

2018-01-01

# Cerium Levels In Fine And Coarse Airborne Particulate Matter In El Paso, Texas - A Geospatial And Temporal Investigation

Esenam Adzo Fumador

*University of Texas at El Paso*, [fumador\\_esenam@yahoo.com](mailto:fumador_esenam@yahoo.com)

Follow this and additional works at: [https://digitalcommons.utep.edu/open\\_etd](https://digitalcommons.utep.edu/open_etd)



Part of the [Environmental Sciences Commons](#)

---

## Recommended Citation

Fumador, Esenam Adzo, "Cerium Levels In Fine And Coarse Airborne Particulate Matter In El Paso, Texas - A Geospatial And Temporal Investigation" (2018). *Open Access Theses & Dissertations*. 70.  
[https://digitalcommons.utep.edu/open\\_etd/70](https://digitalcommons.utep.edu/open_etd/70)

This is brought to you for free and open access by DigitalCommons@UTEP. It has been accepted for inclusion in Open Access Theses & Dissertations by an authorized administrator of DigitalCommons@UTEP. For more information, please contact [lweber@utep.edu](mailto:lweber@utep.edu).

CERIUM LEVELS IN FINE AND COARSE AIRBORNE PARTICULATE MATTER IN EL  
PASO, TEXAS - A GEOSPATIAL AND TEMPORAL INVESTIGATION

FUMADOR ESENAM ADZO

Master's Program in Environmental Science

APPROVED:

---

Nicholas E. Pingitore, Ph.D., Chair

---

Maria Amaya, Ph.D.

---

Benjamin Brunner, Ph.D.

---

Charles Ambler, Ph.D.  
Dean of the Graduate School

## **DEDICATION**

I dedicate this work to my husband Felix Dziejzorm Ziwu (Ph.D.) whose encouragement and support made it possible for me to see this work to a successful completion

CERIUM LEVELS IN FINE AND COARSE AIRBORNE PARTICULATE MATTER IN EL  
PASO, TEXAS - A GEOSPATIAL AND TEMPORAL INVESTIGATION

by

FUMADOR ESENAM ADZO, BSC.

THESIS

Presented to the Faculty of the Graduate School of  
The University of Texas at El Paso  
in Partial Fulfillment  
of the Requirements  
for the Degree of

MASTER OF SCIENCE

Department of Geological Sciences  
THE UNIVERSITY OF TEXAS AT EL PASO

December 2018

## **ACKNOWLEDGEMENTS**

This work was supported by grant number S11 ES013339 from the National Institute of Environmental Health Sciences (NIEHS) and the National Institutes of Health (NIH). Its contents are solely the responsibility of the authors and do not necessarily represent the official views of the NIEHS or NIH. We appreciate the efforts and support of all the faculty and students who participated in this NIEHS ARCH Program. We also thank the TCEQ (Texas Commission on Environmental Quality) and EPWU (El Paso Water Utilities) for their cooperation in providing access to their property and electrical power for the siting of our air samplers.

## ABSTRACT

The Paso Del Norte airshed is shared by two cities, El Paso, Texas, U.S.A. and Ciudad Juarez, Chihuahua, Mexico. Population growth in both cities and their desert climate has created persistent challenges in meeting air quality standards for particulate matter, which is generated from both natural and anthropogenic sources.

In Europe, ceria or cerium dioxide ( $\text{CeO}_2$ ), introduced into diesel road fuel as nanoparticles, has significantly reduced emissions as well as increased vehicle mileage. Concerns have been raised there about the fate and potential health risks associated with the nanoceria (n-Ce) emitted in diesel exhaust. In the U.S.A on-road use of n-Ce additives is still under regulatory study. Because of possible future use, it is important to establish baseline data on current levels of airborne cerium. This is of special interest in El Paso should n-Ce be used in neighboring Cd. Juarez, Mex.

This study analyzed weekly total concentrations of cerium in El Paso air at 8 sampling stations during 2006 to 2009. A  $\text{PM}_{10}$  dichotomous sampler had been used to simultaneously collect  $\text{PM}_C$  (the  $\text{PM}_{10}$  to  $\text{PM}_{2.5}$  fraction) and  $\text{PM}_F$  or  $\text{PM}_{2.5}$ . An X-ray fluorescence instrument had been used to measure 61 elements, of which cerium was one, in the two PM fractions.

Results indicate higher levels of airborne cerium in  $\text{PM}_C$  (~2 ng/m<sup>3</sup> average for all sites for entire study period) than in  $\text{PM}_F$  (~1 ng/m<sup>3</sup>). Higher values for coarse and to a lesser degree for fine PM are associated with sites proximal to the core of the binational contiguous El Paso—Cd. Juarez metropolplex. This indicates a significant anthropogenic contribution to airborne cerium in El Paso; abrasion of vehicle parts that incorporate cerium-doped alloys, residual cerium catalysts from gasoline refining, open burning of solid waste, and other commercial and industrial debris

are the likely sources. No overall seasonal patterns were evident other than a possible decrease in PMC during the summers; this is consistent with a significant anthropogenic contribution.

## TABLE OF CONTENTS

ACKNOWLEDGEMENTS .....	iv
ABSTRACT .....	v
LIST OF TABLES .....	ix
LIST OF FIGURES .....	x
1.0 INTRODUCTION .....	1
1.1 Background .....	1
1.1.1 Particulate matter origin .....	1
1.1.2 Health impact of particulate matter .....	2
1.2 Cerium oxide nanoparticles (n-Ce) .....	3
1.2.1 Effect of n-Ce diesel additives on PM and other air pollutants .....	4
1.3 Introduction of cerium oxide fuel additive in the market .....	5
1.4 Rationale for this Research .....	6
1.5 Research Questions .....	7
1.6 Tasks .....	7
2.0 METHODOLOGY .....	9
2.1 Geography of El Paso, Texas .....	9
2.2 Sampling .....	9
2.3 Physical and chemical Analysis .....	11
2.3.1 Gravimetric determination of mass of PM .....	11
2.3.2 XRF determination of cerium in PM and calculation of ambient cerium levels .....	11
2.4 Data Analysis .....	12
3.0 RESULTS AND DISCUSSION .....	13
3.1 Data .....	13
3.2 General observations .....	16
3.2.1 Cerium levels and air quality regulations .....	16
3.2.2 Source of Cerium .....	18
3.3 Geographic trends and possible sources .....	19
3.4 Seasonal Trends .....	24
3.5 Public Health Implications .....	29



4.0 CONCLUSIONS.....	30
REFERENCES .....	31
VITA.....	38

## LIST OF TABLES

Table 2.1: Description of sampling sites .....	11
Table 3.1: Basic statistics for total coarse and fine PM for the study period .....	15
Table 3.2: Basic statistics for cerium levels at all sites in both $PM_{10}$ and $PM_{2.5}$ .....	15
Table 3.3: Cerium concentration of ambient $PM_{2.5}$ in U.S. cities.....	18

## LIST OF FIGURES

Figure 1.1: Predicted surface-level concentrations of cerium due to use of n-Ce diesel fuel. Modified from Erdakos et al. (2014). .....	5
Figure 2.1: Map of study area showing sampling sites within El Paso County.....	10
Figure 3.1: Average concentration of cerium at all sites for $PM_C$ and $PM_F$ . Error bars correspond to $\pm 2$ SEM. ....	14
Figure 3.2: Scatter plot showing the relationship between cerium in $PM_C$ and $PM_F$ in $ng/m^3$ .....	16
Figure 3.3: Average cerium concentration in $PM_C$ and $PM_F$ monitored for all the sites.....	21
Figure 3.4: Inverse Distance Weighted (IDW) interpolation of cerium concentration in $PM_C$ ....	22
Figure 3.5: Inverse Distance Weighted (IDW) interpolation of cerium concentration in $PM_F$ . ...	23
Figure 3.6: Seasonal average of ambient coarse cerium in spring, summer and fall recorded at all sites from 2006-2009. ....	25
Figure 3.7: Seasonal average of ambient fine cerium in spring, summer and fall recorded at all sites from 2006-2009 .....	26
Figure 3.8: Yearly average of cerium levels by season in $PM_{10}$ .....	27
Figure 3.9: Yearly average of cerium levels by season in $PM_{2.5}$ .....	28

## **1.0 INTRODUCTION**

Aerosols are an important component of the atmosphere influencing climate and human health. In light of this, reducing anthropogenic release of particles in air through innovative technology is important to improving health and protecting the environment. One important emission source of aerosols in the atmosphere is transportation combustion, and because of this the vehicular technology sector is constantly seeking and finding new ways of reducing emissions.

The Paso Del Norte airshed is shared by two cities, El Paso, Texas, U.S.A. and Ciudad Juarez, Chihuahua, Mexico. Increasing population and a desert climate is the reason for persistent challenges in meeting air quality standards for particulate matter resulting from natural and anthropogenic sources in both cities (Lauer et al., 2009). Many elements and compounds have been measured in PM collected from the Paso Del Norte airshed (e.g., Li et al., 2001; Arrieta et al., 2003; Paz et al., 2017), and new elements and compounds are being introduced because of anthropogenic activities. With the use of engineered cerium oxide ( $\text{CeO}_2$ ) fast gaining recognition for its ability to substantially reduce diesel emissions, the potential for introducing nano-ceria particles (n-Ce) into the airshed is possible.

The purpose of this study is to collect and analyze data on baseline cerium levels in the El Paso region of the Paso Del Norte airshed to ascertain its source in air, and its size-range based on  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  fractions.

## **1.1 BACKGROUND**

### **1.1.1 Particulate matter origin**

Particulate matter (PM) is a combination of various particles suspended in air, comprising solid and liquid particles from a wide range of natural and anthropogenic sources such as

industries, crustal matter, sea spray, fugitive dust from construction, resuspended roadside dust petroleum refining and vehicular emissions (Chan et al., 2011; U.S. EPA, 2004). Vehicular sources of particulate matter can be categorized into exhaust and non-exhaust forms. Brake, tire and clutch wear constitute the main source of non-exhaust emissions (Grigoratos and Martini, 2015), whereas exhaust emissions are from fuel combustion and contain a variety of elements and compounds (Stedman et al., 1996) of which cerium can be a part (Perry and Gee, 1995; World Health Organization, 2010; Erdakos et al., 2014). The complexity of particulate matter as a standard air pollutant can be attributed to its sources as well as the physical and chemical characteristics of its constituents (U.S. EPA, 2004). Originating from a wide range of natural and anthropogenic sources with varying sizes, PM emitted directly into the air from varying sources is termed primary particulate matter. Secondary particulate matter forms from the reaction of primary particles in the atmosphere (U.S. EPA, 2004). A major source of primary PM is fuel combustion from vehicles and industries. The introduction of new and improved vehicular technologies as emission control devices and fuel additives containing engineered nanomaterials is aimed at reducing PM emissions. However, this poses a new concern of introducing new and smaller size (nano-size) elements or compounds into the air.

### **1.1.2 Health impact of particulate matter**

Several epidemiological studies have provided evidence of how PM has adverse effects on human health, affecting the respiratory and cardiovascular systems both in children and adults (Dockery, 2001; U.S. EPA, 2004; Jansen et al., 2005; Hansen et al., 2006; World Health Organization, 2013; Olvera et al., 2012; Rohr and Wyzga, 2012). Jansen et al. (2005) showed that airway inflammation in adults with asthma is associated with PM. A pilot study by Dockery (2001) suggests the association between  $PM_{10}/PM_{2.5}$  concentrations and a decrease in heart rate

variability in healthy elderly adults. It also provided evidence that particulate air pollution was associated with acute cardiovascular events (Dockery, 2001). Experimental study by Olvera et al. (2012) found that children are prone to higher lung doses of ultrafine particles than adults, and this is further increased in people with asthmatic conditions and a decrease in particle size.

