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Cerium Levels in Coarse and Fine Airborne Particulate Matter in El Paso, Texas, U.S.A.

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Abstract In Europe, ceria or cerium dioxide (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 nano-ceria (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, Texas, U.S.A., which shares a common air shed with contiguous Ciudad Juarez, Chihuahua, Mexico where n-Ce might also be used. This study analyzed weekly total concentrations of cerium in El Paso air at 8 sampling stations during 2006 to 2009. A PM_{10} dichotomous sampler simultaneously collected PM_C (the PM_{10} to $PM_{2.5}$ fraction) and PM_F or $PM_{2.5}$. An X-ray fluorescence instrument measured cerium in the two PM fractions. Results indicate higher levels of airborne cerium in PM_C (~2 ng/m^3 average for all sites for entire study period) than in PM_F (~1 ng/m^3). Higher values for coarse and to a lesser degree for fine PM are associated with sites proximal to the urban core of the binational El Paso—Cd. Juarez metroplex. This indicates significant anthropogenic contribution to airborne cerium in El Paso; abrasion of vehicle parts that incorporate cerium-doped alloys, residual cerium catalysts from gasoline refining, other commercial and industrial debris, and open-air waste burning are likely sources. No overall seasonal patterns were evident other than a possible decrease in PM_C during the summers; this is consistent with a significant anthropogenic contribution. Background Ce levels are low relative to those anticipated from possible future use of n-Ce additives, and thus any such increases would be readily detectable in future monitoring. Current Ce levels appear to pose no local health risk relative to tentative U.S. Environmental Protection Agency reference concentrations.

Keywords: *cerium, nanoparticles, air pollution, particulate matter, El Paso*

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1. Introduction

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_{10} and $PM_{2.5}$ emissions [1]. Cerium additives shift emitted DPM in the direction of smaller particle sizes, 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 size particles are formed [2]. However, the total amount of particulate matter emitted has been shown to decrease substantially [3]. Nano-ceria additives also lower the emission of ozone and several hazardous air pollutants (HAPs) from mobile diesel sources [1]. Adding cerium-based additives to diesel fuels reduces the organic carbon content of PM but does not influence elemental carbon, but no reason was ascribed to this observation. Ceria particles are also emitted as part of DPM upon the addition of cerium-based additives [2]. The examination of filters in that study revealed n-Ce is emitted in the particle phase within a size range of 20 to 80 nm [2]. This fact was also confirmed when it was determined that ceria particles, whether emitted individually or in association with soot, had a size of approximately 75 nm [4]. Most of the ultrafine particles existed in its Ce^{+4} oxidation state [2]. Other studies also confirm n-Ce particles are emitted in smaller particle sizes composed mostly of CeO_2 and perhaps 40% as aggregations of CeO_2 with soot particles [4]. Further studies confirmed emission reduction of CO_2,

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 engine were measured and compared [5].

1.1. Nano-ceria Fuel Additives in the Market

Currently, Europe, Asia Pacific, Canada, and India permit the use of engineered n-Ce as additives in diesel fuel. It is significant to realize that about one-third of newer passenger cars in Western Europe are diesel-fueled, due in the main to the high cost of vehicular fuel, since diesels yield higher milage than gasoline-powered engines [1,3]. The use of n-Ce in on-road vehicles began in 2003 in the U.K., 2005 in New Zealand, and 2010 in Canada [4].

There are three different brands of cerium-based fuel additives currently being marketed, namely Platinum Plus®, Eolys® and Envirox®. Platinum Plus®, 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_2 limits. Envirox® can only be used in off-road vehicles in the United States but is also currently not registered with the U.S. EPA and cannot be found in the marketplace [1,6]. The current Platinum Plus® formulation for sale 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 (190 x 10^9 l) of fuel yearly, thus emitting 300,000 tons of fine particulates ($PM_{2.5}$) into the atmosphere [1]. Despite the fact that it could lower such emissions, the use of cerium-based fuel additives in diesel fleets remains under regulatory study in the U.S. In the United Kingdom, these additives are widely used in diesel cars, buses and coaches [7].

