TO: Texas Air Research Center

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SUBJECT: Annual Progress Report

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PROJECT TITLE: Detailed elemental characterization of Saharan dust to quantify its contributions to $PM_{2.5}$ and PM_{10} during episodic intrusions in Houston

PROJECT PERIOD: September 1, 2013 – July 15, 2015

DATE: September 1, 2014

Project Description. The arid regions of North Africa are estimated to emit about 800 Tgy^{-1} of soil dust each year, 70% of the global total. Summertime trade winds carry a portion of this North African particulate matter (PM) across the Atlantic Ocean to the Caribbean and the southern continental United States increasing ambient PM_{10} and $PM_{2.5}$ concentrations in Texas typically a few times mostly during June, July, and August. The ability to quantitatively distinguish between locally-emitted versus long-range transported PM is vitally important because it enables us to exclude exceptional events that impact local air quality but which are beyond regulatory control especially when responding to more stringent PM standards.

Objectives. The primary objective of this research is to show that by accurately measuring a suite of major and trace elements in different hypothesized mineral dust sources and in ambient PM in receptor locations, we can distinguish and quantitatively estimate contributions of long-range dust and locally entrained crustal material and local anthropogenic sources. For accurate source apportionment, we developed a representative source profile of aerosols originating in North Africa by collecting samples in a remote location in the Caribbean (Barbados) during dust episodes before they entered the continental United States.

Methodology. Daily $PM_{2.5}$ (n=28) and PM10 (n=27) samples were collected on 47-mm diameter Teflon filters between July 20 and August 2, 2008 at Clinton Drive (Texas Commission on Environmental Quality (TCEQ) CAMS 403; latitude +29.734, longitude -95.258) and Channelview (TCEQ CAMS 15; +29.803, -95.126) using Rupprecht & Patachnick 2025 samplers. African dust impacting Houston had followed trajectories passing over Barbados where aerosol samples were collected at a field station located on a 30m bluff on the east coast of Barbados at Ragged Point (+13.165, -59.432).

Houston PM samples on Teflon filters were acid-digested (HF, HNO_3 and H_3BO_3) in two steps, each for 26min at 200°C and 200psig in Teflon-lined vessels (HP-500 Plus) using a microwave (MARS 5, CEM Corp.). Barbados Saharan dust samples needed an additional pre-digestion step with less aggressive conditions (10-minute ramp to 150°C at 300psig for 26min) using HF and HNO_3 to accommodate violent reactions between

concentrated acids and the cellulosic substrate of Whatman filters. Fifteen main group elements (Na, Mg, Al, Si, K, Ca, Ga, As, Se, Rb, Sr, Sn, Sb, Ba, Pb), 14 transition metals (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Mo, Cd, W) and 14 lanthanoids (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) were quantified by dynamic reaction cell – quadrupole – ICP-MS (ELAN DRCII, PerkinElmer).

Results and discussion. Satellite imagery and back-trajectories show that African dust moved over the region on 25, 26, and 27 July. Over this period the average ambient $PM_{2.5}$ levels doubled: Clinton Drive 14.7±4.0 during routine days before and after the dust intrusion and 28.2±4.3μgm^{-3} during the event; Channelview 11.6±3.0 during routine days and 27.5±3.1μgm^{-3} during the episode. Average PM_{10} concentrations during the three Saharan intrusion days also increased: doubling in Clinton Drive from 49.5±26.4μgm^{-3} to 101.3±27.7μgm^{-3}; 50% increase in Channelview from 49.5±26.4μgm^{-3} to 76.1±8.9μgm^{-3}.

Enrichment factors (EF) of individual elements (X) were calculated referencing Ti in the upper continental crust (UCC) ($EF_X = [X/Ti]_{Sample}/[X/Ti]_{UCC}$). The crustal origins of all elements in Saharan aerosols collected in Barbados were inferred since their EFs were close to 1 with notable exceptions of Se (EF 74) and Cd (EF 33). In Houston, routine enrichment factors of Mg, Si, K, Sc, Ti, Mn, Rb, Sr, Zr, Al, Fe, and Co were close to unity suggesting their crustal origin. Ca, Ba, Cr, Ni, and La were slightly elevated (EF 3.3-9.5) whereas Cu, Ga, As, Se, Mo, Cd, Sn, Sb, W, Pb, V, and Zn were significantly enriched (EF: 16-1270) demonstrating their anthropogenic nature. North African dust intrusion into the Houston area reduced EFs of several industrially emitted metals by 53-88% relative to those measured routinely. Dilution of anthropogenic metals in PM by incursion of huge quantities of crustal elements associated with Saharan dust is shown in Figure 1.