## **1.2 CERIUM OXIDE NANOPARTICLES (N-Ce)**

Cerium belongs to the series of lanthanide rare-earth elements and is the most abundant rare earth element in the earth's crust, making up 0.006 % or 60 ppm by mass (Gambogi, 2014), or some three times greater abundance than lead (Pb). It is a very reactive element (reacting with oxygen to form ceria, or cerium oxide,  $\text{CeO}_2$ ) and a strong oxidizing agent (Cassee et al., 2011). Compared to its surface at microscale, at nanoscale ceria has many defects on its surface, giving it the characteristics of being an efficient oxygen adsorbing compound. These surface defects make the compound a strong oxidizing catalyst. The adsorption of oxygen to its surface makes it available to oxidize soot at temperatures far lower than soot's conventional oxidizing temperature. This mechanism is what makes n-Ce effective in reducing particle emission in diesel powered vehicles (Majestic et al., 2010). Current advances in nanotechnology have seen the application of engineered n-Ce in the fabrication of such products as catalysts, fuel cells, coatings, electronics, biomedical equipment and fuel additives (Majestic et al., 2010; Cassee et al., 2011; Dahle and Arai, 2015). According to Cassee et al. (2011) there is an ongoing exposure of new diesel emissions generated from the use of fuel additives containing engineered n-Ce to a large human population. Despite this fact, very little is known about the impact of cerium nanoparticles on human health and the environment (Majestic et al., 2010; Cassee et al., 2011; Erdakos et al., 2014; Dahle and Arai, 2015) and this poses the challenge of regulating the use of

engineered nano-ceria in different applications and assessing the risk it presents to human health and the environment (Dahle and Arai, 2015).

### **1.2.1 Effect of n-Ce diesel additives on PM and other air pollutants**

Diesel fuels emit a substantial amount of air pollutants (as diesel particulate matter-DPM), and fuels containing nanoceria (n-Ce) additives have been found to generate substantially lower PM<sub>10</sub> and PM<sub>2.5</sub> emissions (Erdakos et al., 2014). According to Erdakos et al. (2014), studies show that cerium additives shift emission distribution in the direction of smaller particle sizes in the nuclei mode, implying that the addition of n-Ce increases the emission of smaller-sized particles. Hence the higher the n-Ce concentration in the additive, the more smaller-sized particles are formed (Skillas et al., 2000). However, the amount of particulate matter emission has been shown to decrease substantially (Jung et al., 2005). n-Ce additives also influence ambient levels of ozone and several hazardous air pollutants (HAPs) (Erdakos et al., 2014). Skillas et al. (2000) observed that adding cerium-based additives to diesel fuels reduces the organic carbon content of PM but does not influence elemental carbon (EC), but no reason was ascribed to this observation. Ceria particles are also emitted as part of DPM upon the addition of cerium-based additives. The examination of filters in the Skillas et al. (2000) study revealed cerium/ceria is emitted in the particle phase within a size range of 20 to 80 nm. This fact was also confirmed by Gantt et al. (2015) when it was determined that ceria particles, whether emitted individually or in association with soot, had a size of approximately 75 nm. Most of the ultrafine particles emitted consisted of cerium metals in situations where an additive was used and existed in its Ce<sup>+4</sup> oxidation state (Skillas et al., 2000). Other studies also confirm n-Ce particles are emitted in smaller particle sizes composed mostly of CeO<sub>2</sub> and as aggregations of CeO<sub>2</sub> associated with soot particles. Also, approximately 40% of CeO<sub>2</sub> is associated with soot

particles (Gantt et al., 2015). Further studies from Zhang et al. (2013) confirmed emission reduction of CO<sub>2</sub>, CO, total particulate mass, formaldehyde, acetaldehyde, acrolein, and several polycyclic aromatic hydrocarbons by ceria-based fuel additives when emission rates for a single cylinder and a four-cylinder were measured and compared (Zhang et al., 2013).

A hypothetical study using the Community Multiscale Air Quality (CMAQ) model for an area covering the eastern part of the United States for Winter and Summer periods (see Figure 1.1) indicates a widespread use of n-Ce would result in ambient cerium concentrations as high as 22 ng/m<sup>3</sup>, a moderate decrease in PM<sub>2.5</sub> and a substantial decrease in elemental carbon (Erdakos et al., 2014).

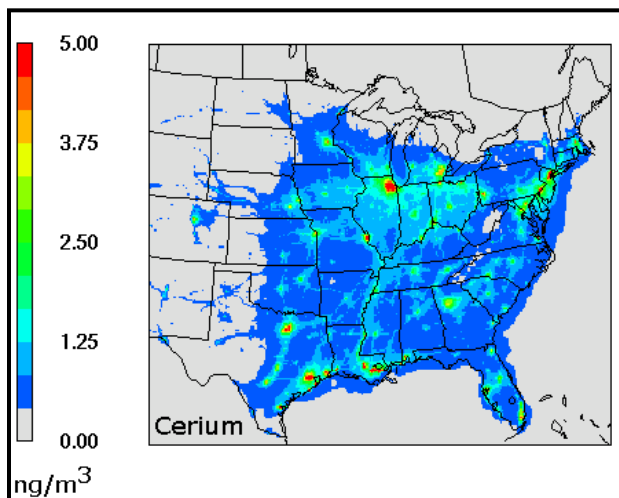


Figure 1.1: Predicted surface-level concentrations of cerium due to use of n-Ce diesel fuel. Modified from Erdakos et al. (2014).

### 1.3 INTRODUCTION OF CERIUM OXIDE FUEL ADDITIVE IN THE MARKET

Currently, Europe, Asia Pacific, Canada and India allow the use of engineered n-Ce as additives in diesel fuel. About a third of new passenger cars in Western Europe are diesel-fueled (Jung et al., 2005; Erdakos et al., 2014). The use of n-Ce for on-road vehicles started in 2003 in



the U.K., 2005 in New Zealand and 2010 in Canada (Gantt et al., 2015). There are three different brands of cerium-based fuel additives currently being marketed, namely Platinum Plus<sup>®</sup>, Eolys<sup>®</sup> and Envirox<sup>®</sup>. Platinum Plus<sup>®</sup>, manufactured by Clean Diesel Technologies (CDTi) based in the United States, was formerly registered with the U.S. EPA and was used in on-road and off-road vehicles until it was discontinued in October 2011 for non-compliance with the 2009 NO<sub>2</sub> limits. Envirox<sup>®</sup> can only be used in off-road vehicles in the United States but is also currently not registered with the U.S. EPA (Majestic et al., 2010; Erdakos et al., 2014). The current formulation in the U.S. does not appear to contain n-Ce. In the United States, it is estimated that diesel vehicles consume 50 billion gallons of fuel yearly, thus emitting 300,000 tons of fine particulates (PM<sub>2.5</sub>) into the atmosphere (Erdakos et al., 2014). Despite this fact, the use of cerium-based fuel additives in diesel fleets is still under regulatory study. In the United Kingdom, these additives are widely used in diesel cars, buses and coaches (Johnson and Park, 2012), but use of these additives is not currently allowed on-road in the United States. A case study in 2007 by CDTi (Clean Diesel Technologies Inc.) showed how Platinum Plus<sup>®</sup> was used in the U.S. to improve fuel economy and reduce soot emission in a fleet of school buses operated by DATTCO Bus Company (CDTi, undated). However, as stated earlier, the product is no longer registered with the U.S. EPA for use.

#### **1.4 RATIONALE FOR THIS RESEARCH**

The potential for engineered n-Ce based fuel additives to reduce the emission of important air pollutants has been demonstrated in several scientific studies (Majestic et al., 2010), and the use of n-Ce in fuel additives is fast gaining prominence in the vehicular technology sector. However, there is growing concern about the lack of information on the health impacts of engineered n-Ce

(Cassee et al., 2011) and the overall effect of any particles in the nano-size range on human health and the environment compared to their micro-sized counterpart.

Being the most abundant rare earth element, cerium is likely to be found in the atmosphere (although in minute quantities) because of mineral dust suspension in air (Gantt et al., 2015). The existence of naturally occurring sources of cerium and the introduction of new and highly dispersive anthropogenic sources provides the premise for investigating this uncommon yet important element. This research is therefore timely, adding to the knowledge gathering process that will influence decision making on the use of n-Ce based fuel additives in the U.S.A. and possible air quality standards for ambient cerium. The study will focus on determining the background cerium concentration in El Paso, Texas, and possible sources of the metal in the city.

## **1.5 RESEARCH QUESTIONS**

- How much cerium is in El Paso PM
- What is the main source of ambient cerium in El Paso, Texas
- How do anthropogenic activities contribute to the presence of cerium in El Paso air
- Is there evidence of transboundary influence on the recorded levels of cerium in El Paso
- What are the possible health implications, if any, of current cerium levels in the Paso del Norte airshed

## **1.6 TASKS**

The aim of this research is to build a baseline for ambient airborne cerium levels in El Paso Texas. This will help develop a database that will form the basis for setting future standards for engineered n-Ce concentration in El Paso airshed.

- To determine the baseline concentrations of cerium (Ce) in the city of El Paso from August 2006 to December 2009 at eight different locations.
- To ascertain possible temporal (season) and spatial (geographical) variations in cerium levels in El Paso, Texas, during the study period.
- Statistically analyze the available data for possible trends and patterns.
- Examine the possible health implications of having cerium particles in air.

## **2.0 METHODOLOGY**

### **2.1 GEOGRAPHY OF EL PASO, TEXAS**

This research was carried out in El Paso County, Texas, located in the southwestern United States. The city of El Paso and Fort Bliss military base comprise most of the county area. There are approximately 825,000 residents in the county, with another estimated 1,500,000 residents directly across the Rio Grande in Ciudad Juarez, Chihuahua, Mexico. The two cities are contiguous, separated only by the relatively narrow river and associated border buffer zones.

The cities lie at an average elevation of approximately 1150 m above sea level, with a Chihuahuan high-altitude desert climate. Cool-to-cold winters can produce sub-freezing temperatures, particularly during the night. Annual rainfall is less than 25 cm, with most falling in the months of July, August and September, a so-called summer monsoon. The spring is arid and often windy, giving rise to occasional dust storms.

### **2.2 SAMPLING**

Sampling was carried out at eight different sites (see Table 2.1) for a period of 3.4 years, from August 2006 to December 2009. The sampling sites were spread across El Paso County as can be seen in Figure 2.1. Most sites were located at existing Texas Commission on Environmental Quality Community Air Monitoring Stations and El Paso Water Utilities monitoring stations because each site required security and access to electricity (Paz et al., 2017). Weekly samples for fine and coarse PM were collected at each site. Sampling was done with a PM<sub>10</sub> dichotomous sampler (Thermo Electron Corporation Series 241; Thermo Electron Corp., Waltham, MA, U.S.A.) following the U.S. EPA's Compendium Method IO-2.2 as a guide. Samples were collected on 37-mm Teflon<sup>®</sup> filters, preconditioned at  $25 \pm 5$  °C and  $30 \pm 5\%$

relative humidity for 24 hours, weighed, and stored in petri dishes for less than 30 days prior to sampling (Li et al., 2001).