A case study in 2007 by CDTi (Clean Diesel Technologies Inc.) showed how n-Ce-containing Platinum Plus® was tested in the United States and shown to improve fuel economy and reduce soot emission in a fleet of school buses operated by DATTCO Bus Company [8]. However, as stated earlier, the product is no longer registered with the U.S. EPA for use.

1.2. Nano-ceria and Health

There is reasonable concern about the release of any natural or manufactured nano-particles into the environment [9]. The particles may present threats due to, among other factors, shape, elemental content, surface reactivity, radioactivity, sorbed species, etc. Of particular concern is the deep penetration of nano-particles into the respiratory tract, and their ability, in some cases, to be transported to distant organs, e.g., the brain [10].

According to [11] 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 [1,6,11,12]. 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 [12].

There are few studies of the human effects of respiration of n-Ce, and even fewer about tail-pipe emissions of n-Ce, the surfaces of which particles can be coated with adsorbed diesel soot. As examples, [13] found that 20-nm-sized ceria particles significantly and sequentially decreased viability in lung-cancer cell lines with increased dosages and exposure times. Likewise, both cerium nano-particles and micro-particles were found to be cytotoxic and genotoxic in an allium test (a standard test for environmental monitoring) of root meristematic cells [14]. On the other hand, some positive health effects of n-Ce have been noted. Because of its catlytic properties that can scavange free radicals, it has been suggested that n-Ce can be employed as a well-tolerated (in murine studies) therapy for chronic inflammation [15].

1.3. Cerium Natural Occurrence and Uses

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, or an abundance some three times greater than that of lead (Pb) [16]. It is a very reactive element (reacting with oxygen to form ceria, or cerium oxide, CeO_2) and a strong oxidizing agent [11].

Cerium is found in the atmosphere, although in minute quantities, because of mineral dust suspension in air [4]. The element is incorporated at high concentrations in such cerium source minerals as the Ce-rich forms of allanite ($\{CaCe\}\{Al_2Fe^{2+}\}(Si_2O_7)(SiO_4)O(OH)$, monoclinic), as well as in monazite ($CePO_4$, monoclinic), and bastnaesite ($Ce(CO_3)F$, hexagonal) [17]. It also occurs as a minor or trace element in numerous other minerals.

Important industrial uses for cerium include glass polishing powders, *Mischmetal* for lighter flints and other applications, catalysts for petroleum refining, automotive catalytic converters, metal alloys, a catalyst in the walls of self-cleaning ovens, fuel additives, and various electronic and optoelectonic devices [6,11,12]. For all rare earths as a group, the U.S. Geological Survey estimates their usage as: catalysts, 55%; ceramics and glass, 15%; metallurgical applications and alloys, 10%; polishing, 5%; and other, 15% [18]. According to the U.S. Geological Survey the United States imported its entire supply of 2,700 tonnes of cerium compounds in 2017 [18].

The powerful catalytic properties of ceria arise from its reversible Ce^{3+}/Ce^{4+} redox pair and its surficial acid-base effects. In addition, the surface of engineered n-Ce hosts numerous oxygen-vacancy defects, providing additional sites for catalytic activity [19].

As a diesel additive, the adsorption of oxygen to the n-Ce surface makes it available to oxidize soot at temperatures far lower than soot's conventional oxidizing temperature. This mechanism makes n-Ce effective in reducing particle emission in diesel powered vehicles [6].

1.4. Rationale: Establish Baseline Ce Levels for Possible Monitoring in the Future

The potential for engineered n-Ce based fuel additives to reduce the emission of important air pollutants has been demonstrated in several scientific studies, and the use of n-Ce in fuel additives is prominent in the vehicular

technology sector outside of the U.S. [6]. There is a reasonable chance that at some point in the near future n-Ce could be approved for on-road use in the U.S. Therefore, to validate possible future monitoring for this element it is important to establish "pre-approval" background levels of cerium in urban settings.

In addition, an understanding of current natural (geologic) and anthropogenic sources of cerium also is of interest, from both a scientific and reguatory standpoint. Thus this study focuses on determining the background cerium concentration in El Paso, Texas, and possible current sources of the metal in the city.

