust oxide mass from the $PM_{2.5}$ mass, as well as the FM mass fraction.

The average $PM_{2.5}/PM_{10}$ aerosol mass fraction for the period of study was 0.28, but reached levels of 0.76 for the pollution event on 30 August and a low of 0.087 for the dust event on 22 September. This high variability further confirms the complexity of the aerosol and the importance of both the anthropogenic and natural components to the regional air quality. To understand the contributions to both, we first focus on the chemical analysis of the CM aerosols.

3.2 Coarse Mode Composition

As the coarse mode dominates total particle mass from PM_{10} and $PM_{2.5}$ and, as discussed below, dust can serve as a sink for anthropogenic gases, we need to thoroughly understand its nature if we are to understand the chemical properties of the fine mode. While dust minerals obviously dominate the CM aerosols, the location of the MAARCO at a coastal site near an urban center and several offshore drilling rigs allows us to observe the interaction between the dust aerosols, sea salt aerosols and the anthropogenic component. Dust minerals, assumed to be in their simplest oxide form, comprised $76\% \pm 7\%$ of the CM aerosols, while sea salt comprised $5\% \pm 2\%$, and nitrate and sulfate together comprised an average of $11\% \pm 3\%$.

Both the residual and the overestimation of the CM aerosol mass seen in Figure 2(a) are likely due to the oversimplification of the dust mineral chemical composition. As stated in Section 2, fresh dust in this region likely takes the form of silicate, kaolinite, hematite, calcite, dolomite and feldspar, and other minor constituents which would account for the residual. The composition of the dust is complex and varies significantly by region. In previously published work analyzing

the dust concentrations encountered during the UAE² campaign, Reid et al. (2008a) used the dust mineral composition shown in Figure 2 (specifically the ratio of major elements to Fe), CM size distributions measured by the Aerodynamic Particle Sizer (APS) aboard the South African Weather Service Aerocommander 690A, and HYSPLIT back trajectory analysis to identify six major groupings of dust and their likely source region. Figure 3 illustrates the variability of the mineral composition depending on their source region. While the mass percentage of iron oxide to all major dust minerals remains somewhat constant at ~5%, making it an excellent marker for airborne dust mass, there is more variability associated with the mass percentage of silicon, aluminum, and in particular calcium depending on the source of the dust.

As the dust is exposed to urban pollution, the oxidation of anthropogenic SO₂ and NO_x gases can replace the anions associated with the dust minerals with sulfate and nitrate, leading to overestimation of the CM aerosol mass (Herring et al., 1996). Laboratory and field studies confirm SO₂ and NO_x can condense onto dust particles, either at the surface of the dust particle, changing the dust aerosol from hydrophobic to hydrophilic, or as complete replacement of the carbonate (e.g. Wu and Okada, 1994; Gao and Anderson, 2001), with the uptake rates enhanced with increasing RH (Fairlie et al., 2010). In the absence of dust, sulfate is found primarily in the fine mode as ammonium sulfate, while nitrate can be associated with the ammonium in the fine mode or with sodium from sea salt in the CM (Song and Carmichael, 2001). Both field campaigns and model simulations encountering polluted Asian dust plumes found intrusions of nitrate and sulfate into the dust-dominated coarse mode during the INTEx-B campaign as well as the TRACE-P campaign (Fairlie et al., 2010; Jordan et al., 2003).

The conditions required for dust processing are met by the urban Abu Dhabi environment, with high levels of SO₂ and NO_x gases emitted by the local petrochemical industry and mobile sources, and an observed increase in the RH (~ 61%) caused by the proximity of the Arabian Gulf as compared to the interior desert. During UAE², sulfate was present in the CM at $5.7 \pm 3.9 \mu\text{g}/\text{m}^3$ and at $13.1 \pm 8.5 \mu\text{g}/\text{m}^3$ in the PM_{2.5} aerosols, showing a preference for existing as ammonium sulfate. With the presence of calcite, dolomite and sea salt in the CM, nitrate existed almost exclusively in the CM ($5.6 \pm 3.9 \mu\text{g}/\text{m}^3$, compared with $0.8 \pm 0.9 \mu\text{g}/\text{m}^3$ in the PM_{2.5} mode).

Trace metals present in the CM could be due to natural minerals associated with the dust emissions or due to anthropogenic contamination of the dust particles, commonly termed road dust, or a combination of the two. To determine which trace metals had natural origins, the correlation coefficients of the trace metals with iron concentrations, used as a proxy for dust, were examined and the results are shown in Figure 4. With 51 pairs, R^2 values greater than 0.26 are considered significant with p-values $< .001$. This leads us to conclude that copper, zinc and lead, all commonly found in vehicle part emissions (e.g. brake pad wear) and petroleum refining and combustion emissions, are primarily anthropogenic in origin and are present in the CM in the form of contaminated road dust. Nickel, manganese, chromium and vanadium appear to be primarily natural in origin, although anthropogenic sources such as flaring emissions could contribute to the total trace metal concentrations. This is in partial agreement with previous studies of regional road dust, which used enrichment factors to identify anthropogenic enhancement of trace metals on mineral dust. Rashed (2008) found high enrichment factors of lead and manganese in Aswan City, Egypt, and Khodeir et al. (2012) found enrichment factors greater than ten of lead and zinc in urban dust in Jeddah City, Saudi Arabia, and thus these trace metals were attributed to anthropogenic contaminants, specifically the combustion of fossil fuel and construction. The discrepancy of our results may be attributed to differing methodology. For comparison, using iron as a representative crustal element and Taylor et al. (1964) as a source for mean crustal abundances, consistent with the Rashed (2008) and Khodeir (2012) methodology, lead and nickel have a mean enrichment factor of greater than 5, indicating a possibility of anthropogenic sources. However, as nickel co-varies strongly with iron, we suggest that nickel has a natural source in our campaign that is higher than the global mean.