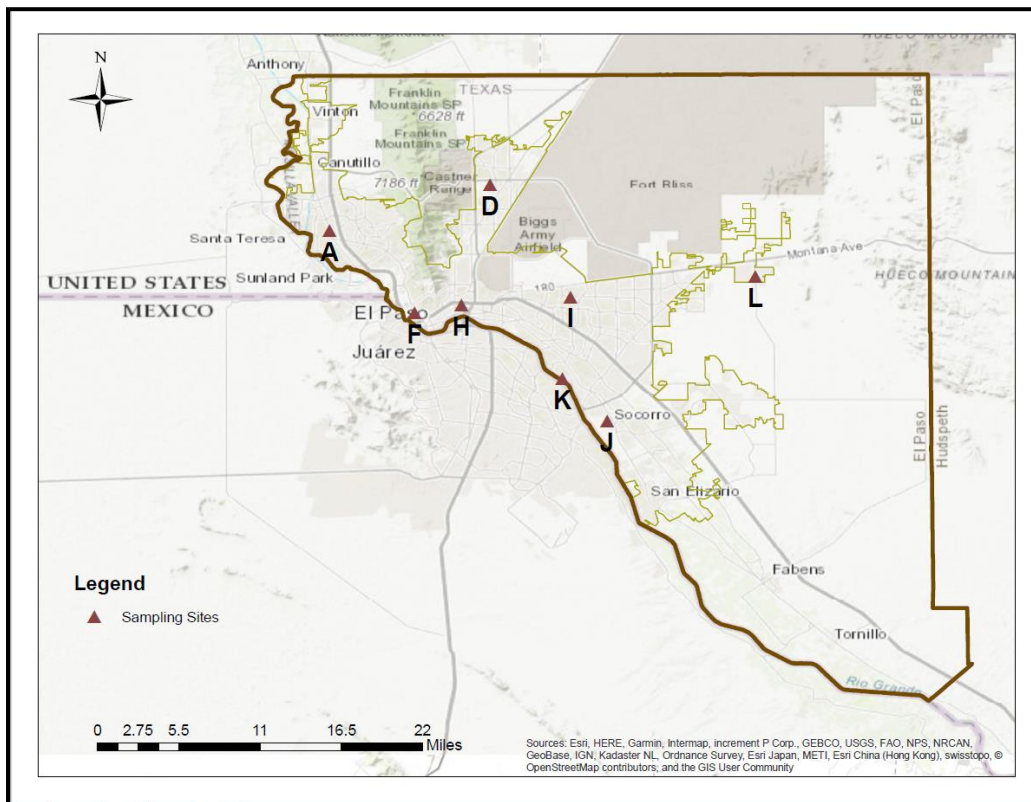


Figure 2.1: Map of study area showing sampling sites within El Paso County

Table 2.1: Description of sampling sites

Site	Description
A	Predominantly residential area in west El Paso, adjacent to railroad tracks.
D	Northeast El Paso, close to Highway 54 and Yvette Road. Classified as a residential location.
F	Adjacent to the campus of the University of Texas at El Paso (UTEP).
H	Adjacent to the International Bridge of the Americas, a major U.S.—Mexico border crossing and truck route.
I	Predominantly residential area in east El Paso, near Album Park.
J	Southwest area of El Paso, the mixed urban—rural Mission Valley.
K	Southwest area of El Paso (Mission Valley).
L	Monte Vista, newer residential area easternmost El Paso.

## 2.3 PHYSICAL AND CHEMICAL ANALYSIS

### 2.3.1 Gravimetric determination of mass of PM

The mass concentrations of  $PM_C$  and  $PM_F$  were gravimetrically determined for each sample according to U.S. EPA Compendium Method IO-2.2 (U.S. EPA, 1999).

### 2.3.2 XRF determination of cerium in PM and calculation of ambient cerium levels

Cerium concentrations on the filters had been determined using a PANalytical Epsilon5 energy dispersive X-ray fluorescence (XRF) instrument, which is purposely designed to meet the requirements of U.S. EPA Method IO-3.3 for elemental analysis of air filter PM (U.S. EPA, 1999; Paz et al., 2017). For calibration of the XRF instrument, U.S. National Institute for Standards and Technology (NIST) Standard Reference Materials (SRMs), together with Micrometer<sup>TM</sup> commercial thin-film single-element standards were employed (Paz et al., 2017). For each sample the mass concentration of cerium per square centimeter of exposed filter

( $\mu\text{g}/\text{cm}^2$ ) was determined and results used to calculate the total mass of cerium collected on the filter (the X-ray beam impinges upon only a portion of the filter). The 1-sigma lower limit of detection (per U.S. EPA Method IO-3.3) on the Epsilon5 for  $\text{PM}_{\text{C}}$  was  $0.02 \text{ ng}/\text{m}^3$  and for  $\text{PM}_{\text{F}}$   $0.002 \text{ ng}/\text{m}^3$ .

## **2.4 DATA ANALYSIS**

Microsoft™ Excel was used in cleaning and analyzing the data obtained on cerium levels in the PM sample filters. Using statistical and graphical tools in Excel, averages were determined for cerium in both fine and coarse samples, seasonal and yearly averages were computed and there were compared to total averages for both fine and coarse cerium levels. Geospatial maps were developed using the Inverse Distance Weighted (IDW) Average tool in ArcGIS to extrapolate concentration of cerium for the nearest vicinity of sampling points. This provided an estimate of the cerium levels within the El Paso County at unsampled locations.

### 3.0 RESULTS AND DISCUSSION

#### 3.1 DATA

Over 2000 samples had been collected and analyzed from all eight locations for both coarse particulate matter ( $PM_C$ ) and fine particulate matter ( $PM_F$ ), and after excluding invalid or incomplete samples 1,995 samples were studied, with concentrations ranging from 0.00 to 13.2  $ng/m^3$ . Figure 3.1 is a bar graph showing the mean concentration of cerium in both  $PM_C$  and  $PM_F$  for the period 2006 to 2009 at each sample site, with error bars depicting the standard deviation for each particle fraction for the entire study. Figure 3.2 shows the regression model and statistics describing the relationship between coarse and fine cerium concentrations recorded in the study. Figures 3.3 and 3.4 are IDW interpolation maps developed from ArcGIS showing the extrapolation of cerium concentrations for El Paso County. Table 3.1 displays the basic statistics (means, standard deviations, standard error mean, minimum and maximum concentrations and the first and second quartile (Q1 and Q3) values for cerium concentrations in both PM fractions for the entire study. Table 3.2 shows the same basic statistics for cerium levels in both PM fractions for all sites during the study.

Analysis of the data provides evidence of the continual presence of airborne cerium in the Paso Del Norte airshed. Yearly average cerium level recorded for the entire study period was 2.02  $ng/m^3$  for  $PM_C$  and 1.12  $ng/m^3$  for  $PM_F$ , with standard deviations of 1.66 and 1.04 respectively (see Table 3.1). The highest cerium levels recorded were 13.2  $ng/m^3$  at site F and 5.32  $ng/m^3$  at site L for coarse and fine PM respectively (see Table 3.2). Based on the values in Table 3.2, it is evident that coarse PM consistently recorded higher values for cerium concentrations at each site compared to fine PM. Figure 3.2 shows no statistically significant



correlation between coarse and fine cerium concentration. This general disconnect between  $PM_C$  and  $PM_F$  levels suggests that their sources differ at least in part.

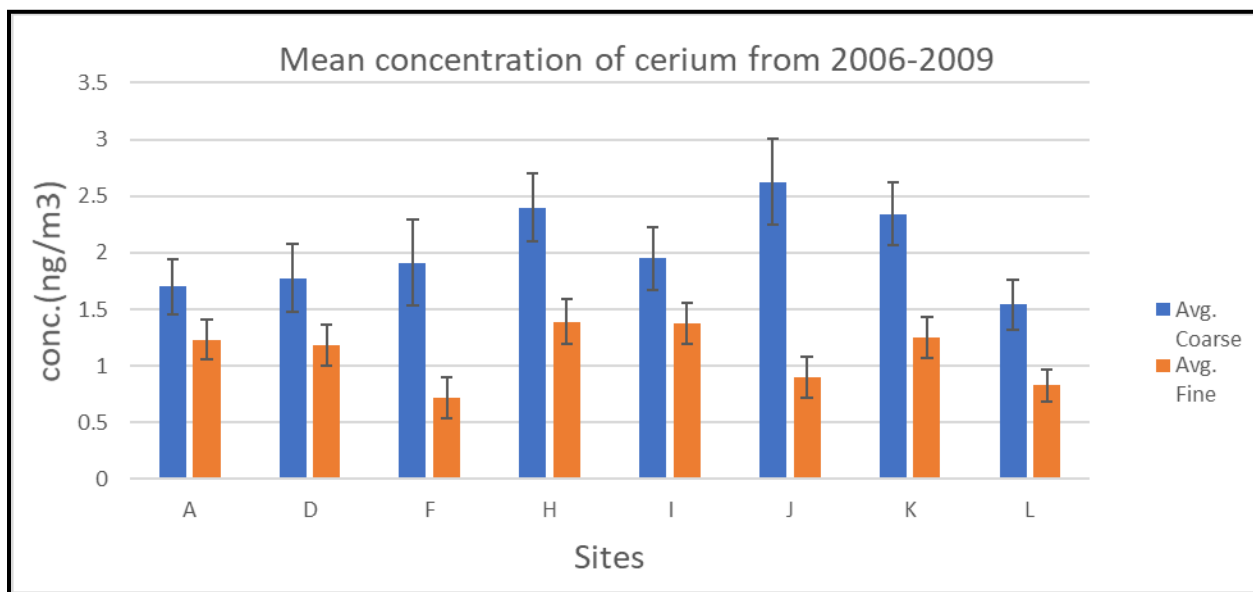


Figure 3.1: Average concentration of cerium at all sites for  $PM_C$  and  $PM_F$ . Error bars correspond to  $\pm 2$  SEM.

The highest average cerium level computed for  $PM_C$  was  $2.63 \text{ ng/m}^3$ , which occurred at site J. Three sites, H, J and K recorded averages higher than the yearly average of  $\sim 2 \text{ ng/m}^3$  of cerium in  $PM_C$ . In total,  $PM_F$  recorded lower concentrations of cerium for all sites, with sites H and I recording the highest average value of  $1.4 \text{ ng/m}^3$ . Sites A, D, H, I and K recorded averages above the yearly average of  $1 \text{ ng/m}^3$  for cerium levels in  $PM_F$ . Other studies (Hughes et al., 1998; Cass et al., 2000; Kulkarni et al., 2007) recorded varying background levels of cerium in  $PM_{2.5}$  in different cities in the U.S., shown in Table 3.3. Background cerium levels recorded in Houston, TX in 2006 (Kulkarni et al., 2007, supporting document) for ambient  $PM_{2.5}$  of  $\sim 0.38 \text{ ng/m}^3$  was about three times lower than that recorded for fine  $PM_F$  in El Paso, TX in this study.