It should be emphasized that the collecting equipment used in this study, and in most scientific and monitoring studies, measures only the level of the element cerium. It does not speciate, or determine the compound(s) that incorporate cerium, or indicate whether the cerium is in a nano-sized particle. Such information is beyond the capability of routine regulatory monitoring and is addressed normally only in advanced scientific studies. Any future monitoring for cerium, should n-Ce additives be permitted in the U.S., would most likely involve conventional sampling for unspeciated total airborne cerium.

1.5. El Paso Setting – Geography and Climate

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. Because of their proximity, the twin cities share a common air mass, often designated the *Paso del Norte* ("pass of the north") air shed. With the Rio Grande as the national boundary and its floodplain as a low point, the region exhibits a bowl-shaped topography, ringed in part by low mountains.

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. Materials and Methods

2.1. Sampling

Sampling was carried out at eight different sites (see Figure 1 and Table 1) for a period of 3.4 years, from August 2006 to December 2009. Sampling sites were spread across El Paso County to achieve a wide areal coverage of the more populated parts of the county. 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 equipment security and access to electricity [20]. Filters were exposed for a full week collection period for fine and coarse PM at each site.

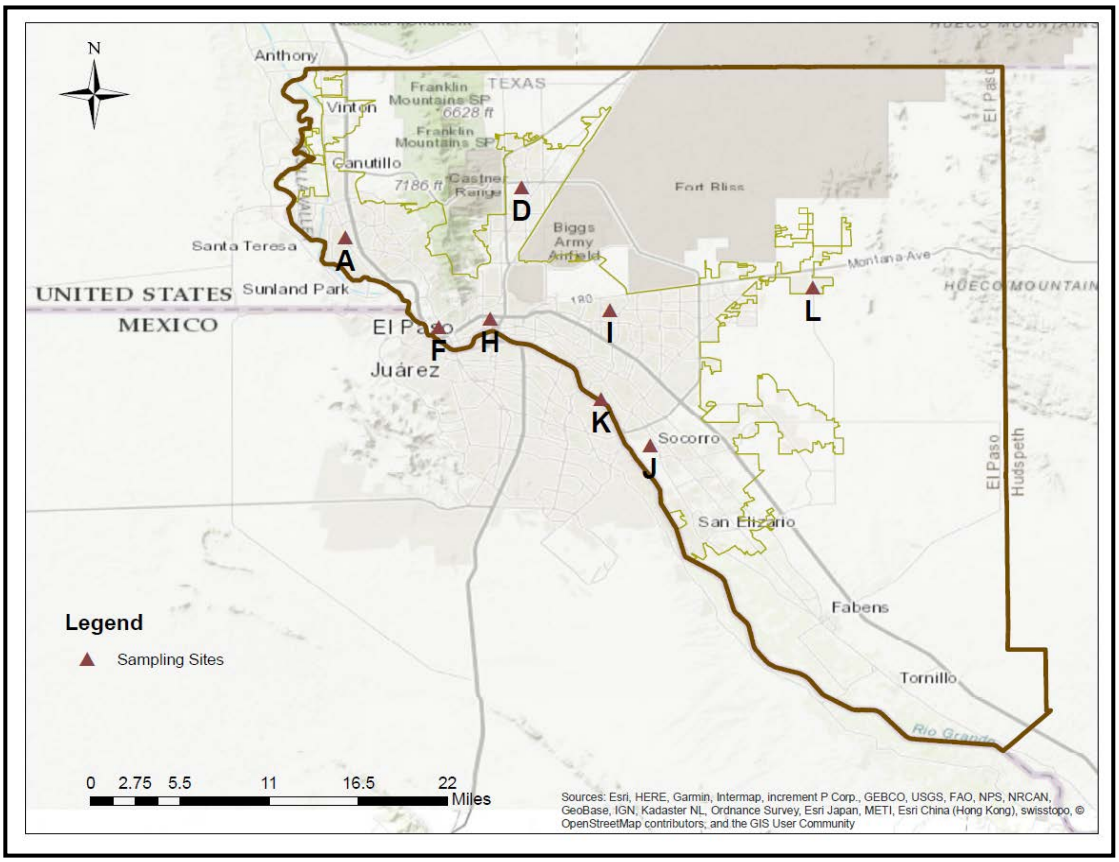

Figure 1. (Color online) Map of study area showing sampling sites within El Paso County (bold outline)

Table 1. Description of sampling sites in El Paso, Texas [20]

Site	Description
A	Predominantly residential area in west El Paso, adjacent to railroad tracks.
D	Northeast El Paso, classified as a residential location.
F	Adjacent to the campus of the University of Texas at El Paso (UTEP). Residential and some commercial.
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	Far southwest area of El Paso, the mixed urban—rural Mission Valley.
K	Southwest area of El Paso (Mission Valley), chiefly residential.
L	Monte Vista, newer residential area in easternmost El Paso, proximal to desert.