3.3 PM_{2.5} and Anthropogenic Fine Mode Composition

While the dust contributes to the majority of the PM₁₀ aerosol particle mass burden in the Arabian Gulf region, it has been analyzed in previous field work and is the better understood of the aerosol modes. Less work has been done to analyze the anthropogenic contribution to the PM₁₀ Arabian aerosol burden despite its significant presence. Due to the high aerosol cut point of 2.5 μm of the filter impactor, there is significant CM creep into the fine mode chemical speciation. Reid et al., (2008a) found the actual cutoff at ambient RH is less than 1 μm , and found no evidence of a fine mode in the dust population. However, dust metals alone account for 22% of the PM_{2.5} mass. The residual, comprising 2% on average of the PM_{2.5} aerosol mass, is

likely the carbonates, hydroxides and oxides associated with dust aerosols and organic materials. As expected, ammonium and sulfate concentrations are highly correlated ($\text{NH}_4^+ = 3.38 \times \text{SO}_4^{2-} + 2.90$, $R^2 = 0.83$), while ammonium shows no correlation with nitrate. Furthermore, the average molar ammonium to sulfate ratio, $[\text{NH}_4^+]/(2[\text{SO}_4^{2-}])$ is 0.55 ± 0.21 , indicating that the available ammonium is fully neutralized and that the regional anthropogenic emissions produce acidic $\text{PM}_{2.5}$. Even accounting for nitrate in the $\text{PM}_{2.5}$ aerosols, only one case of non-acidic $\text{PM}_{2.5}$ aerosols exists (17/9/04; $[\text{NH}_4^+]/(2[\text{SO}_4^{2-}] + [\text{NO}_3^-]) = 1.0$). Without an available basic cation, nitric acid generally does not partition onto fine mode aerosols. The observed acidity of the $\text{PM}_{2.5}$ aerosols, demonstrating the lack of ammonium available to react with nitrate in the anthropogenic aerosols, and the lack of correlation between nitrate and ammonium reinforces that sulfate occurs primarily in the fine mode, while nitrate is preferentially scavenged by sea salt and dust.

Organic measurements were only made for the $\text{PM}_{2.5}$ aerosols and indicated that organics contribute to a surprisingly small portion of the total $\text{PM}_{2.5}$ mass. Organic carbon is present at $3.2 \pm 1.2 \mu\text{g}/\text{m}^3$, and black carbon is present at $1.6 \pm 0.7 \mu\text{g}/\text{m}^3$, respectively accounting for 10% and 5% of the total $\text{PM}_{2.5}$ aerosol mass. A study of oil plumes in the Gulf of Mexico indicated that the dominant organic aerosol mass spectral signal was $\text{C}_2\text{H}_3\text{O}^+$ (Bahreini et al., 2012). Using this to estimate the contribution of oxygen and carbon (e.g. $\text{OC} \times 1.79$), the organics contribute approximately 20% to the $\text{PM}_{2.5}$ mass and 5% to PM_{10} .

Trace metals associated with anthropogenic pollution are present at levels above the limit of detection, comprising 0.2% of the $\text{PM}_{2.5}$ mass. Vanadium and nickel, two tracers for oil combustion, are present at significant levels in all but two samples with a mean of $6 \text{ ng}/\text{m}^3$ for both metals. The V/Ni mass ratio is 1.1 ± 0.7 , consistent to what was found in and downwind of the Kuwaiti oil plumes over two decades earlier (1.7 ± 0.4 and 1.4 ± 0.9 , respectively; Cahill et al., 1992).

3.4 Particle size and size-resolved chemistry analysis

Examination of single elements from the DRUM data set may provide us with a finer timescale of the dust events occurring during UAE² as well as the interaction between anthropogenic trace metals and the CM dust. Figure 5 demonstrates that CM (defined as $2.5 - 10 \mu\text{m}$ diameter for

the DRUM series) silicon or calcium concentrations are adequate to capture all the dust events observed in the region.

Exploring the mean size distribution of the elements collected by the DRUM sampler allows us to further verify some of our hypotheses. Figure 6(a) demonstrates the dominance of dust in the CM. As observed by Reid et al. (2008a), dust mass is primarily limited to the supermicron mode. Examining the four common dust metals provided in the DRUM analysis (Al, Si, Ca, Fe), while 19% of the mass on average lay below the 2.5 μm diameter cut point, only 1% lay below the 0.75 μm diameter cut point, emphasizing the lack of submicron mode in the dust mass distribution in the Arabian Gulf region. Figure 6(a-b) show similar mean mass distributions for the dust minerals and trace metals of natural origin. The trace dust metals show a similar pattern, with 4% by mass lying below the 2.5 μm diameter cut point and only 0.1 % below the 0.75 μm diameter cut point.

In contrast, trace metals we identified as being primarily of anthropogenic origin have a distinct bimodal behavior (Figure 6(c)), with 39% of the mass below the 2.5 μm diameter cut point and 9% below the 0.75 μm diameter cut point. Vanadium, a trace metal that has both natural and anthropogenic origins, has a strong CM presence, but also has 59% of the mass below the 2.5 μm diameter cut point and 33% below the 0.75 μm diameter cut point.

Size distribution data for the submicron mode was available from the PCASP aboard the Aerocommander research aircraft and was correlated to the MAARCO station during flybys. Flybys were not performed on every day and on the occasions that multiple fly-bys were performed on a single day, they were usually contained within an hour. Thus, while they can provide a snapshot of the submicron mode aerosols present at the MAARCO station, they are not necessarily representative of the entire submicron aerosol population collected on a filter with an exposure time of 24 hours.

Normalized number, surface area, and volume distribution populations are shown in Figure 7 and Table 1, and can be clearly separated into three populations based on median particle diameter and geometric standard deviation. The 30 August case is distinct in its narrow distribution, indicative of a fresh pollution event. This is confirmed by the mass loadings of the $\text{PM}_{2.5}$ filter, with a mass of 98 $\mu\text{g}/\text{m}^3$, compared to a mean mass of $21 \pm 7 \mu\text{g}/\text{m}^3$ for the other events. This event was high in ammonium and sulfate (12.4 and 53.1 $\mu\text{g}/\text{m}^3$, respectively, with an ammonium

to sulfate molar ratio of 0.70), but contained almost no nitrate, indicating separate sources and sinks for these pollutants. TC was also high for this event, at $7.1 \mu\text{g}/\text{m}^3$ compared to an average of $4.2 \pm 1.1 \mu\text{g}/\text{m}^3$ for the other events captured in Figure 7.

The other days can be divided up into two categories based on their size distributions and confirmed using aerosol chemistry measurements. The 12, 28 and 29 Sept. observations (referred to hereafter as Population 1) have smaller mean diameters and broader geometric standard deviations (means $0.19 \mu\text{m}$ and 1.6 , respectively) compared to the observations made 31 Aug., and 7, 27, and 30, Sept. (referred to hereafter as Population 2) with a mean and standard deviation of $0.23 \mu\text{m}$ and 1.48 , respectively. These two populations differentiate themselves chemically as well, with Population 1 containing significantly more nitrate than Population 2 ($0.49 \pm 0.26 \mu\text{g}/\text{m}^3$ and $0.07 \pm 0.09 \mu\text{g}/\text{m}^3$, with molar ammonium to sulfate ratios of 0.55 and 0.68 , respectively). There are no other significant chemical differences between the populations. As there is no significant pattern in the HYSPLIT back trajectories and all of the flybys occurred in the morning hours, this leads us to conclude that there was a local source of NO_x that was present on some days but not on others.

Table 1: PCASP Aerosol Size Distribution, including mean particle diameter (D_p) and standard deviation (σ) for number, surface area (SA) and volume distributions.