Table 3.1: Basic statistics for total coarse and fine PM for the study period

<b>ng/m<sup>3</sup> Ce</b>	<b>N*</b>	<b>Mean</b>	<b>SE Mean</b>	<b>Std Dev</b>	<b>Minimum</b>	<b>Q1** *</b>	<b>Median</b>	<b>Q3*** *</b>	<b>Maximum</b>
<b>Coarse</b>	970	2.02	0.053	1.66	0.00	0.83	1.75	2.87	13.2
<b>Fine</b>	1025	1.12	0.032	1.04	0.00	0.17	0.95	1.73	5.33

\* number of cases included; \*\* Q1 1st quartile; \*\*\*Q3 3rd quartile

Table 3.2: Basic statistics for cerium levels at all sites in both PM<sub>10</sub> and PM<sub>2.5</sub>

<b>SIT E</b>	<b>Variable (ng/m<sup>3</sup>)</b>	<b>N</b>	<b>Mean</b>	<b>SE Mean</b>	<b>Std Dev</b>	<b>Minimum</b>	<b>Q1</b>	<b>Median</b>	<b>Q3</b>	<b>Maximum</b>
<b>A</b>	<b>Coarse</b>	130	1.70	0.12	1.31	0.00	0.80	1.55	2.39	7.46
	<b>Fine</b>	134	1.23	0.09	1.03	0.00	0.30	1.16	1.89	4.20
<b>D</b>	<b>Coarse</b>	117	1.77	0.15	1.65	0.00	0.51	1.40	2.48	8.14
	<b>Fine</b>	140	1.187	0.09	1.08	0.00	0.35	1.00	1.92	4.85
<b>F</b>	<b>Coarse</b>	108	1.91	0.19	1.94	0.00	0.45	1.60	2.88	13.23
	<b>Fine</b>	114	0.73	0.09	0.97	0.00	0.00	0.22	1.38	4.11
<b>H</b>	<b>Coarse</b>	117	2.40	0.15	1.62	0.00	1.23	2.13	3.33	7.80
	<b>Fine</b>	118	1.39	0.10	1.05	0.00	0.49	1.29	2.06	5.21
<b>I</b>	<b>Coarse</b>	129	1.95	0.14	1.58	0.00	0.79	1.68	2.78	8.60
	<b>Fine</b>	132	1.37	0.09	1.03	0.00	0.64	1.14	2.07	4.40
<b>J</b>	<b>Coarse</b>	108	2.63	0.19	1.92	0.00	1.36	2.28	3.52	10.41

	Fine	11 3	0.90	0.09	0.99	0.00	0.00	0.67	1.52	4.63
K	Coarse	13 6	2.34	0.14	1.68	0.00	0.91	2.08	3.21	9.82
	Fine	14 1	1.25	0.09	1.09	0.00	0.34	1.09	1.93	5.32
L	Coarse	12 5	1.54	0.11	1.30	0.00	0.42	1.33	2.36	5.90
	Fine	13 3	0.83	0.07	0.83	0.00	0.00	0.64	1.36	3.76

\*number of cases included; \*\* Q1 1st quartile; \*\*\*Q3 3rd quartile

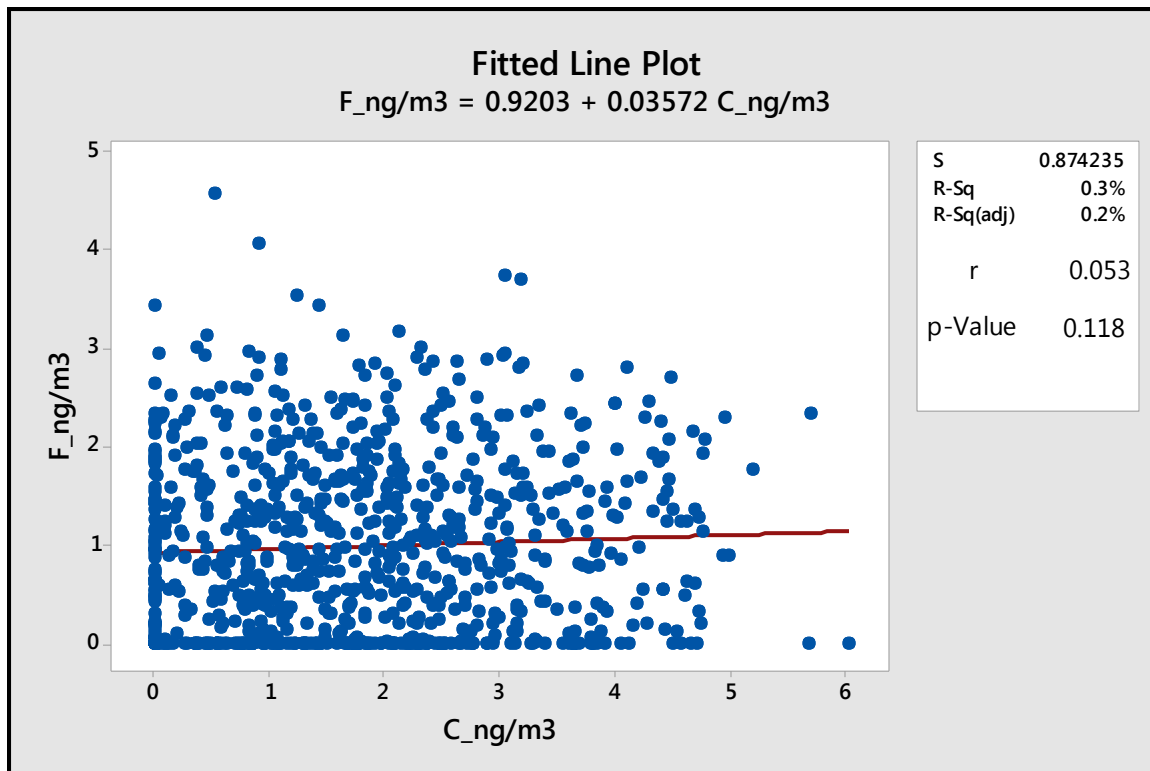


Figure 3.2: Scatter plot showing the relationship between cerium in  $PM_C$  and  $PM_F$  in  $\text{ng/m}^3$ .

## 3.2 GENERAL OBSERVATIONS

### 3.2.1 Cerium levels and air quality regulations

The annual average ambient PM concentrations (mass of PM) for the study period were  $37.2 \mu\text{g}/\text{m}^3$  and  $9.9 \mu\text{g}/\text{m}^3$  for coarse and fine particulate matter respectively, within the set limit of  $150 \text{ ng}/\text{m}^3$  and  $12.0 \text{ ng}/\text{m}^3$  for both  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  respectively by the U.S. The current  $\text{PM}_{10}$  standard is based on a 24-hour averaging time and is used in the absence of an annual standard because of a lack of evidence linking long term exposure to  $\text{PM}_{10}$  and public health (U.S. EPA, 2012).

Available information on ambient cerium in the U.S. is mainly from chemical characterization of  $\text{PM}_{2.5}$  or ultrafine particles. Table 3.3 shows background concentration of cerium in  $\text{PM}_{2.5}$  in some U.S. cities along with the average values recorded in this study. Research in 187 counties within the United States also revealed the presence of cerium in  $\text{PM}_{2.5}$ , with the annual average being  $29.5 \text{ ng}/\text{m}^3$  (Bell et al., 2007). The reason for the much higher values in this study based on U.S. EPA data is uncertain; unfortunately, the Supporting Data accompanying the Bell et al. (2007) study were not accessible. Background  $\text{PM}_{2.5}$  cerium levels in El Paso, TX are almost three times higher than those recorded in Houston, TX, where ambient cerium was used as an indicator for refinery activities (Kulkarni et al., 2007). In the United Kingdom, baseline cerium concentrations in  $\text{PM}_{10}$  were recorded at three locations *prior* to the introduction of n-Ce based fuel additive in on-road vehicles. The concentrations were 0.15, 0.20, and  $0.65 \text{ ng}/\text{m}^3$  at Newcastle, Greenwich and London respectively (Park et al., 2008). These  $\text{PM}_{10}$  values in the U.K are lower at each site compared to the average measured in this study for cerium in  $\text{PM}_{10}$  (i.e.  $\sim 3 \text{ ng}/\text{m}^3$ ;  $\text{PM}_C + \text{PM}_F$ ).

Table 3.3: Cerium concentration of ambient PM<sub>2.5</sub> in U.S. cities

City	Average cerium (ng/m <sup>3</sup> )		
El Paso - TX	1.12	PM <sub>2.5</sub>	This study
Houston - TX	0.38 (2007)	PM <sub>2.5</sub>	Kulkarni et al.
Central Los Angeles - CA	1.20 (1998)	PM <sub>2.5</sub>	Hughes et al.
Pasadena - CA	0.37 (2000)	PM <sub>2.5</sub>	Cass et al.
London – U.K.	0.65 (2008)	PM <sub>10</sub>	Park et al.
Greenwich – U.K.	0.20 (2008)	PM <sub>10</sub>	Park et al.
Newcastle – U.K.	0.15 (2008)	PM <sub>10</sub>	Park et al.

### 3.2.2 Source of Cerium

The entrainment of local soils, as well as regional desert soils, in the form of dust, which is a frequent occurrence in El Paso due to the regional climate, is one possible source of the airborne cerium found in the PM samples. Cerium is present in some soils to the west of El Paso at concentrations greater than 150 ppm in the upper 20 cm of the soil (Shacklette and Boerngen, 1984).

As the most abundant REE, cerium can be found in several mineral classes, carbonates being the largest mineral group containing the metal (Dahle and Arai, 2015). Important mining sources of the metal are the carbonate mineral bastnaesite (Ce,La)CO<sub>3</sub>(F,OH) and the phosphate mineral monazite (Ce,La,Nd,Th)PO<sub>3</sub>. Cerium also occurs as a trace constituent in many minerals and has an average crustal abundance of 60 ppm (Gambogi, 2014).

In addition to geologic sources, the use of cerium in industrial processes serves as an anthropogenic source of the metal in the environment. As demonstrated by Park et al. (2008) and Gantt et al. (2015), mobile sources such as diesel-powered vehicles using n-Ce based fuel additives emit airborne cerium particles, although not in the U.S. Cerium is a component of wear

of iron, magnesium and aluminum alloys containing cerium (e.g., HSLA – High-Strength-Low Alloy steel) used in vehicular parts (Johnson and Park, 2012) and also contributes to anthropogenic cerium in air.

Examples of stationary sources of this metal include Fluid Catalytic Cracking Units (FCCUs) of refineries, glass and ceramic manufacturing and steel industries. These release dust and air pollutants with cerium compounds (Reimann and de Caritat, 2011) into the atmosphere. Fuel oil and coal burning in power stations also emit rare earth elements.

*Potential* stationary local sources in El Paso would include Daltile™ ceramics and Western Refining, now Andeavor (Andeavor, 2018), a 135,000-barrel-per-day crude oil refinery that incorporates FCCUs. Daltile™ lies to the north and east of station D, a location with relatively low levels of airborne cerium. That suggests that this ceramic plant is not a significant contributor, if at all, to El Paso's cerium levels. Western Refining lies east and north of station H, toward station I. Although Kulkarni et al. (2007) provided documentation of FCCUs releasing lanthanides, chiefly lanthanum, in Houston, TX air due to equipment breakdowns, similar evidence does not exist for El Paso. The Houston equipment breakdowns resulted in lanthanide spikes 33-106 times background levels. Such occasional cerium spikes did not appear in our data set for the surrounding stations.

### **3.3 GEOGRAPHIC TRENDS AND POSSIBLE SOURCES**

Average cerium levels in both  $PM_C$  and  $PM_F$  varied with each sampling location, showing consistently higher values for  $PM_C$  compared to  $PM_F$ . Sites H, K and J recorded above yearly average ( $\sim 2 \text{ ng/m}^3$ ) values for  $PM_C$  (see Figure 3.1). Sites A, D, H, I and K recorded values above  $1 \text{ ng/m}^3$  for fine PM in the study.

Locations A, D, F, I and L recorded  $PM_C$  cerium levels lower than those at sites H, J, and K. Note that these four sites are peripheral to the core urban El Paso—Cd. Juarez metroplex, suggesting the influence of a regional source (windblown dust) in the distribution of coarse airborne cerium in El Paso. Site L shows the lowest  $PM_C$  cerium average level, and the second lowest  $PM_F$  level. It lies at the outskirts of the city, surrounded in the main by desert. Thus, it can serve as a benchmark for natural background airborne cerium levels in the region.