2.2. Samples

Sampling was done with a PM_{10} 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 [21]. Samples were collected on 37-mm Teflon® filters, preconditioned at 25 ± 5°C and 30 ± 5% relative humidity for 24 hours, weighed, and stored in petri dishes for less than 30 days prior to sampling [22].

2.3. Physical and Elemental Analysis

The mass concentrations of PM_C and PM_F were gravimetrically determined for each sample collected according to U.S. EPA Compendium Method IO-2.2 [21]. Cerium concentrations on the filters were 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 [20,23]. For calibration of the XRF instrument, U.S. National Institute for Standards and Technology (NIST) Standard Reference Materials (SRMs), together with Micromatter commercial thin-film single-element standards were employed [20]. For each sample the mass concentration of cerium per square centimeter of exposed filter ($\mu g/cm^2$) 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 Epsilon 5 for PM_C was 0.02 ng/m^3 and for PM_F 0.002 ng/m^3.

2.4. Data Analysis

Microsoft™ Excel was used in cleaning (elimination of missing samples, checks for misprints, etc.) 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 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 near vicinity of sampling points. This provided an estimate of the cerium levels within El Paso County at unsampled locations.

2.5. Data Compilation: Seasonality and Geography

Following the protocols of an earlier paper on lead in El Paso, the weekly PM data were combined to create three "seasons" per year to reflect the local climate regime. February 15th through June 15th was selected as spring, a dry and typically windy period [20]. Summer in El Paso is characterized by high temperatures and a late-summer rainy "monsoon," with brief, often intense, precipitation. This season ran from June 16th through October 15th in our construct. Winter was taken as October 16th through February 14th. The season is commonly characterized by atmospheric temperature inversions that can trap particulate matter near the surface, particularly in the more dense neighborhoods of El Paso and contiguous Cd. Juarez. Because of the altitude, winter temperatures at night can result in hard freezes.

By compacting the data from weekly to seasonal, it becomes simpler to make geographic, annual, and seasonal comparisons. It should be further noted that annual sums can represent the total exposure of a resident to cerium. By geographic comparisons, the exposure of different neighborhoods can be evaluated.

3. Results and Discussion

3.1. Presentations of Data

After excluding missing or invalid data, 1,995 samples were studied, with concentrations ranging from 0.00 to 13.2 ng/m^3. Figure 2 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, and error bars depicting the standard deviation for each particle fraction for the entire study. Figure 3 presents these averages at their geographic locations. Figure 4 and Figure 5 are IDW interpolation maps developed from ArcGIS showing the extrapolation of cerium concentrations for El Paso County. Figure 6 and Figure 7 are seasonal averages of cerium plotted at each site for the entire study period. Figures 8 and 9 are the seasonal averages, by year, of cerium levels in bar-graph format. Table 2 displays the basic statistics (number of samples, means, standard error of the mean, and maximum concentrations) for cerium concentrations in both PM fractions for the entire study. Table 3 shows the same basic statistics for cerium levels in both PM fractions for each site during the entire study period.

3.2. Overview

Analysis of the data provides evidence of the continual and prevasive presence of airborne cerium at detectable levels in the *Paso Del Norte* airshed. 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 errors of the

mean of 0.053 and 0.032 respectively (see Table 2). The highest cerium levels recorded were 13.2 ng/m^3 at site F and 5.32 ng/m^3 at site K for coarse and fine PM respectively (Table 3). Based on the values in Table 3, it is evident that coarse PM consistently recorded higher values for cerium concentrations at each site compared to fine PM. There is 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.