Date	Number D_p	Number σ	SA D_p	SA σ	Volume D_p	Volume σ
30 Aug	0.26	1.3	0.29	1.2	0.30	1.2
31 Aug	0.17	1.6	0.23	1.5	0.26	1.4
7 Sept	0.18	1.6	0.24	1.4	0.27	1.3
12 Sept	0.13	1.4	0.18	1.6	0.22	1.6
27 Sept	0.14	1.6	0.22	1.6	0.40	2.3
28 Sept	0.13	1.5	0.18	1.6	0.23	1.7
29 Sept	0.13	1.5	0.20	1.6	0.28	1.9
30 Sept	0.16	1.4	0.21	1.4	0.24	1.4

437

438 **3.5 Chemical apportionment of the PM_{2.5} and coarse mode aerosols**

439 The filter analysis of the UAE² field campaign revealed a complex mixture of aerosols in the
440 PM_{2.5} and coarse modes. To better understand the sources of these aerosols, Positive Matrix
441 Factorization (PMF) was applied to the Teflon and quartz chemical analysis results, using the
442 methodology described in Section 2. For both the CM and DRUM mode analyses, six sources
443 resulted in reproducible solutions with the lowest levels of rotational ambiguity and a high
444 percentage of mappings onto each of the six base factors based upon the DISP, BS, and BS-DISP
445 error analysis contained in the EPA PMF v5.0, and documented in Table 2. However, PM_{2.5}
446 source analyses were limited to five results due to a large level of rotational ambiguity observed
447 in the six factor solution. Solutions were chosen and errors are reported based upon the
448 recommendations outlined by Brown et al., 2015, by minimizing the Q values and the number of
449 cases with swaps occurring during element displacement, while maximizing factor mapping.

450 **3.5.1 Analysis of Coarse Mode PMF results**

451 The three largest contributors to CM mass variation (Figure 8) are, unsurprisingly, strongly
452 associated with the known dust metals (Mg, Al, Si, K) and identified dust trace metals (Mn, Ti,
453 Cr, Ni), totaling 70% of the total variability. However, these three factors differentiate
454 themselves based on the non-mineral dust metals with which they are also associated.

455 Factor one (red) is most probably road dust, likely locally sourced, as the dust minerals are
456 loaded equally with the industrially-emitted metals copper, zinc, and lead, suggesting that a
457 significant percentage of the total dust sampled has been chemically modified in the urban
458 MAARCO sampling environment. There is also a possibility that factor one is simply a
459 uniquely-sourced desert dust containing a unique chemical signature of trace metals and
460 metalloids. Factor two (blue), termed continental dust, appears to be relatively fresh dust with no
461 loadings of copper, zinc, or lead indicating no contamination from car emissions. However,
462 small loadings of nitrate and sulfate indicate that even fresh dust contains some anthropogenic
463 influences in the highly polluted Arabian Gulf region. Factor three (yellow) contains a mixture of
464 metals associated with dust and sodium, likely from marine origins. We termed this factor
465 marine dust, proposing it contains dust that has spent significant time over the Arabian Gulf,

causing it to be well mixed with sea salt aerosols, although a possible contribution of ophiolites to the mineral dust chemical composition cannot be eliminated (e.g. Ghazi et al., 2010).

To confirm the two distinct dust sources suggested in the PMF analysis, a time series of the factor contributions was compared to 72-hour back trajectory analyses computed for each filter collection time using the ARL HYSPLIT model. As expected for the region, winds were highly variable, at times north-easterly with sources originating in Iraq and traveling across the Arabian Gulf before reaching the MAARCO station in the UAE, at times northerly from Iran, at times circular in pattern indicating a period of stagnation over UAE, and at times southerly or southwesterly with winds originating in Oman and travelling across the Arabian peninsula to reach the MAARCO station. Local meteorology was further influenced by the daily land/sea breeze pattern at the coast. This is explored in more detail in Reid et al., (2008a). Focusing on the 24-hour-averaged back trajectory analysis provided by ARL HYSPLIT, a strong period of southwesterly winds from 23 August – 28 August, 2004 coincided with a near zero normalized contribution of the PMF factor marine dust and a high loading of the continental dust factor (Figure 9). Conversely, an earlier period ranging from 11 August – 16 August showed 72-hour air mass history originating NE in Iraq and traveling across the Gulf before arriving at the MAARCO station. These air masses, containing dust from Iraq and sea salts from the Arabian Gulf, have strong contributions from the marine dust PMF factor and low normalized contributions from the continental dust factor.

The three remaining factors (Figure 8(a)) include fresh sea salt (green), with strong loadings of sodium and chloride, and secondary sulfate (maroon), which is co-emitted with lead, zinc, vanadium and copper (indicating an association with vehicular emissions and/or plumes originating from oil refineries). The small loading of this factor on the dust metals, but not on sodium, is in agreement with the earlier postulate that sulfate will condense on dust particles, but not sea salt. The secondary nitrate factor (cyan) contains nitrate with loadings of metals associated with sea salt, dust, and trace metals associated with industrial emissions. This suggests nitrate, co-emitted as gaseous NO_x with other industrial pollutants such as vanadium and lead, ultimately deposits on CM sea salt and dust. It is worth noting that nitrate does not appear to have a preference for calcium, suggesting that it does not react preferentially with the alkaline dust calcite or dolomite or that this calcium dust takes a less soluble form. The influence of

anthropogenic pollution on the CM variability is significant, with secondary sulfate and secondary nitrate contributing in sum 17% to the total CM mass variability (Figure 8(b)).

Linear regression allows us to predict the CM mass when measurements (in $\mu\text{g}/\text{m}^3$) of only a few elements are available. Total mass is most closely related, unsurprisingly, to dust minerals, with silicon alone regressing on to total mass with a squared correlation value of 0.83, significant with a p-value $< .001\%$. Adding a pollution tracer in the form of nitrate increases the agreement to $R^2=0.96$, but the best agreement occurs when iron and calcium are used together, representing two dust sources, resulting in a squared correlation coefficient of 0.98:

$$\text{CM Mass} = 3.38 \cdot \text{Ca} + 22.64 \cdot \text{Fe} - 4.04 \quad (1)$$

3.5.2 Analysis of $\text{PM}_{2.5}$ PMF results

Looking at $\text{PM}_{2.5}$ receptor model results (Figure 10), we see some similarity with the CM factor analysis due to the significant creep of dust and sea salt into $\text{PM}_{2.5}$. Factor one (red) is termed dust due to its high loadings of dust metals. Factor two, labeled sea salt, contains strong loadings of sodium and chloride. The nitrate loading on these two factors demonstrates the affinity of gaseous NO_x to condense on sea salt and dust aerosols.