Locations H, K, and J, sited in the core of the El Paso—Cd. Juarez metroplex, exhibit higher levels of  $PM_C$  cerium. This suggests that a portion of the  $PM_C$  cerium load is generated by anthropogenic activity. Site H is of special interest because it recorded the highest levels of the metal in both coarse and fine PM, and slightly higher than site K which has a similar pattern for cerium concentration. Located within 150 m from the U.S.—Mexico border crossing station and surrounded by a maze of interstate highways, cerium levels in site H can be attributed to intense vehicular traffic occurring at the border between El Paso and Cd. Juarez, Mexico. However, since the on-road use of n-Ce based additives is not currently allowed in the U.S. and there is no evidence of the use of the additive in Cd. Juarez, Mexico, likely anthropogenic mobile sources of the metal would be from abrasion of vehicular parts made from cerium, iron, aluminum and magnesium alloys (Johnson and Parker, 2012), and cerium that remains in gasoline because of the FCCU crude oil refining process (Kulkarni et al, 2007). Nearer to and downwind of the U.S.-Mexico border, with no topographic obstruction to wind flow from the west, sites J and K exhibit similar records of cerium in  $PM_C$  as site H. Presumably these levels are associated with the large, densely populated urban (1,500,000 inhabitants) area just to the west.

$PM_F$  levels are generally the same for stations A, D, H, I, and K. Stations F, J, and L cluster at considerably lower cerium levels. No explanation of this pattern is evident.

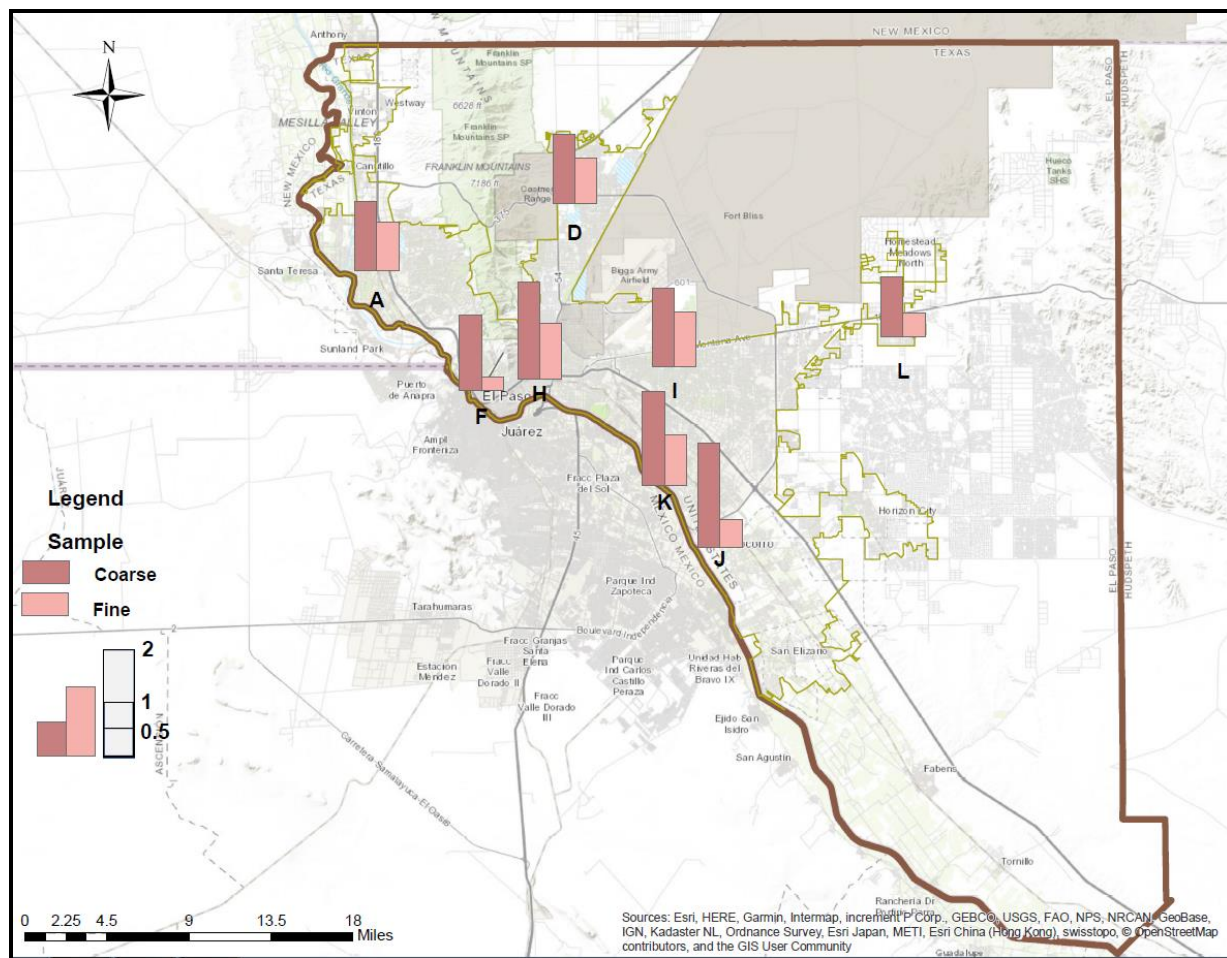


Figure 3.3: Average cerium concentration in  $PM_C$  and  $PM_F$  monitored for all the sites

Using ArcGIS Inverse Distance Weighted (IDW) interpolation, contour maps of generalized cerium levels in coarse and fine PM were generated for the study area, seen in Figs. 3.4 and 3.5.



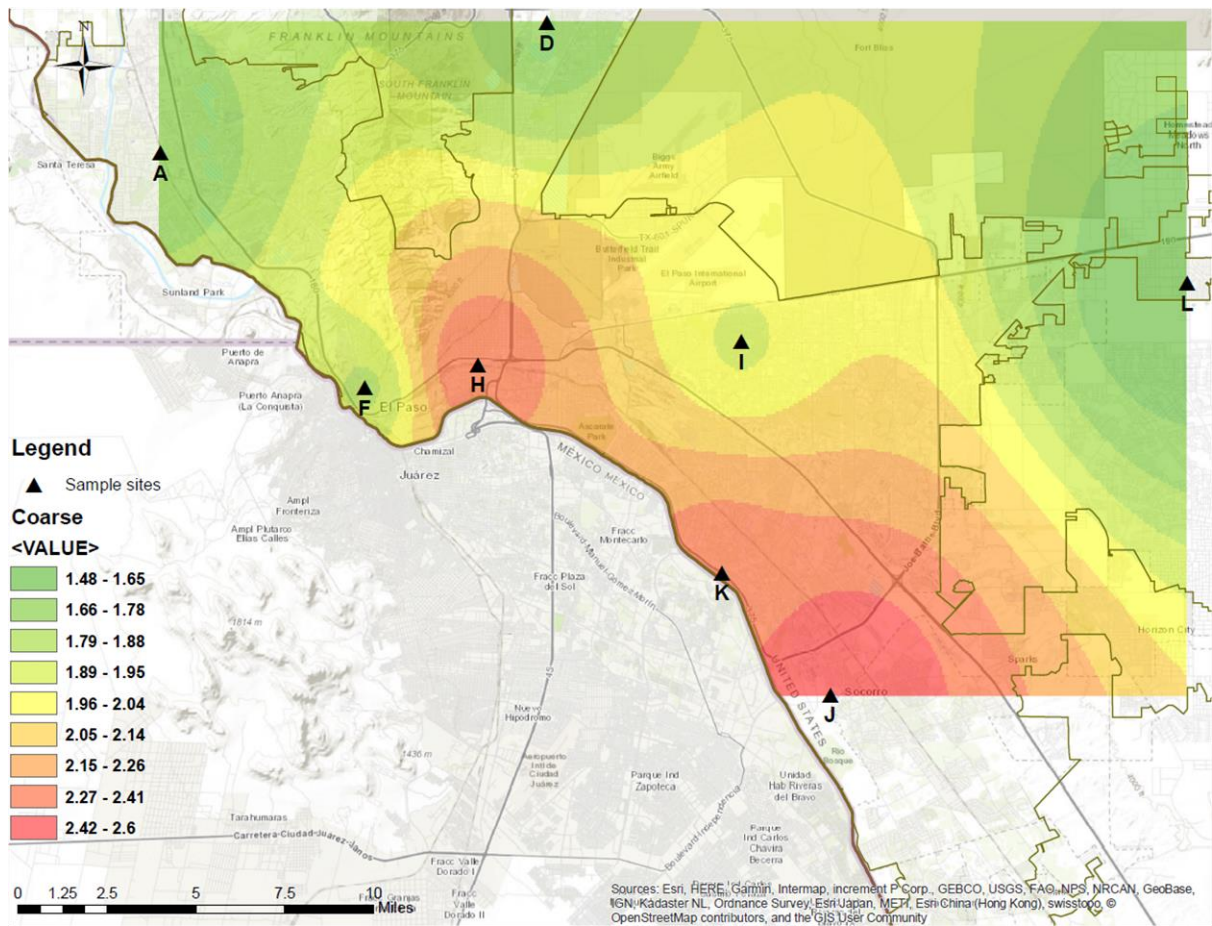


Figure 3.4: Inverse Distance Weighted (IDW) interpolation of cerium concentration in PM<sub>C</sub>.

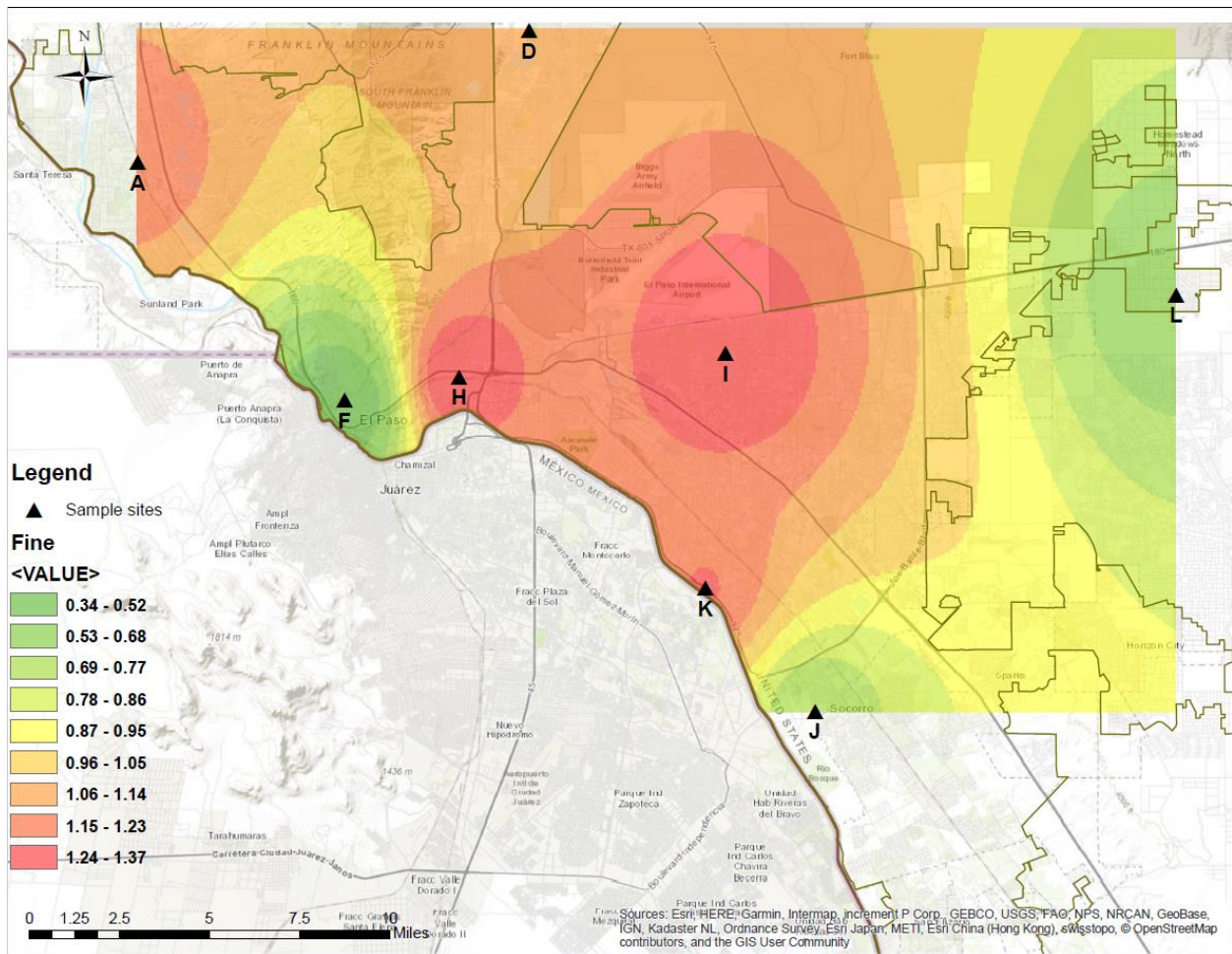


Figure 3.5: Inverse Distance Weighted (IDW) interpolation of cerium concentration in  $PM_F$ .