The highest average cerium level computed for PM_C was 2.63 ng/m^3, which occurred at site J. Three sites, H, J and K recorded averages higher than the yearly average of ~2 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 ng/m^3. Sites A, D, H, I and K recorded averages above the yearly average of 1 ng/m^3 for cerium levels in PM_F.

Table 2. Basic Statistics for Cerium in PM_C & PM_F, All Sites, for 4-year Study Period, in ng/m^3

PM	N cases	Mean	Std Error	Maximum
Coarse	970	2.02	0.053	13.2
Fine	1025	1.12	0.032	5.32

Table 3. Statistics for Cerium in PM_C & PM_F At Each Site, for 4-year Study Period, in ng/m^3

Site		N cases	Mean	Std Error	Maximum
A	PM_C	139	1.70	0.12	7.46
	PM_F	134	1.23	0.09	4.20
D	PM_C	117	1.77	0.15	8.14
	PM_F	140	1.19	0.09	4.85
F	PM_C	108	1.91	0.19	13.2
	PM_F	114	0.73	0.09	4.11
H	PM_C	117	2.40	0.15	7.80
	PM_F	118	1.39	0.10	5.21
I	PM_C	129	1.95	0.14	8.60
	PM_F	132	1.37	0.09	4.40
J	PM_C	108	2.63	0.19	10.41
	PM_F	113	0.90	0.09	4.63
K	PM_C	136	2.34	0.14	9.82
	PM_F	141	1.25	0.09	5.32
L	PM_C	125	1.54	0.11	5.90
	PM_F	133	0.83	0.07	3.76

3.3. Comparison to Other Cities

Other studies [24,25,26] recorded varying background levels of cerium in $PM_{2.5}$ in different cities in the U.S., shown in Table 4. Background cerium levels recorded in Houston, Texas in 2006 for ambient $PM_{2.5}$ of ~ 0.38 ng/m^3 was about three times lower than that recorded for fine PM_F in El Paso, Texas in this study [26]. Values presented for cerium in PM_{10} in the U.K. all were taken before use of n-Ce was introduced in that nation.

Table 4. Cerium concentrations of $PM_{2.5}$ in U.S. cities and of PM_{10} in U.K. cities

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

3.4. Cerium Levels and Air Quality Regulations

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 ng/m^3 and 900 ng/m^3 for micro-sized cerium developed by the U.S. EPA for toxicological purposes [27,28]. These RfCs have been used as guideline values in some studies [1,4] 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 [4,29].

3.5. Possible Source(s) 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 [30].

As the most abundant REE, cerium can be found in several mineral classes, carbonates being the largest mineral group containing the metal [12]. Important mining sources of the metal are the carbonate mineral bastnaesite ($(Ce,La)CO_3(F)$, hexagonal) and the phosphate mineral monazite ($(Ce,La,Nd,Th)PO_4$, monoclinic). Cerium also occurs as a trace constituent in many minerals and has an average crustal abundance of 60 ppm [16].

In addition to geologic sources, the incorporation of cerium in industrial processes serves as an anthropogenic source of the metal in the environment. Vehicular sources of particulate matter can be categorized into exhaust and non-exhaust forms. Brake, tire and clutch wear constitute the main sources of non-exhaust emissions [31], whereas exhaust emissions are from fuel combustion and contain a variety of elements and compounds [32] of which cerium can be a part [1,33,34,35]. As demonstrated by [4,29], 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 and also contributes to anthropogenic cerium in air [7].

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 into the atmosphere [36]. Fuel oil and coal burning in power stations also emit rare earth elements as does open burning of solid waste.

Potential stationary local sources in El Paso would include Daltile™ ceramics and Western Refining, now Andeavor, a 135,000-barrel-per-day crude oil refinery that incorporates FCCUs [37]. 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 [26] provided documentation of FCCUs releasing lanthanides, chiefly lanthanum, in Houston, Texas air due to equipment breakdowns, similar evidence does not exist for El Paso. Those breakdowns resulted in lanthanide spikes 33-106 times background levels. Such occasional spikes did not appear in our data set for the proximal sampling sites.

3.6. Geographic Clues to 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 (~2 ng/m^3) values for PM_C (see Figure 3 and Figure 4). Sites A, D, H, I and K recorded values above 1 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 4 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.