Factor three (yellow) contains primarily ammonium and sulfate, representing secondary anthropogenic sulfate aerosol formation. Also found in this factor are strong loadings of organic and black carbon and trace metals associated with industrial emissions such as lead and zinc. Factor four (green), with strong loadings of vanadium, nickel, lead, and organic carbon and black carbon, was attributed to the petrochemical industry. Vanadium, nickel and lead are all tracers for oil combustion, and the strong loading of ammonium sulfate on this factor indicates that the oil undergoing combustion is unrefined. Factor five (maroon) contains similar loadings of vanadium and nickel, but smaller loadings of sulfate, and ammonium, leading us to attribute this factor to refined oil combustion from mobile sources. Although implementation of low sulfur fuel regulations across the region has not been uniform, it is expected that unrefined fuel emissions should have higher sulfate loading than refined fuel. Factor five also contains copper, which may be due to brake lining wear of the mobile sources (Denier van der Gon et al., 2007).

These $\text{PM}_{2.5}$ PMF results also confirm the Aug. 30 unique pollution event identified by the PCASP (Fig. 7). The normalized factor contributions to the $\text{PM}_{2.5}$ aerosols show the dominance

of the ammonium sulfate factor contributing to ~90% of the observed aerosol composition that day, with the oil refinery factor contributing ~8% of the aerosol composition. This pollution event is further discussed in Reid et al., (2008b), identifying the source of this high pollution event as the abundant petroleum extraction and processing facilities in the area.

Anthropogenic pollution contributes most to the PM_{2.5} mass variability, as seen in Figure 10(b). Ammonium sulfate aerosols and aerosols from oil combustion contribute a total of 58% to the total mass variability. However the influence of CM aerosols included in the PM_{2.5} aerosol analysis is significant, with sea salt and road dust concentrations contributing 42% to PM_{2.5} mass variability. Unsurprisingly, the best tracers to estimate PM_{2.5} mass are sulfate and iron concentrations, representing pollution and dust. The equation, in µg/m³ with a squared correlation coefficient of 0.96 is:

$$\text{PM}_{2.5} \text{ Mass} = 1.52 \cdot \text{SO}_4^{2-} + 30.07 \cdot \text{Fe} + 0.30 \quad (2)$$

3.5.3 Analysis of DRUM filter PMF results

Finally the PMF was applied to the fine mode chemistry data as measured by the DRUM samplers below the 0.75 µm cutoff (Fig. 11). This allowed us to identify the sources of true fine mode aerosols without dust intrusion. Factor one (red), with its high loadings of zinc and copper, and strong loadings of other contaminant metals such as nickel and manganese could result from a nearby zinc and/or copper smelter. Similarly, with its high calcium loadings, factor four (green) is likely the result of a cement factory in the nearby industrial zone. Vanadium and nickel are common tracers for fuel oil emissions (factor six – cyan), while unrefined fuel burnings due to flare emissions of nearby refineries contain more concentrated phosphate (factor five, purple). The chloride co-emitted in the flare emissions factor, while not as easily explained, was also seen in aerosol emissions resulting from the Kuwait oil fires a decade before (Cahill et al., 1992). Factor three (yellow) contains high levels of bromine and lead, which may be a tracer for a popular vehicular fuel additive. Finally, factor two (blue) contains numerous heavy metals found in electronic and car parts and is thus speculated to be waste combustion.

Table 2: Error analysis of positive matrix factorization (PMF) coarse mode (CM), PM_{2.5}, and DRUM data using the bootstrap (BS) analysis, displacement (DISP) analysis, and the combined bootstrap-displacement (BS-DISP) for the three sets of aerosol source analysis, as recommended by Brown et al., 2015. Q is the PMF object function.

	CM	PM _{2.5-5}	DRUM
Number of species	19	22	18
Number of samples	51	51	254
BS block size	1	6	20
DISP dQ^{max}	4,8,15,25	4,8,15,25	4,8,15,25
DISP active species	All	All	All
BS-DISP active species	Zn, SO ₄ ²⁻ , Cl ⁻ , NO ₃ ⁻ , Si, Na ⁺	Cl ⁻ , Si, Z, SO ₄ ²⁻ , Ni	Zn, Mg, Br, Ca, P, V
Q _{expected}	549	757	2940
Q _{true}	934.8	10933.4	13370.1
Q _{robust}	902.0	6388.0	11395.7
Q _{robust} /Q _{expected}	1.64	6.38	3.88
Species with Q/ Q _{expected} >10	None	OC, BC, Cl, NO ₃ ⁻ , Na ⁺ , Ca, Ni, Cu, Zn, Pb	K
DISP % dQ	0.2%	0.1%	8%
DISP swaps	0	0	0
Factors with BS mapping < 100%	1(95%); 2(90%); 5(96%); 6(91%);	1(95%); 3(98%); 4(94%); 5(83%);	3(91%); 4(99%); 6(95%)
BS_DISP % cases with swaps	4%	5%	1%

555

556 **4. Discussions and Conclusions**

The aerosol mixture present in the Arabian Gulf provides a particularly complex environment to understand. Mineral dust oxides dominate the PM_{10} aerosol mass in this region at $72\% \pm 11\%$ by mass, but the dust appears to be significantly processed by the urban and industrial environment, increasing the hygroscopicity of the dust and its ability to serve as cloud condensation nuclei (a topic for a future paper). We saw strong evidence of scavenging of gaseous SO_2 and NO_x by the dust particles, with a strong presence of sulfate in the CM and an almost exclusive preference of nitrate for CM dust aerosols. The presence of dust also complicates the $PM_{2.5}$ aerosol composition due to the dominance of the dust mass in the $PM_{2.5}$ aerosol loadings.

The impact of dust on the anthropogenic aerosol mass is complicated. The scavenging of these reactive gases coupled with suppression of photochemical processes due to light scattering and photochemical oxidant uptake supports the hypothesis that the presence of dust would inhibit new particle formation, thus decreasing the $PM_{2.5}$ aerosol number concentration. But new studies indicate that dust may enhance new particle formation by serving as a surface for heterogeneous photochemical processes, thereby increasing $PM_{2.5}$ aerosol number concentrations (Nie et al., 2014). The presence of dust also impacts the behavior of the trace metals associated with anthropogenic emissions. Vanadium, copper, zinc and lead all have a clear bimodal mass distribution, indicating that their presence is primarily due to anthropogenic emissions, most likely vehicle emissions and petrochemical processing emissions, but that they can exist in the fine mode or condense onto dust particles.