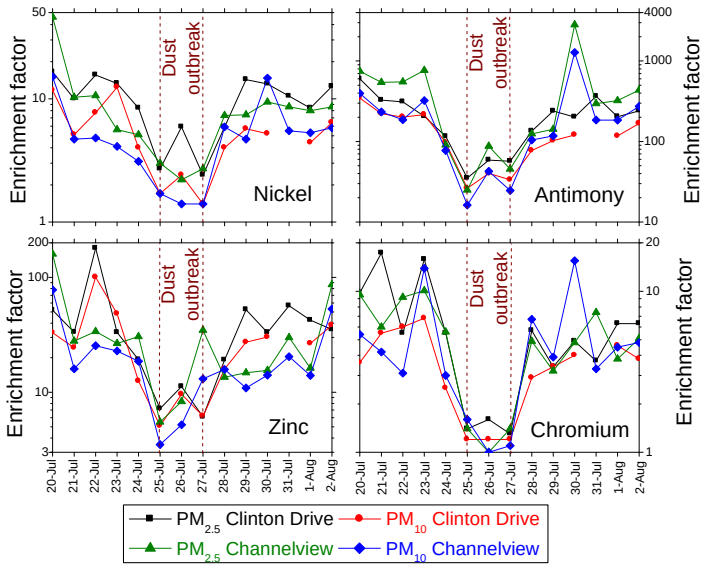

Figure 1. Enrichment factors with respect to crustal Ti for selected anthropogenic elements at Clinton Drive and Channelview showing their dilution during Saharan dust intrusion.

Simultaneous variations in La, Ce, and Sm concentrations were investigated using ternary plots (Figure 2) after normalization so that average UCC abundances appeared at the centroid. Such triangular diagrams are being increasingly employed to investigate concurrent changes in PM elemental concentrations. The light lanthanoid signature of Saharan dust from Barbados and local Houston soil predictably clustered near the UCC due to their crustal origins. Since petroleum refining catalysts are believed to be primarily responsible for lanthanoid enrichment in Houston's atmosphere, five FCC catalysts are also shown. Catalysts' anthropogenic nature and their strong La-enrichment are evidenced by their shift towards the La apex. Three component variations of La, Ce, and Sm in routine ambient PM followed a highly linear trend spanning the entire distance between the La apex and the UCC centroid signifying that light lanthanoids almost solely arose from the mixing of petroleum refining emissions and crustal aerosols. Even during the three dust outbreak days, ambient PM_{10} and $PM_{2.5}$ did not deviate from the linear relationship; composition simply moved closer towards the centroid symptomatic of greater contributions from Saharan dust. Long-range North African dust transport was confirmed by overlapping La/Ce ratios that were < 1 during the 3-day outbreak, close to the average value of 0.49±0.01 in Barbados samples. In contrast, La/Ce was > 1 during non-Saharan days validating the strong influence of FCC catalysts on routine PM. These further validate the importance of measuring lanthanoid composition of PM to distinguish various sources. This analysis provides incontrovertible and qualitative evidence for North African dust intrusion into the greater Houston area on July 25-27, 2008. Contributions of long-range transport to measured ambient PM mass concentrations were also quantified through chemical mass balancing.

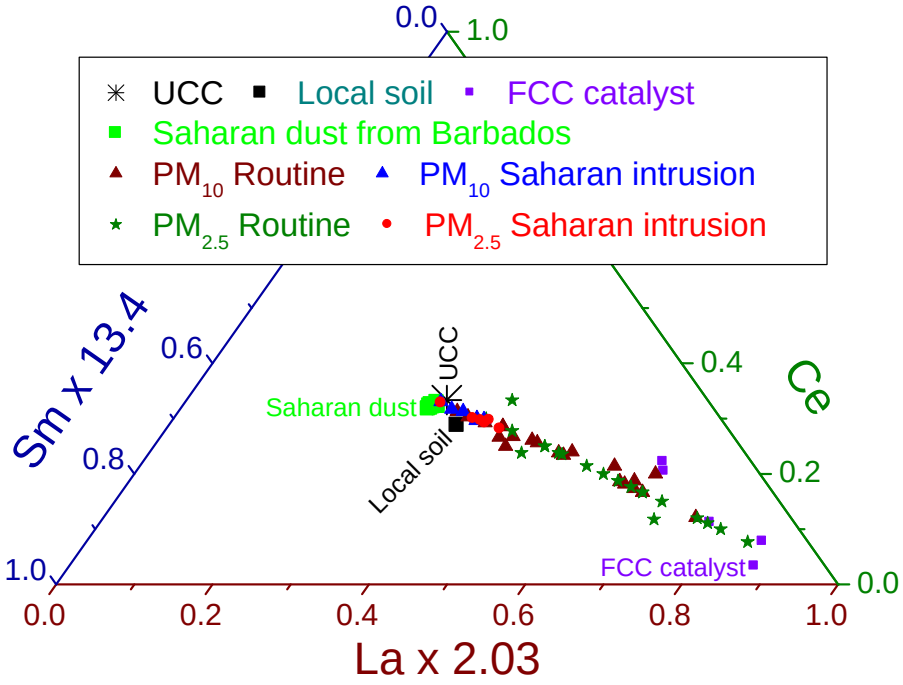

Figure 2. La, Ce, Sm ternary diagram showing ambient $PM_{2.5}$ and PM_{10} in the Houston Ship Channel area during routine days and the Saharan dust outbreak. North African dust from Barbados analyzed as a part of this study, petroleum refining catalysts, and local soil are also shown. Concentrations were normalized using upper continental crust values so that it appears at the centroid.