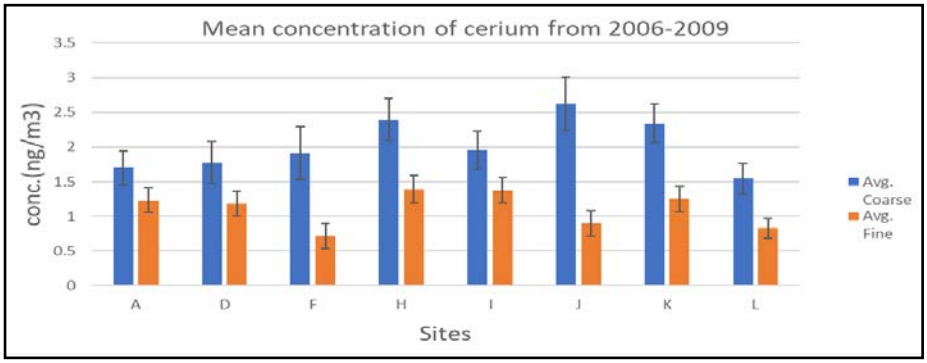

Figure 2. (Color online) Mean concentration of cerium at all sites for PM_C and PM_F (Error bars correspond to ± 2 SEM)

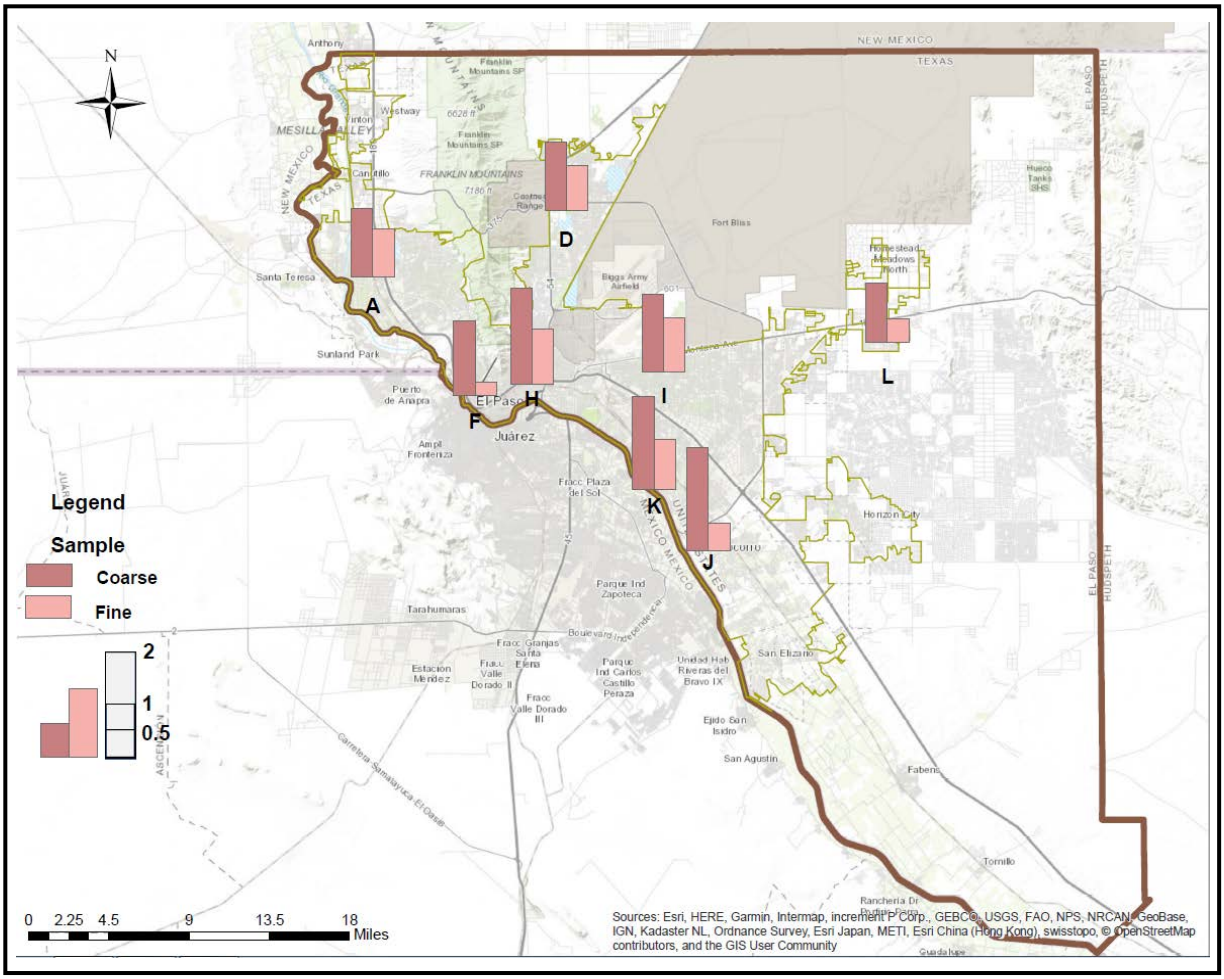