Sea salt mass was found in both the $PM_{2.5}$ mode and the CM, compromising only a small percentage of the observed aerosol loading, averaging 3%, or $1.2 \mu g/m^3$ of the $PM_{2.5}$ mode aerosol mass and 5.3%, or $5.4 \mu g/m^3$ of the CM aerosols. However, this is in agreement with marine environments globally. Jaeglé et al., (2011) found measured mean sea salt concentrations at 10 m above sea level in the open ocean ranging from $0.11 - 0.83 \mu g/m^3$ on average in the fine mode, and $5.1 - 8.0 \mu g/m^3$ in the CM. The slightly higher value observed in the UAE² fine mode is easily explained by the higher cut point used by the UAE² filters ($2.5 \mu m$ compared to $1 \mu m$ used in the studies cited by Jaeglé et al., (2011)). Thus, due to the locally high aerosol concentration, sea salt plays a minor role in the regional aerosol chemistry.

Heavy metals were found in the aerosol burden in significant levels, as shown in Table 3. The predominance of Mn, Ti, Cr, and Ni in the CM, along with the monomodal size distribution and

covariance with Fe is consistent with the theory that these metals are found naturally in dust minerals of the region. However, V, Cu, Zn and Pb are also found in the CM, although to a lesser degree. Their presence in the fine mode indicates they have anthropogenic sources, products of oil refineries (e.g. V) or brake wear from mobile sources (e.g. Cu) for example, but Table 3 also indicates that they are associated with dust in the CM, forming what is referred to as road dust. There are some significant regional differences in mean concentrations compared to a recent study of Makkah, Saudi Arabia where specifically Ni and Cr were found to be concentrated more in the PM_{2.5} aerosols (Habeebullah, 2014b). All trace metal levels were found to be below WHO suggested guidelines (WHO, 2000) established to prevent neurological and carcinogenic effects in human populations.

Table 3. Mean and standard deviation trace metal concentrations (in ng/m³) observed during UAE² for the coarse mode (CM), PM_{2.5} mode, and the WHO suggested limit.

Mean Heavy metal concentrations			
Metal	CM	PM _{2.5}	WHO guideline suggested limit
Mn	53±28	12±8	150 (annual)
Ti	196±103	35±26	N/A
Cr	15±9	2±2	N/A
Ni	19±13	6±3	N/A
V	10±5	6±5	1000 (24-hours)
Cu	1±2	10±9	N/A
Zn	11±9	26±11	N/A
Pb	3±2	10±6	500 (annual)

The high concentrations of both the PM₁₀ and PM_{2.5} mode aerosols measured by MAARCO near the urban Abu Dhabi collection site warrant significant attention. The WHO recommends

that annual PM_{10} concentration limits of $20 \mu g/m^3$ and annual $PM_{2.5}$ concentrations limits of $10 \mu g/m^3$, with 24 hour means not to exceed $50 \mu g/m^3$ and $25 \mu g/m^3$, respectively. The government of Dubai recommends 24 hour averages of PM_{10} remain below $150 \mu g/m^3$ (Air Quality Monitoring in Dubai). The EPA further classifies 24-hour mean particulate matter concentrations into five separate air quality indices (AQI): good, moderate, unhealthy for sensitive groups, unhealthy and very unhealthy. However, the high annual aerosol concentrations in the Arabian Gulf region frequently exceed all recommendations.

The 24-hour averages of the $PM_{2.5}$ and PM_{10} concentrations observed during the intensive UAE² campaign (Figure 12) reinforces the potential hazards of local aerosol concentrations to human health in the region. The top graph shows $PM_{2.5}$ and the bottom graph represents PM_{10} concentrations, both color-coded as defined by the EPA's AQI. Five days reach unhealthy levels for $PM_{2.5}$ concentrations and eight days reach unhealthy levels for PM_{10} concentrations. While the annual PM mean concentrations are not available from this campaign, the two month mean of $PM_{2.5} = 36.2 \pm 16.5 \mu g/m^3$ and $PM_{10} = 153.6 \pm 76.9 \mu g/m^3$ indicate annual mean concentrations are likely above the safe level recommended by the EPA and the WHO.

The fine mode aerosols, while difficult to resolve due to the high aerosol diameter cut point of the filters, were present in high concentrations at MAARCO near Abu Dhabi and warrant significant attention in this polluted atmosphere. The use of a PM_1 sampler in a future campaign would provide the region with more information regarding the fine mode aerosols. Even with mineral dust oxides subtracted from the $PM_{2.5}$ mass, anthropogenic emissions would have reached unhealthy levels on one day and unhealthy for sensitive groups on four days, over the 52 days sampled. This suggests that while, up until now the dust aerosol loadings of the region have primarily been the area of focus of most regional field campaigns, anthropogenic aerosols warrant further attention, both with regards to global aerosol burden and forcing and with regards to regional health concerns.

5. Acknowledgements

The UAE² mission required the help and assistance of a number of individuals from all of the participating organizations as listed in the author list. Particular thanks are to the staff of the Department of Water Resource Studies (DAS; now the UAE National Centre of Meteorology

and Seismology) and the South African air and ground maintenance crews and the Advanced Light Source at Lawrence Berkley National Laboratory. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. This research was supported by the Office of Naval Research Code 32, the Naval Research Laboratory Base Program and the NASA Radiation Sciences Program.

6. References

- Air Environment Regulations: Environmental Regulations No.:EN/001 (<http://www.ehss.ae/forms/07.28regulationno.en-001airenvironment1steditionjuly2010.pdf>). Last accessed April 2015.
- Alam, K., Trautmann, T., Blaschke, T., Subhan, F., 2014. Changes in aerosol optical properties due to dust storms in the Middle east and Southwest Asia. *Rem. Sens. of Environ.*, 143, 216-227. <http://dx.doi.org/10.1016/j.rse.2013.12.021>.
- Ali-Mohamed, A.Y., Ali, H.A., 2001. Estimation of atmospheric inorganic water-soluble particulate matter in Muharraq Island, Bahrain, (Arabian Gulf), by ion chromatography. *Atmos. Environ.*, 35 (4), 761-768.
- Atwood, S.A., Reid, J.A., Kreidenweis, S.M., Cliff, S.S., Zhao, Y., Lin, N.-H., Tsay, S.-C., Chu, Y.-C., Westphal D.L., 2013. Size resolved measurements of springtime aerosol particles over the northern South China Sea. *Atmos. Environ.* 78, 134-143.
- Bahreini, R., Middlebrook, A.M., Brock, C. A., de Gouw, J.A., McKeen, S.A., Williams, L.R., Daumit, K.E., Lambe, A.T., Massoli, P., Canagaratna, M.R., Ahmadov, R.A., Carrasquillo, J., Cross, E.S., Ervens, B., Holloway, J.S., Hunter, J.F., Onasch, T.B., Pollack, I.B., Roberts, J.M., Ryerson, T.B., Warneke, C., Davidovits, P. Worsnop, D.R., Kroll J.H., 2012. Mass spectral analysis of organic aerosol formed downwind of the Deepwater Horizon oil spill: Field studies and laboratory confirmations. *Environ. Sci. Technol.*, 46 (15), 8025-8034.
- Brown, S. G., Eberly, S., Paatero, P., Norris, G. A., 2015. Methods for estimating uncertainty in PMF solutions: Examples with ambient air and water quality data and guidance on reporting PMF results. *Sci. Tot. Environ.*, 518, 626-635.