The salient feature of the maps is the overall concentration of higher cerium levels toward the core of the bi-national metroplex. This is pronounced on the  $PM_C$  map, less so on the  $PM_F$  map. This suggests the importance of urban, presumably anthropogenic, sources of airborne cerium. The seeming bulge of stations H—I—K on the  $PM_F$  map could be caused by the longer transport of fine particles toward the urban periphery by generally eastward air flow.

This outcome is in line with the study conducted by Powell et al. (2002) that revealed the presence of anthropogenic cerium in residential dust collected in inner city Syracuse, NY in the

spring of 1999. This documented the importance of urban areas as an anthropogenic source of cerium. In addition, open air burning of solid waste is common in Cd. Juarez and this practice is a documented source of airborne cerium (Reff et al., 2009).

### **3.4 SEASONAL TRENDS**

Figures 3.6 and 3.7 are maps showing the average concentrations of coarse and fine cerium in spring, summer and winter.

#### **Coarse PM**

Figure 3.6 reveals a weak trend of lower coarse cerium concentrations in the summer for most of the locations, compared to the spring and winter seasons. This outcome could be explained by the fact that the summer monsoon rainfall results in atmospheric washout of larger particles resulting in lower levels of cerium being recorded in  $PM_C$ . There also is a shift in wind direction in summer, with the monsoon rains coming up from the Gulf of Mexico to the southeast. The elevated concentrations of the element in spring and winter can be explained by the occurrence of high wind velocity mostly experienced in the spring and the thermal inversion in the winter that prevents the dispersion of atmospheric particles. The pattern observed in the levels of coarse cerium recorded for all three seasons is consistent with a mix of urban core anthropogenic and regional geologic sources.

#### **Fine PM**

Figure 3.7 indicates that the concentrations of cerium in fine particles do not seem to be influenced by the seasonal changes.

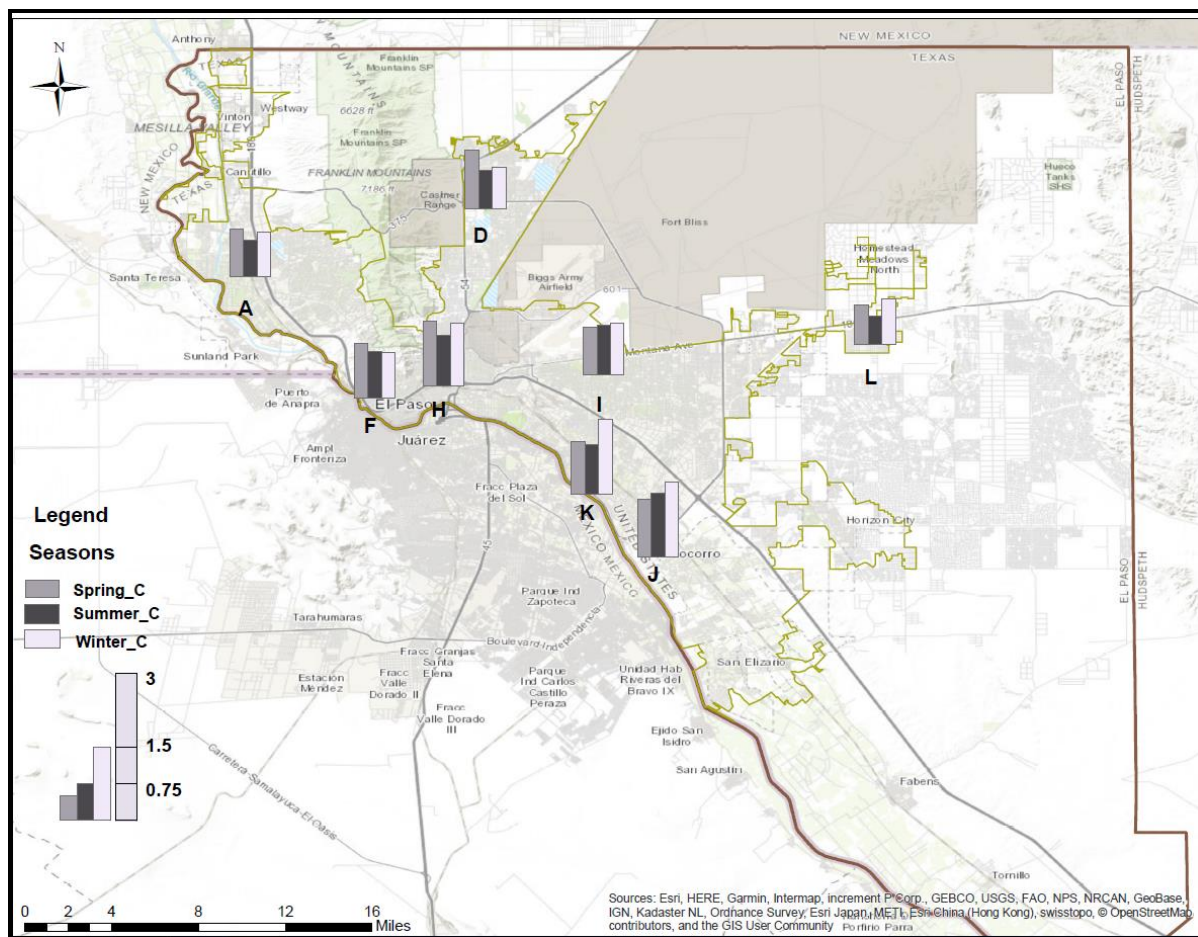


Figure 3.6: Seasonal average of ambient coarse cerium in spring, summer and fall recorded at all sites from 2006-2009.



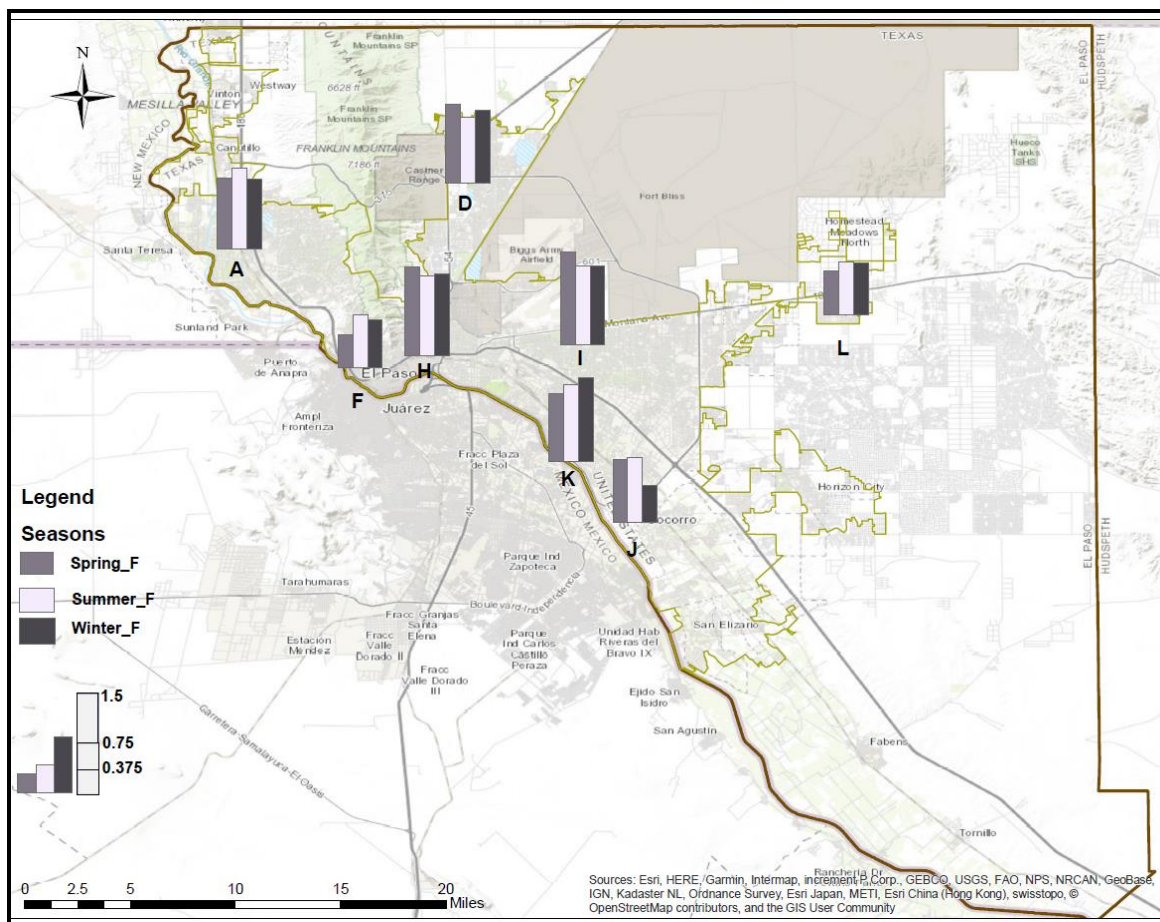


Figure 3.7: Seasonal average of ambient fine cerium in spring, summer and fall recorded at all sites from 2006-2009

Figures 3.8 and 3.9 show the average cerium recorded for each season from 2006 to 2009 for, respectively, coarse and fine airborne particulates for the individual sites in El Paso. Notice the scale difference in both coarse and fine graphs and the absence of data for spring 2006 for both PM fractions. No trend is discernable, further supporting the observation that cerium concentrations are not significantly influenced by seasonal change. Likewise, no obvious secular trend emerges from the graphs.