On average 50.4% and 72.4% of the measured $PM_{2.5}$ and PM_{10} masses were apportioned to primary emissions, consistent with significant contributions from secondary formation in summertime aerosols in southeast Texas, especially $PM_{2.5}$. Mineral dust sources i.e., cement manufacturing (Ca-rich), and soil and road dust dominated both PM_{10} and $PM_{2.5}$ during the 11-days immediately before and after the North African dust outbreak. Importantly, small but nevertheless significant amounts of Saharan dust were also present routinely at both sites. Source contribution estimates of the total mineral material during the non-Saharan period averaged 26.5% for $PM_{2.5}$ and 58.2% for PM_{10} at Clinton Drive and 25.2% for $PM_{2.5}$ and 42.1% for PM_{10} at Channelview. During this timeframe, a Ca-rich source (i.e. cement manufacturing) contributed significantly at Clinton Drive (19.5% to $PM_{2.5}$ and 25.9% to PM_{10}) but had minimal impact at Channelview (8.6% only to PM_{10}). Cement, drywall, and plaster manufacturing facilities are located at (29.731297; -95.261092) and (29.723725; -95.244773) near Clinton Drive reinforcing our source identification. Resuspension of local soil and road dusts also added significant mass averaging 22.4% of PM_{10} and 12.7% of $PM_{2.5}$. 10.1% of $PM_{2.5}$ mass and 8.7% of PM_{10} mass emanated from motor vehicles, with higher contributions at Clinton Drive similar to earlier results obtained using organic markers. Sea salt, vegetative burning, oil and coal combustion, and petroleum refineries also contributed small amounts to airborne PM.

Importantly, chemical mass balancing quantified the impact of North African dust, estimating Saharan aerosols to account for 54.4% of $PM_{2.5}$ mass and 63.0% of PM_{10} mass measured during July 25-27 (9.6-20.5 μgm^{-3} of $PM_{2.5}$ and 45.8-56.3 μgm^{-3} of PM_{10}). Additionally, during the 3-day dust outbreak, total African mineral material contributions were approximately 64.0% of $PM_{2.5}$ and 85.4% of PM_{10} far exceeding mineral dust contributions from other local anthropogenic sources as discussed in the next section. Immediately following this period, the trend of measured ambient PM at the two sites diverges: $PM_{2.5}$ and PM_{10} levels at Channelview and $PM_{2.5}$ levels at Clinton Drive decrease to levels roughly equivalent to those measured before the episode; in contrast PM_{10} levels at Clinton Drive remain elevated. Without further analytical detail and analysis, the causes of this behavior are not immediately clear and warrant further investigation.

Implications. Various lines of evidence demonstrated that dust-laden African air masses reached the southern and eastern United States in late July 2008 and had a major impact on air quality even overwhelming local emissions in Houston. To our knowledge, this is the first work to quantify the impact of African dust on airborne ambient PM in the USA and to place it in the context of other suspected local and regional sources. This was accomplished using detailed elemental measurements of PM samples, including African dust, combined with source attribution using CMB. It is emphasized that the PM monitoring and X-ray fluorescence measurements routinely made in air quality studies may not be sufficient to quantitatively assess desert dust impacts in urban environments because of their limited sensitivity and the smaller number of marker elements that are measured, coupled with the lower frequency of elemental speciation measurements that are typically undertaken. This limitation would be particularly important in less industrialized urban regions where soil and road dust resuspension might dominate PM levels thus making it difficult to discriminate between local and global dust sources. We are currently analyzing more dust episodes to better

establish the applicability of the presented approach and to ascertain the minimum number of elements that would suffice to identify such events.

Future Work. A second Saharan dust episode was identified in the Southern Texas region (including Houston) between June 28 and July 2, 2008 using satellite imagery and meteorology. We also have archived $PM_{2.5}$ and PM_{10} filters from this period and five days immediately preceding and succeeding this event. Similar laboratory analysis and receptor modeling will be performed using these samples to characterize and quantify a second Saharan dust episode.

List of Publications and Presentations.

1. Bozlaker, A., J.M. Prospero, M.P. Fraser, and S. Chellam (2013). Quantifying the Contribution of Long-Range Saharan Dust Transport on Particulate Matter Concentrations in Houston, Texas, using Detailed Elemental Analysis. *Environmental Science and Technology,* **47** 10179-10187.

2. Bozlaker, A., N.J. Spada, M.P. Fraser, and S. Chellam (2014). Elemental Characterization of $PM_{2.5}$ and PM_{10} Emitted from Light Duty Vehicles in the Washburn Tunnel of Houston, Texas: Release of Rhodium, Palladium, and Platinum. *Environmental Science and Technology,* **48** (1) 54-62.

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