662 Cahill, T. A., Wilkinson, K., Schnell, R., 1992. Composition analyses of size-resolved aerosol
663 samples taken from aircraft downwind of Kuwait, spring 1991. *J. Geophys. Res. Atmos.*, 97
664 (D13), 14513-14520.

665 Chow, J. C., Watson, J. G., Lowenthal, D. H., Magliano, K. L., 2005. Loss of PM_{2.5} nitrate from
666 filter samples in central California. *Journal of the Air & Waste Management Association*, 55(8),
667 1158-1168.

668 Denier van der Gon, H.A.C., Hulskotte, J.H.J., Visschedijk, A.J.H., Schaap, M., 2007. A revised
669 estimate of copper emissions from road transport in UNECE-Europe and its impact on predicted
670 copper concentrations. *Atmos. Environ.* 41 (38), 8697-8710.

671 Draxler, R.R., Hess, G.D., 1998. An overview of the HYSPLIT_4 modelling system for
672 trajectories. *Aus. Met. Mag.* 47, (4), 295-308.

673 DRI EAF capabilities: <http://www.dri.edu/eaf-capabilities?showall=1>. Last accessed July 2015.

674 Eck, T.F., Holben, B.N., Reid, J.S., Sinyuk, A., Dubovik, O., Smirnov, A., Giles, D., O'Neill,
675 N.T., Tsay, S.-C., Ji, Q., Al Mandoos, A., Ramzan Khan, M., Reid, E.A., Schafer, J.S., Sorokine,
676 M., Newcomb, W., Slutsker, I., 2008. Spatial and temporal variability of column-integrated
677 aerosol optical properties in the southern Arabian Gulf and United Arab Emirates in summer, *J.*
678 *Geophys. Res.*, 113 (D01204). <http://dx.doi.org/10.1029/2007JD008944>.

679 Engelbrecht, J.P., McDonald, E.V., Gillies, J.A., Jayanty, R.K.M., Casuccio, G., Gertler A.W.,
680 2009a. Characterizing mineral dusts and other aerosols from the Middle East-Part 1: Ambient
681 sampling. *Inhal. Toxic.* 21 (4), 297-326.

682 Engelbrecht, J.P., McDonald, E.V., Gillies, J.A., Jayanty, R.K.M., Casuccio, G., Gertler, A.W.
683 2009b. Characterizing mineral dusts and other aerosols from the Middle East-Part 2: Grab
684 samples and re-suspensions, *Inhal. Toxic.* 21 (4), 327-336.

685 Fairlie, T.D., D.J. Jacob, J.E. Dibb, B. Alexander, M.A. Avery, A.V. Donkelaar, Zhang, L.,
686 2010. Impact of mineral dust on nitrate, sulfate, and ozone in transpacific Asian pollution
687 plumes, *Atmospheric Chemistry and Physics*, 10 (8), 3999-4012.

688 Gao, Y., Anderson, J.R., 2001. Characteristics of Chinese aerosols determined by individual
689 particle analysis, *J. Geophys. Res.*, 106, 18,037–18,045.

690 Ghazi, J. M., Moazzen, M., Rahgoshay, M., Moghadam, H. S., 2010. Mineral chemical
691 composition and geodynamic significance of peridotites from Nain ophiolite, central Iran,
692 Journal of Geodynamics, 49 (5), 261-270, <http://dx.doi.org/10.1016/j.jog.2010.01.004>.

693 Habeebullah, T.M., 2014a. Modeling particulate matter (PM10) in Makkah, Saudi Arabia,-A
694 view point of health impact, J. Clean Energy Tech., 2, 196-200.

695 Habeebullah, T.M., 2014b. An analysis of Heavy Metals of atmospheric aerosols in
696 Makkah. Journal of Natural Sciences and Mathematics, 7 (1), 21-35.

697 Hansell, R.A., Liou, K.N., Ou, S.C., Tsay, S.-C., Ji, Q., Reid J.S., 2008. Remote sensing of
698 mineral dust aerosol using AERI during the UAE²: A modeling and sensitivity study. J.
699 Geophys. Res.-Atmos., 113 (D18). <http://dx.doi.org/10.1029/2008JD010246>.

700 Hering, S., Cass, G., 1999. The magnitude of bias in the measurement of PM_{2.5} arising from
701 volatilization of particulate nitrate from Teflon filters. J. Air & Waste Management Association,
702 49 (6), 725-733.

703 Herring, J.A., Ferek, R.J., Hobbs, P.V., 1996. Heterogeneous chemistry in the smoke plumes
704 from the 1991 Kuwait oil fires, J. Geophys. Res., 101, 14, 451-14,463.

705 Hobbs, P.V., Radke, L.F., 1992. Airborne studies of the smoke from the Kuwait oil
706 fires. Science, 256 (5059), 987-991.

707 Hsu, N.C., Gautam, R., Sayer, A.M., Bettenhausen, C., Li, C., Jeong, M.J., Tsay, S.-C.,
708 Holben, B.N., 2012. Global and regional trends of aerosol optical depth over land and ocean
709 using SeaWiFS measurements from 1997 to 2010, Atmos. Chem. Phys., 12, 8037-8053.
710 <http://dx.doi.org/doi:10.5194/acp-12-8037-2012>.

711 Jaeglé, L., Quinn, P.K., Bates, T.S., Alexander, B., Lin J.-T., 2011. Global distribution of sea salt
712 aerosols: new constraints from in situ and remote sensing observations, Atmos. Chem. Phys., 11,
713 3137-3157.

714 Jordan, C.E., Dibb, J.E., Anderson, B.E., Fuelberg, H.E., 2003. Uptake of nitrate and sulfate on
715 dust aerosols during TRACE-P. J. Geophys. Res., 108(D21),
716 <http://dx.doi.org/10.1029/2002JD003101>.

717 Kahn, R. A., Nelson, D. L., Garay, M. J., Levy, R. C., Bull, M. A., Diner, D. J., Martonchik, J.
718 V., Paradise, S. R., Hansen, E. G., Remer, L. A. 2009. MISR aerosol product attributes and
719 statistical comparisons with MODIS. *Geoscience and Remote Sensing, IEEE Transactions on*,
720 47(12), 4095-4114.