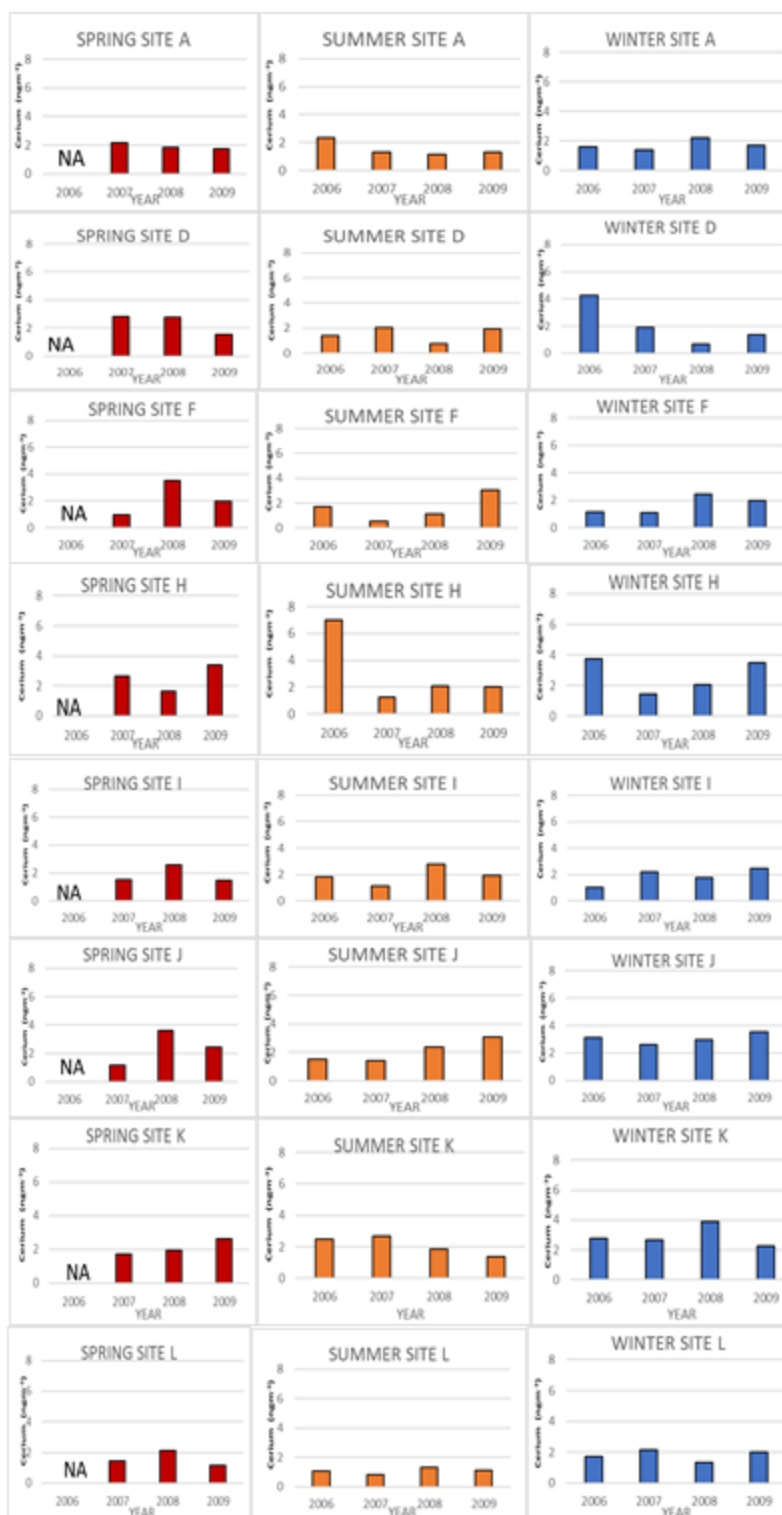


Figure 3.8: Yearly average of cerium levels by season in PM<sub>10</sub>

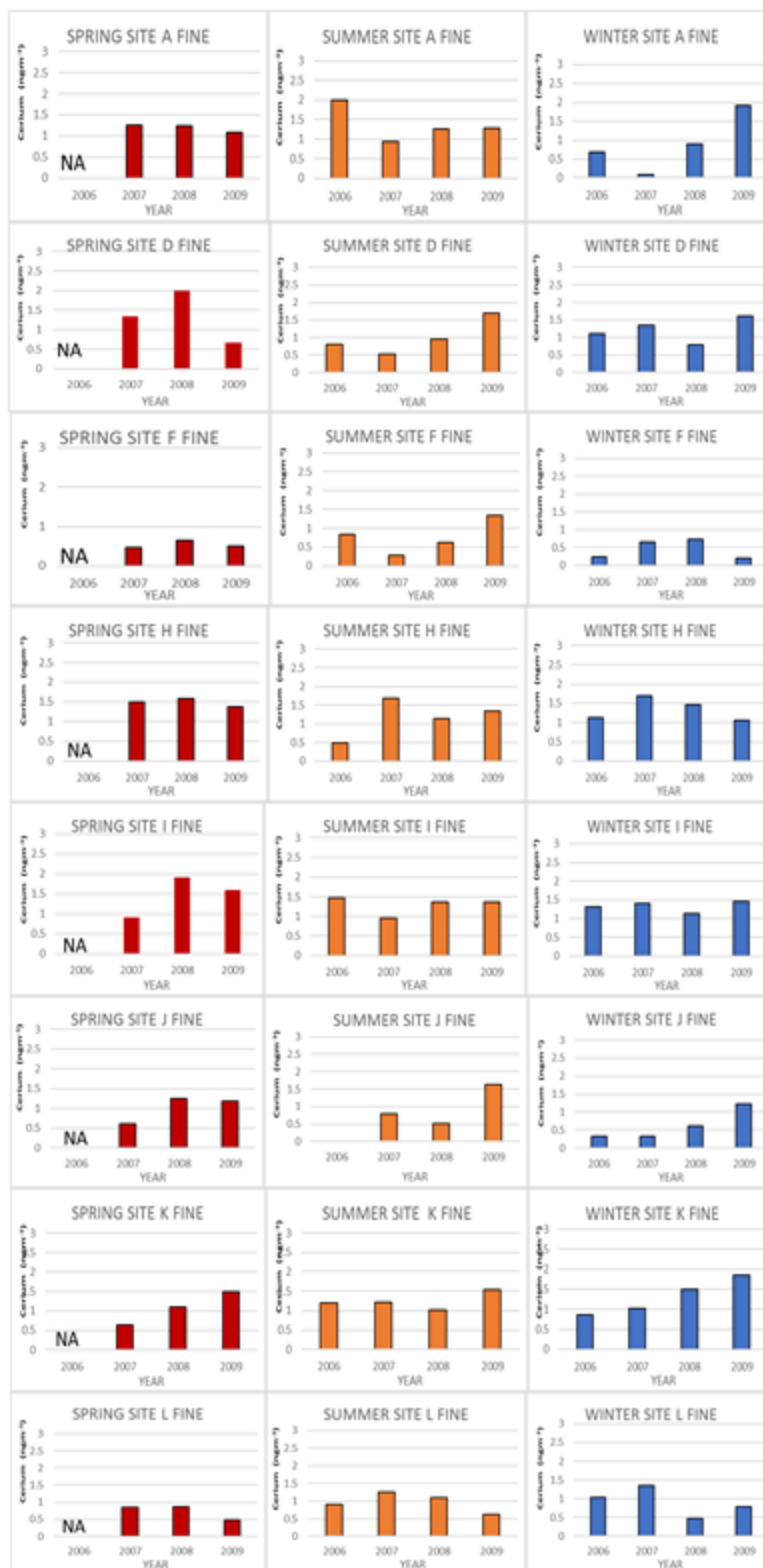


Figure 3.9: Yearly average of cerium levels by season in PM<sub>2.5</sub>

### 3.5 PUBLIC HEALTH IMPLICATIONS

Nanoscale ( $<0.1\ \mu\text{m}$ ) cerium particles can reach deeper regions of the respiratory system compared to their microscale counterparts. This study reveals the presence and exposure levels of ambient cerium particles in El Paso. These particles could exist in particulate matter as either cerium oxide or other forms of cerium compounds because of the metal's high reactivity and inability to exist in elemental form in the environment (Lewis, 2001; Powell et al., 2002; EPA, 2009). Based on the higher levels of cerium detected in  $\text{PM}_{10}$ , effective exposure to El Paso residents is low, however the occurrence of approximately 1/3 of airborne cerium in the fine particulate fraction ( $<2.5\ \mu\text{m}$ ) indicates the possible existence of ambient anthropogenic nanoscale ( $<0.1\ \mu\text{m}$ ) cerium particles in El Paso.

Currently, there is no established National Ambient Air Quality Standard (NAAQS) for cerium in the U.S., as well as in Europe, where extensive research is available on the metal because of its widespread use in diesel fuel additive. However, there are two tentative inhalation reference concentrations (RfCs) of  $200\ \text{ng}/\text{m}^3$  and  $900\ \text{ng}/\text{m}^3$  for micro-sized cerium developed by the U.S. EPA for toxicological purposes (U.S. EPA, 2005; U.S. EPA, 2009). These RfCs have been used as guideline values in some studies (Edarkos et al., 2014; Gantt et al., 2015) to determine the importance of cerium measured or predicted at a location. In like manner, comparing the ambient cerium levels measured for El Paso with both RfCs, it is obvious that cerium in both PM fractions is lower by two orders of magnitude or more. This suggests that there is at present little health threat to El Paso residents from airborne cerium, as is the case in other studies (Park et al., 2008; Gantt et al., 2015).



## 4.0 CONCLUSIONS

The levels of airborne cerium recorded in El Paso, TX for this study are higher in coarse particulate matter (overall average  $\sim 2 \text{ ng/m}^3$ ) compared to fine particulate matter ( $\sim 1 \text{ ng/m}^3$ ). Geographical variation indicated that a heavily trafficked urban core location (site H) recorded high levels of airborne cerium, in both  $\text{PM}_C$  and  $\text{PM}_F$ . High values also were recorded at sites close to the international border between Ciudad Juarez, Chihuahua, Mexico and contiguous (separated only by the narrow Rio Grande) El Paso, Texas, U.S.A. The lowest overall values were encountered at the site most distant from the urban core, with few residents or commercial activities in the area. A geospatial interpolation map of the data from sampling locations highlighted this pattern.

There was a small seasonal variation in  $\text{PM}_C$ , with lower values in the summer. No seasonal variations were apparent in the  $\text{PM}_F$ .

Given the emerging use of nanoceria in diesel vehicular technology to reduce particulate matter emission in other developed countries, these baseline data on ambient particulate cerium in El Paso are important for future monitoring should cerium-based diesel fuel additives be permitted for on-road in the U.S. Erdakos et al. (2014) predicted an average contribution of  $0.5 \text{ ng/m}^3$  in  $\text{PM}_F$  from the potential use of n-Ce, and up to  $22 \text{ ng/m}^3$  in urban areas. Given the urban density of El Paso, anticipated increases should be detectable relative to current local  $\text{PM}_F$  levels of cerium.

The absence of an established U.S. EPA standard for cerium in air makes it impossible to definitively determine if the levels obtained in this study are safe for human health. However, comparing the current results with the tentative U.S. EPA inhalation reference concentrations (RfC), it appears safe to assume ambient cerium levels El Paso pose no current health threat.