Figure 3. (Color online) Average cerium concentration in PM_C and PM_F monitored for all the sites

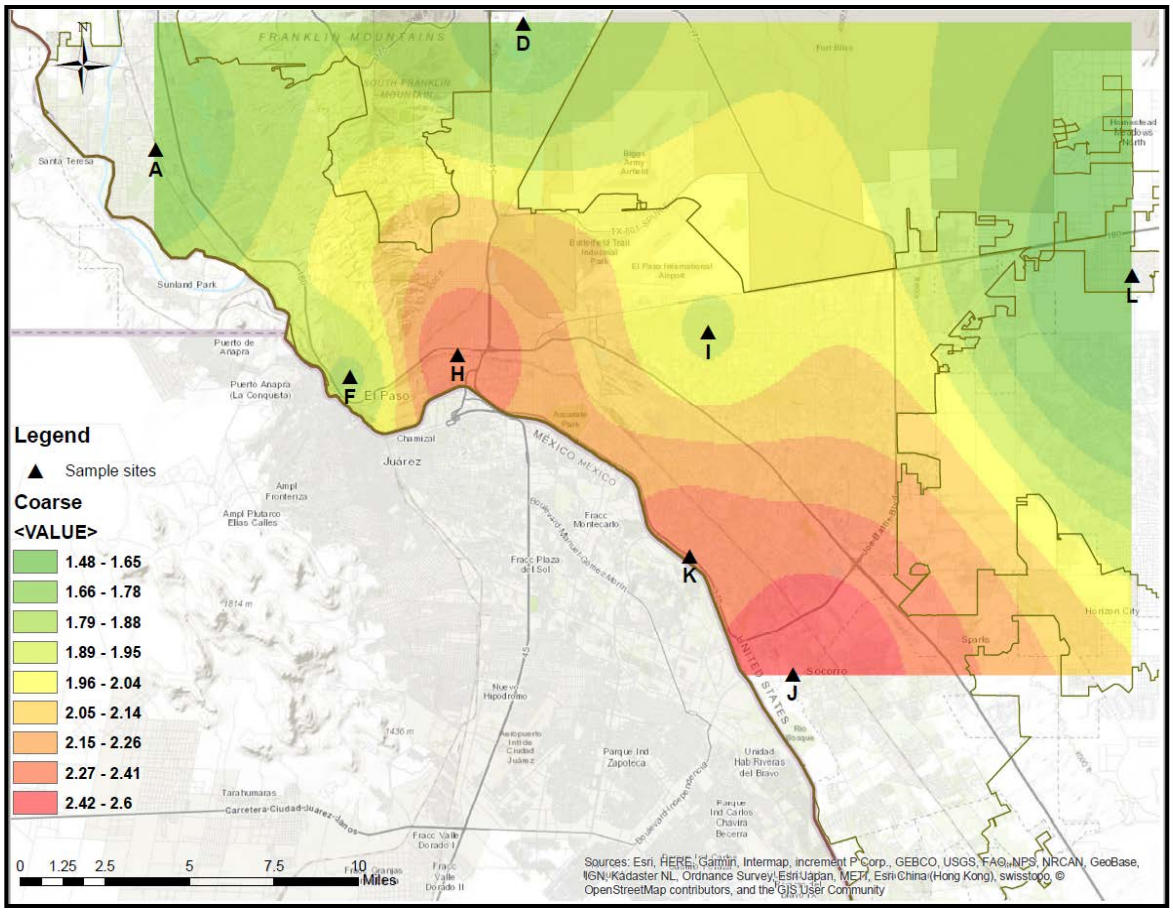

Figure 4. (Color online) Inverse Distance Weighted (IDW) interpolation of cerium level in PM