721 Kampa, M, Castandas, E., 2008. Human health effects of air pollution. *Environ. Poll.*, 151 (2),
722 pp. 362-367.

723 Kaku, K.C., Reid, J.S., O'Neill, N.T., Quinn, P.K., Coffman, D.J., Eck T.F., 2014. Verification
724 and application of the extended Spectral Deconvolution Algorithm (SDA+) methodology to
725 estimate aerosol fine and coarse mode extinction coefficients in the marine boundary layer.
726 *Atmos. Meas. Tech.*, 7. <http://dx.doi.org/10.5194/amt-7-3399-2014>.

727 Kim, D., Chin, M., Yu, H., Eck, T.F., Sinyuk, A., Smirnov, A., Holben, B.N., 2011. Dust optical
728 properties over North Africa and Arabian Peninsula derived from the AERONET dataset, *Atmos.*
729 *Chem. Phys.*, 11, 10733-10741. <http://dx.doi.org/10.5194/acp-11-10733-2011>.

730 Kim, E., Hopke, P.K., Edgerton, E.S., 2003. Source identification of Atlanta aerosol by positive
731 matrix factorization. *J. Air Waste Manag. Assoc.*, 53 (6), 731-739.

732 Khodeir, M., Shamy, M., Alghamdi, M., Zhong, M., Sun, H., Costa, M., Chen, L-C.,
733 Maciejczyk, P., 2012. Source apportionment and elemental composition of PM_{2.5} and PM₁₀ in
734 Jeddah City, Saudi Arabia. *Atmos. Poll. Res.*, 3 (3), 331.

735 Kunte, P. D., Aswini, M. A., 2015. Detection and monitoring of super sandstorm and its impacts
736 on Arabian Sea—Remote sensing approach. *Atmos. Res.*, 160, 109-125.

737

738 Modaihsh, A. S. 1996. Characteristics and composition of the falling dust sediments on Riyadh
739 city, Saudi Arabia. *J. Arid Environ.* 36 (2), 211-223.

740 Nie, W., Ding, A., Wang, T., Kerminen, V. M., George, C., Xue, L., Pataja, T., Qi, X., Gao, X.,
741 Wang, X., Yang, X., Fu, C., Kulmala, M., 2014. Polluted dust promotes new particle formation
742 and growth. *Scientific Reports*, 4. <http://dx.doi.org/10.1038/srep06634>.

743 Norris, G., Duvall, R., Brown, S., Bai, S., 2014. EPA Positive Matrix Factorization (PMF) 5.0:
744 Fundamentals and User Guide Available at:
745 http://www.epa.gov/heads/documents/PMF_5.0_User_Guide.pdf (last accessed Jan. 2015).

746 Levy, R.C., Mattoo, S., Munchak, L.A., Remer, L.A., Sayer, A.M., Patadia, F., Hsu, N.C., 2013.
747 The Collection 6 MODIS aerosol products over land and ocean, *Atmos. Meas. Tech.*, 6, 2989-
748 3034. <http://dx.doi.org/10.5194/amt-6-2989-2013>.

749 O'Neill, N.T., Eck, T.F., Reid, J.S., Smirnov, A., Pancrati, O., 2008. Coarse mode optical
750 information retrievable using ultraviolet to short-wave infrared Sun photometry: Application to
751 United Arab Emirates Unified Aerosol Experiment data. *J. Geophys. Res.-Atmos.*, 113, D05212.
752 <http://dx.doi.org/10.1029/2007JD009052>.

753 Paatero, P., Tapper, U., 1994. Positive matrix factorization: a nonnegative factor model with
754 optimal utilization of error estimates of data values, *Environmetrics*, 5, 111–126.

755 Paatero, P., Eberly, S., Brown, S. G., Norris, G. A., 2014. Methods for estimating uncertainty in
756 factor analytic solutions. *Atmos.Meas.Tech.*, 7(3), 781-797.

757 Pacyna, J. M., Pacyna, E. G., 2001. An assessment of global and regional emissions of trace
758 metals to the atmosphere from anthropogenic sources worldwide. *Environ. Rev.* 9 (4), 269-298.

759 Pandolfi, M., Gonzalez-Castanedo, Y., Alastuey, A., Jesus, D., Mantilla, E., de la Campa, A.S.,
760 Querol, X., Pey, J., Aato, F., Moreno, T., 2011. Source apportionment of PM10 and PM2. 5 at
761 multiple sites in the strait of Gibraltar by PMF: impact of shipping emissions. *Environ. Sci. Poll.*
762 *Res.* 18 (2), 260-269.

763 Peyridieu, S., Chédin, A., Capelle, V., Tsamalis, C., Pierangelo, C., Armante, R., Crevoisier, C.,
764 Crépeau, L., Siméon, M., Ducos, F., Scott, N.A., 2013. Characterisation of dust aerosols in the
765 infrared from IASI and comparison with PARASOL, MODIS, MISR, CALIOP, and AERONET
766 observations. *Atmos. Chem. Phys.*, 13, 6065-6082. <http://dx.doi.org/10.5194/acp-13-6065-2013>.

767 Prospero, J.M., Ginoux, P., Torres, O., Nicholson, S.E., Gill, T.E., 2002. Environmental
768 characterization of global sources of atmospheric soil dust identified with the Nimbus 7 Total
769 Ozone Mapping Spectrometer (TOMS) absorbing aerosol product. *Rev. Geophys.*, 40 (1).
770 <http://dx.doi.org/10.1029/2000RG000095>.

771 Rashed, M.N., 2008. Total and extractable heavy metals in indoor, outdoor and street dust from
 772 Aswan City, Egypt. *Clean*, 36 (10-1), 850-857.

773 Reid, J. S., H. H. Jonsson, H. B. Maring, A. A. Smirnov, D. L. Savoie, S. S. Cliff, E. A. Reid, M.
 774 M. Meier, O. Dubovik, Tsay, S.-C., 2003. Comparison of size and morphological measurements
 775 of coarse mode dust particles from Africa, *J. Geophys. Res.*, 108(D19), 8593,
 776 doi:[10.1029/2002JD002485](https://doi.org/10.1029/2002JD002485).

777 Reid, J.S., Reid, E.A., Walker, A., Piketh, S., Cliff, S., Mandoos, A.A., Tsay, S.C., Eck T.F.,
 778 2008a. Dynamics of southwest Asian dust particle size characteristics with implications for
 779 global dust research. *J. Geophys. Res.-Atmos.* 113 (D14).
 780 <http://dx.doi.org/10.1029/2007JD009752>.

781 Reid, J.S., Piketh, S.J., Walker, A.L., Burger, R.P., Ross, K.E., Westphal, D.L., Bruinjes, R.T.,
 782 Holben, B.N., Hsu, C., Jensen, T.L., Kahn, R.A., Kuciauskas, A.P., Mondoos, A.A., Mangoosh,
 783 A.A., Miller, S.D., Porter, J.N., Reid, E.A., Tsay S.-C., 2008b. An overview of UAE² flight
 784 operations: Observations of summertime atmospheric thermodynamic and aerosol profiles of the
 785 southern Arabian Gulf. *J. Geophys. Res.-Atmos.* 113 (D14213).
 786 <http://dx.doi.org/10.1029/2007JD009435>.