## REFERENCES

- Andeavor, “El Paso,” 2018. <http://www.andeavor.com/refining/el-paso/>
- Angelone, M., Spaziani, F., Cremisini, C., Salluzzo, A., “Determination of PGE and REE in urban matrices and fingerprinting of traffic emission contamination,” *Highway and Urban Environment*, Springer, Dordrecht, G.M.Morrison, S. Rauch, eds., 271-281, 2007.
- Arrieta, D.E., Ontiveros, C.C., Li, W-W., Garcia, J.H., Denison, M.S., McDonald, J.D., Burchiel, S.W., Washburn, B.S., “Aryl hydrocarbon receptor-mediated activity of particulate organic matter from the Paso del Norte airshed along the U.S.-Mexico border,” *Environmental Health Perspectives*, 111(10). 1299-1305, 2003.
- Bell, M.L., Dominici, F., Ebisu, K., Zeger, S.L., Samet, J.M., “Spatial and temporal variation in PM<sub>2.5</sub> chemical composition in the United States for health effects studies,” *Environmental Health Perspectives*, 115(7). 989-995, 2007.
- Cass, G.R., Hughes, L.A., Bhave, P., Kleeman, M.J., Allen, J.O., Salmon, L.G., “The chemical composition of atmospheric ultrafine particles,” *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, 358(1775), 2581-2592. 2000.
- Cassee, F.R., van Balen, E.C., Singh, C., Green, D., Muijsers, H., Weinstein, J., Dreher, K., “Exposure, health and ecological effects review of engineered nanoscale cerium and cerium oxide associated with its use as a fuel additive,” *Critical Reviews in Toxicology*, 41(3). 213-229, 2011.
- CDTi, “Case Studies: DATTCO Bus Company – Platinum Plus – DPF problem solver.” (undated). (DPF = Diesel Particulate Filter).  
[www.cdti.com/content/americas/applications/casestudies/dattco.htm](http://www.cdti.com/content/americas/applications/casestudies/dattco.htm)

- Chan, Y.C., Hawas, O., Hawker, D., Vowles, P., Cohen, D.D., Stelcer, E., Simpson, R., Golding, G., Christensen, E., “Using multiple type composition data and wind data in PMF analysis to apportion and locate sources of air pollutants,” *Atmospheric Environment*, 45(2). 439-449, 2011.
- Dahle, J.T., Arai, Y., “Environmental geochemistry of cerium: applications and toxicology of cerium oxide nanoparticles,” *International Journal of Environmental Research and Public Health*, 12(2). 1253-1278, 2015.
- Dockery, D.W., “Epidemiologic evidence of cardiovascular effects of particulate air pollution,” *Environmental Health Perspectives*, 109(Suppl 4). 483-486, 2001.
- Erdakos, G.B., Bhawe, P.V., Pouliot, G.A., Simon, H., Mathur, R., “Predicting the effects of nanoscale cerium additives in diesel fuel on regional-scale air quality,” *Environmental Science and Technology*, 48(21). 12775-12782, 2014.
- Gambogi, J., Minerals Yearbook, U.S. Geological Survey.  
<https://pubs.er.usgs.gov/publication/70048194>, 2014.
- Gantt, B., Hoque, S., Fahey, K.M., Willis, R.D., Delgado-Saborit, J.M., Harrison, R.M., Zhang, K.M., Jefferson, D.A., Kalberer, M., Bunker, K.L., Conny, J.M., Bhawe, P.V., Weinstein, J.P., Pye, H.O.T., “Factors affecting the ambient physicochemical properties of cerium-containing particles generated by nanoparticle diesel fuel additive use,” *Aerosol Science and Technology*, 49(6). 371-380, 2015.
- Grigoratos, T., Martini, G., “Brake wear particle emissions: a review,” *Environmental Science and Pollution Research*, 22(4). 2491-2504, 2015.
- Hansen, D.A., Edgerton, E., Hartsell, B., Jansen, J., Burge, H., Koutrakis, P., Rogers, C., Suh, M., Chow, J., Zielinska, B., McMurry, P., Mulholland, J., Russell, A., Rasmussen, R.,

- “Air quality measurements for the aerosol research and inhalation epidemiology study,” *Journal of the Air and Waste Management Association*, 56(10). 1445-1458, 2006.
- Hughes, L.S., Cass, G.R., Gone, J.E.C., Ames, M., Olmez, I., “Physical and chemical characterization of atmospheric ultrafine particles in the Los Angeles area,” *Environmental Science and Technology*, 32(9). 1153-1161, 1998.
- Jansen, K.L., Larson, T.V., Koenig, J.Q., Mar, T.F., Fields, C., Stewart, J., Lippmann, M., “Associations between health effects and particulate matter and black carbon in subjects with respiratory disease,” *Environmental Health Perspectives*, 113(12). 1741-1746, 2005. doi: 10.1289/ehp.8153
- Johnson, A.C., Park, B., “Predicting contamination by the fuel additive cerium oxide engineered nanoparticles within the United Kingdom and the associated risks,” *Environmental Toxicology and Chemistry*, 31(11). 2582-2587, 2012. doi: 10.1002/etc.1983
- Jung, H., Kittelson, D.B., Zachariah, M.R., “The influence of a cerium additive on ultrafine diesel particle emissions and kinetics of oxidation,” *Combustion and Flame*, 142(3). 276-288, 2005.
- Kulkarni, P., Chellam, S., Fraser, M.P., “Tracking petroleum refinery emission events using lanthanum and lanthanides as elemental markers for PM<sub>2.5</sub>,” *Environmental Science and Technology*, 41(19). 6748-6754, 2007.
- Lauer, F.T., Mitchell, L.A., Bedrick, E., McDonald, J.D., Lee, W.Y., Li, W-W., Olvera, H., Amaya, M.A., Berwick, M., Gonzales, M., Currey, R., Pingitore, N.E., Burchiel S.W., “Temporal–spatial analysis of U.S.–Mexico border environmental fine and coarse PM air sample extract activity in human bronchial epithelial cells,” *Toxicology and Applied Pharmacology*, 238(1). 1-10, 2009.

- Li, W-W., Orquiz, R., Garcia, J.H., Espino, T.T., Pingitore, N.E., Gardea-Torresdey, J., Chow, J., Watson, J.G., “Analysis of temporal and spatial dichotomous PM air samples in the El Paso-Cd. Juarez air quality basin,” *Journal of the Air and Waste Management Association*, 51(11). 1551-1560, 2001.
- Lewis, R.J., editor, *Hawley's Condensed Chemical Dictionary*, New York, John Wiley and Sons, 229–231, 2001.
- Majestic, B.J., Erdakos, G.B., Lewandowski, M., Oliver, K.D., Willis, R.D., Kleindienst, T.E., Bhave, P.V., “A review of selected engineered nanoparticles in the atmosphere: sources, transformations, and techniques for sampling and analysis,” *International Journal of Occupational and Environmental Health*, 16(4). 488-507, 2010.
- Olvera, H.A., Perez, D., Clague, J.W., Cheng, Y.S., Li, W-W., Amaya, M.A., Burchiel, S.W., Berwick, M., Pingitore, N.E., “The effect of ventilation, age, and asthmatic condition on ultrafine particle deposition in children,” *Pulmonary Medicine*, Article ID 736290. 9 pages, 2012.
- Park, B., Donaldson, K., Duffin, R., Tran, L., Kelly, F., Mudway, I., Morin, J.P., Guest, R., Jenkinson, P., Samaras, Z., Giannouli, M., Kouridis, H., Martin, P., “Hazard and risk assessment of a nanoparticulate cerium oxide-based diesel fuel additive - a case study,” *Inhalation Toxicology*, 20(6). 547-66, 2008. doi: 10.1080/08958370801915309.
- Paz L.M., Amaya M.A., Clague J.W., Li W-W., Olvera H.A., Berwick M., Burchiel S.W., Pingitore N.E., “Airborne Lead in El Paso, Texas, U.S.A.” *Journal of Atmospheric Pollution*, 5(2). 47-54, 2017. doi: 10.12691/jap-5-2-2.
- Perry, R., Gee, I.L., “Vehicle emissions in relation to fuel composition,” *Science of the Total Environment*, 169(1-3). 149-156, 1995.

- Pingitore Jr, N.E., Clague, J., Amaya, M.A., Maciejewska, B., Reynoso, J.J., “Urban Airborne Lead: X-ray Absorption Spectroscopy Establishes Soil as Dominant Source,” *Public Library of Science One (PLoS One)*, 4(4). e5019, 2009.  
<http://www.plosone.org/article/info:doi/10.1371/journal.pone.0005019>.
- Powell, J.W.D., Hunt, A., Abraham, J.L., “Anthropogenic vanadium-chromium-iron and cerium-lanthanum-iron particles in settled urban house dust: CCSEM identification and analysis, *Water, Air, and Soil Pollution*, 135(1-4). 207-217, 2002.
- Reff, A., Bhawe, P.V., Simon, H., Pace, T.G., Pouliot, G.A., Mobley, J.D., Houyoux, M., “Emissions inventory of PM<sub>2.5</sub> trace elements across the United States,” *Environmental Science & Technology*, 43(15). 5790-5796, 2009.
- Reimann, C., de Caritat, P., Chemical Elements in the Environment. Berlin: Springer Verlag; 2011.
- Rohr, A.C., Wyzga, R.E., “Attributing health effects to individual particulate matter constituents,” *Atmospheric Environment*, 62. 130-152, 2012.
- Shacklette, H.T., Boerngen, J.G., “Element concentrations in soils and other surficial materials of the conterminous United States,” *U.S. Geological Survey Professional Paper 1270*, U.S. Department of the Interior, Washington, D.C., United States Government Printing Office. 1984.
- Skillas, G., Qian, Z., Baltensperger, U., Matter, U., Burtscher, H., “The influence of additives on the size distribution and composition of particles produced by diesel engines,” *Combustion Science and Technology*, 154(1). 259-273, 2000.
- Stedman, D.H., Bishop, G., McLaren, S., U.S. Patent No. 5,498,872. Washington, DC: U.S. Patent and Trademark Office. 1996.

- U.S. EPA, “Method IO-3.3 Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence (XRF) Spectroscopy, “*Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air*,” EPA/625/R-96/010a, Environmental Protection Development, June 1999.
- U.S. EPA, “Air Quality Criteria for Particulate Matter,” EPA 600/P-99/002af-bF. Research Triangle Park, NC, U.S. Environmental Protection Agency, 2004.
- U.S. EPA, “Provisional Peer Reviewed Toxicity Value for Cerium (CASRN 7440-45-1),” 2005.  
[https://hero.epa.gov/hero/index.cfm/reference/download/reference\\_id/88346](https://hero.epa.gov/hero/index.cfm/reference/download/reference_id/88346)
- U.S. EPA, “Toxicological review of cerium oxide and cerium compounds (CAS No. 1306-38-3) in support of the summary information on the Integrated Risk Information System (IRIS),” Washington, DC, U.S. Environmental Protection Agency, 2009.  
[https://cfpub.epa.gov/ncea/iris/iris\\_documents/documents/toxreviews/1018tr.pdf](https://cfpub.epa.gov/ncea/iris/iris_documents/documents/toxreviews/1018tr.pdf)
- U.S. EPA, “Revised air quality standards for particle pollution and updates to the Air Quality Index (AQI),” *The national ambient air quality standard for particle pollution*, 2012.  
[https://www.epa.gov/sites/production/files/2016-04/documents/2012\\_aqi\\_factsheet.pdf](https://www.epa.gov/sites/production/files/2016-04/documents/2012_aqi_factsheet.pdf)
- U.S. EPA, “Particulate Matter (PM) Standards - Table of Historical PM NAAQS,” *Reviewing National Ambient Air Quality Standards (NAAQS)*, 2016.  
[https://www3.epa.gov/ttn/naaqs/standards/pm/s\\_pm\\_history.html](https://www3.epa.gov/ttn/naaqs/standards/pm/s_pm_history.html)
- WHO (World Health Organization), “Nanotechnology and human health: Scientific evidence and risk governance,” *Report of the WHO expert meeting 10–11 December 2012, Bonn, Germany*, Copenhagen, WHO Regional Office for Europe, 2013.
- Zhang, J., Nazarenko, Y., Zhang, L., Calderon, L., Lee, K.B., Garfunkel, E., Schwander, S., Tetley, T.D., Chung, K.F., Porter, A.E., Ryan, M., Kipen, H., Liroy, P.J., “Impacts of a

nanosized ceria additive on diesel engine emissions of particulate and gaseous pollutants,” *Environmental Science and Technology*, 47(22). 13077-13085, 2013.



## **VITA**

Esenam Adzo Fumador was born in Ho-Ghana in West Africa on November 8 1982. She attended Aburi Girls Senior High School for her senior secondary certificate and continued with her undergraduate study at the University of Cape Coast in 2003. She graduated with a bachelors degree in Environmental Science in May 2007. She had a career as a liaison officer with several oil marketing companies in Ghana and also worked as an Environmental Consultant with SAL Consult Limited Ghana. In the spring of 2016, she entered the Graduate School of the University of Texas at El Paso (UTEP) to pursue a masters degree in Environmental Science. She was a Teaching Assistant and a Part-time faculty during the course of her study at UTEP. She plans to pursue a PhD in the future.