787 Rushdi, A.I., Al-Mutlaq, K.F., Al-Otaibi, M., El-Mubarak, A.H., Simoneit, B.R., 2013. Air
 788 quality and elemental enrichment factors of aerosol particulate matter in Riyadh City, Saudi
 789 Arabia. *Arabian Journal of Geosciences*, 6 (2), 585-599.

790 Shaltout, A.A., Boman, J., Al-Malawi, D.A.R., Shehadeh, Z.F., 2013. Elemental composition of
 791 PM_{2.5} particles sampled in industrial and residential areas of Taif, Saudi Arabia. *Aerosol and Air*
 792 *Quality Research*, 13 (4), 1356-1364.

793 Smirnov, A., Holben, B.N., Dubovik, O., O'Neill, N.T., Eck, T.F., Westphal, D.L., Goroch, A.K.,
 794 Pietras, C., Slutsker, I., 2002. Atmospheric aerosol optical properties in the Persian Gulf. *Journal*
 795 *of the atmospheric sciences* 59 (3), 620-634.

796 Song, C.H., Carmichael, G.R., 2001. A three-dimensional modeling investigation of the
 797 evolution processes of dust and sea-salt particles in East Asia. *J. Geophys. Res.-Atmos.*
 798 106. <http://dx.doi.org/10.1029/2000JD900352>.

799 Taylor, S.R., 1964. Abundance of chemical elements in the continental crust: a new table.
800 *Geochim. et Cosmo. Acta.* 28, 1273–1285.

801 World Health Organization (WHO), 2000, (World Health Organization). Air Quality Guidelines
802 for Europe. WHO Regional Publications, Series No. 91, European Office, Copenhagen.

803 Wu, P.-M., Okada, K., 1994. Nature of coarse nitrate particles in the atmosphere—A single
804 particle approach. *Atmos. Environ.* 28, 2053–2060.

805 Zhang, J., and Christopher, S. A., 2003. Longwave radiative forcing of Saharan dust aerosols
806 estimated from MODIS, MISR, and CERES observations on Terra. *Geophys. Res. Lett.* 30,
807 (2188), doi:[10.1029/2003GL018479](https://doi.org/10.1029/2003GL018479).

808 Zhang, J., Reid, J.S., 2010. A decadal regional and global trend analysis of the aerosol optical
809 depth using a data-assimilation grade over-water MODIS and Level 2 MISR aerosol
810 products. *Atmos. Chem. Phys.* 10 (22), 10949-10963.

811

813

814 **Fig. 1.** The Multi-angle Imaging SpectroRadiometer (MISR) 0.558 μm Aerosol Optical Depth

815 (AOD) from 2004-2006 over the UAE² study period (Aug.-Sept, 2004). The star shows

816 approximately where the MAARCO station was located. Details on the retrieval process can be

817 found in Zhang and Christopher (2003) and Kahn et al. (2009).

Fig. 2. Chemical analysis results of (a) the $PM_{2.5}$ aerosols and (b) the coarse mode (CM: PM_{10} - $PM_{2.5}$) aerosol chemical speciation. The results are shown as a percentage of the total mass fraction as calculated using the gravimetric filter mass. All of the dust oxides (K_2O , CaO , Fe_2O_3 , SiO_2 , TiO_2 , MgO , Al_2O_3) are combined into one bar. Trace metals and metalloids (Cu, Ni, Zn, Mn, V, Pb, Cr) contribute less than 1% to the total mass. Total carbon (TC: organic carbon + black carbon) was only measured for the $PM_{2.5}$ aerosols. Graph (c) shows the CM and $PM_{2.5}$ gravimetric mass ($\mu g/m^3$) and the bottom graph (d) shows the fine mode (FM) fraction (FM mass divided by the PM_{10} mass) as well as the FM mass ($\mu g/m^3$; $PM_{2.5}$ mass with the dust oxides subtracted).

830

831 **Fig. 3.** A breakdown of major coarse mode (CM) dust metals and metalloids (top) and natural

832 and anthropogenic CM trace metals (bottom) by source determined by Reid et al. (2008a).

833 Source regions include United Arab Emirates (UAE), Iraq, and Interior Arabian Peninsula (AP).

834 Titanium dioxide composed less than 1% of the major dust metals in all groups.

Fig. 4. A time series of trace metals and iron during the UAE² campaign. The squared Pearson correlation coefficient value in the legend indicates the correlation between the trace metal and iron, a tracer for dust.

Fig. 5. DRUM time series analysis of stage 1 (5 – 10 μm diameter) silicon and calcium

Fig. 6. Average mass concentration distributions from DRUM data results for (a) dust metals, converted into their common oxide forms, (b) trace metals of natural origin, and (c) trace metals of anthropogenic origin. The tendency of anthropogenic pollutants to condense onto dust is observed in the third graph.

Fig. 7. Normalized number, surface area and volume distributions of the daily-averaged fine mode aerosol distribution from PCASP fly-by observations. Table 1 indicates the median aerosol diameter and geometric standard deviation of the fitted lognormal distribution.

Fig. 8. Positive matrix factorization (PMF) results showing (a) Coarse mode (CM: $\text{PM}_{10} - \text{PM}_{2.5}$) aerosol chemical speciation fingerprints and (b) a pie chart showing factor contributions to the CM mass loading variation.

Fig. 9. Normalized coarse mode factor contributions as a function of filter collection time for the Continental Dust and Marine Dust factors.

Fig. 10. PMF results showing (a) $\text{PM}_{2.5}$ aerosol chemical speciation fingerprints and (b) a pie chart showing factor contributions to the $\text{PM}_{2.5}$ mass loading variation.

867

868

869 **Fig. 11.** PMF results showing the sub-0.75 µm DRUM aerosol chemical speciation fingerprints.

870

871

872 **Fig. 12.** Histograms of the PM_{2.5} aerosol mass concentration (top) and the PM₁₀ aerosol
 873 concentration (bottom) observed during the UAE² campaign. The colors correspond to the Air
 874 Quality Index (AQI) as defined by the EPA. The classifications for PM_{2.5} (in µg/m³) are Healthy:
 875 0-12, Moderate: 13-35, Unhealthy for Sensitive Groups: 36-55, Unhealthy: 56-150, and Very

876 Unhealthy: >150. The classifications for PM₁₀ (in µg/m³) are Healthy: 0-54, Moderate: 55-154,
877 Unhealthy for Sensitive Groups: 155-254, Unhealthy: 255-354, and Very Unhealthy: >355.