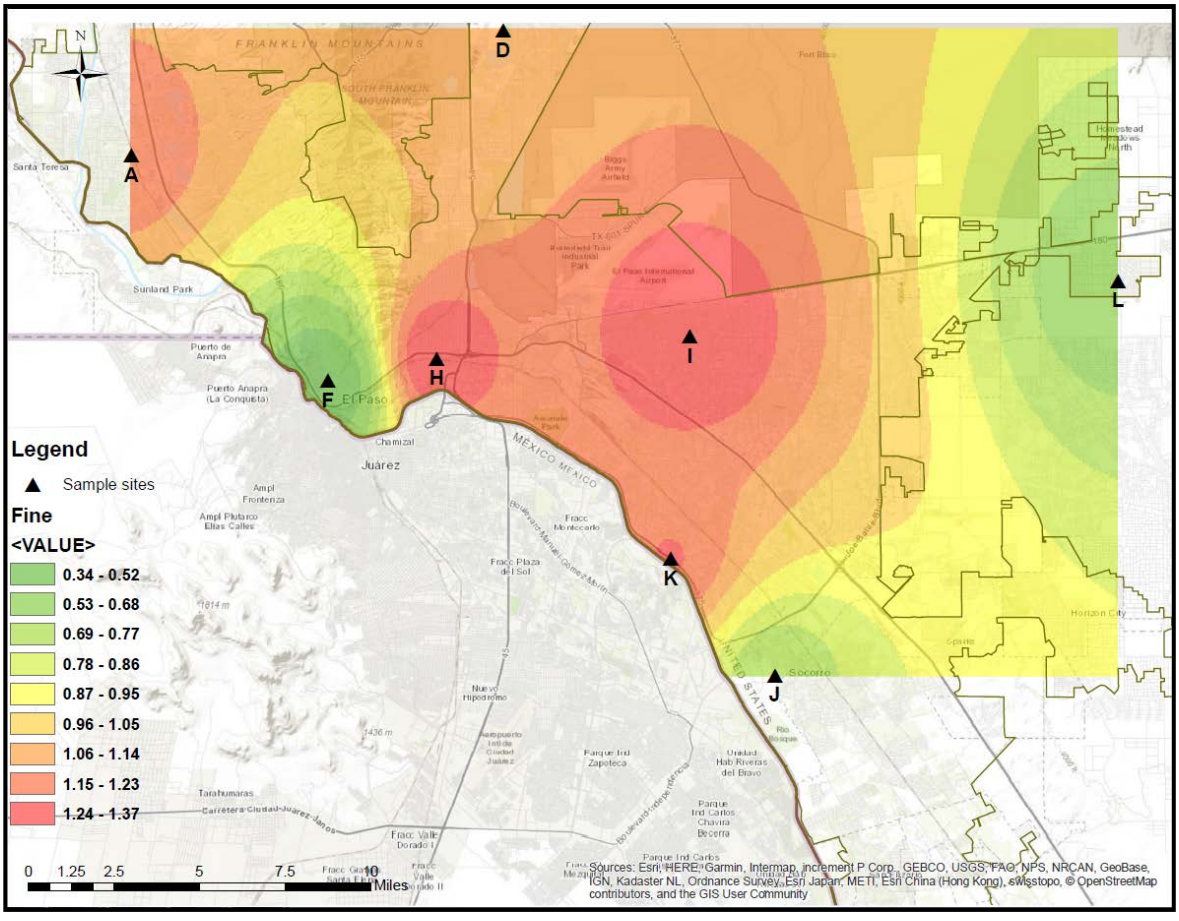

Figure 5. (Color online) Inverse Distance Weighted (IDW) interpolation of cerium level in PM_F

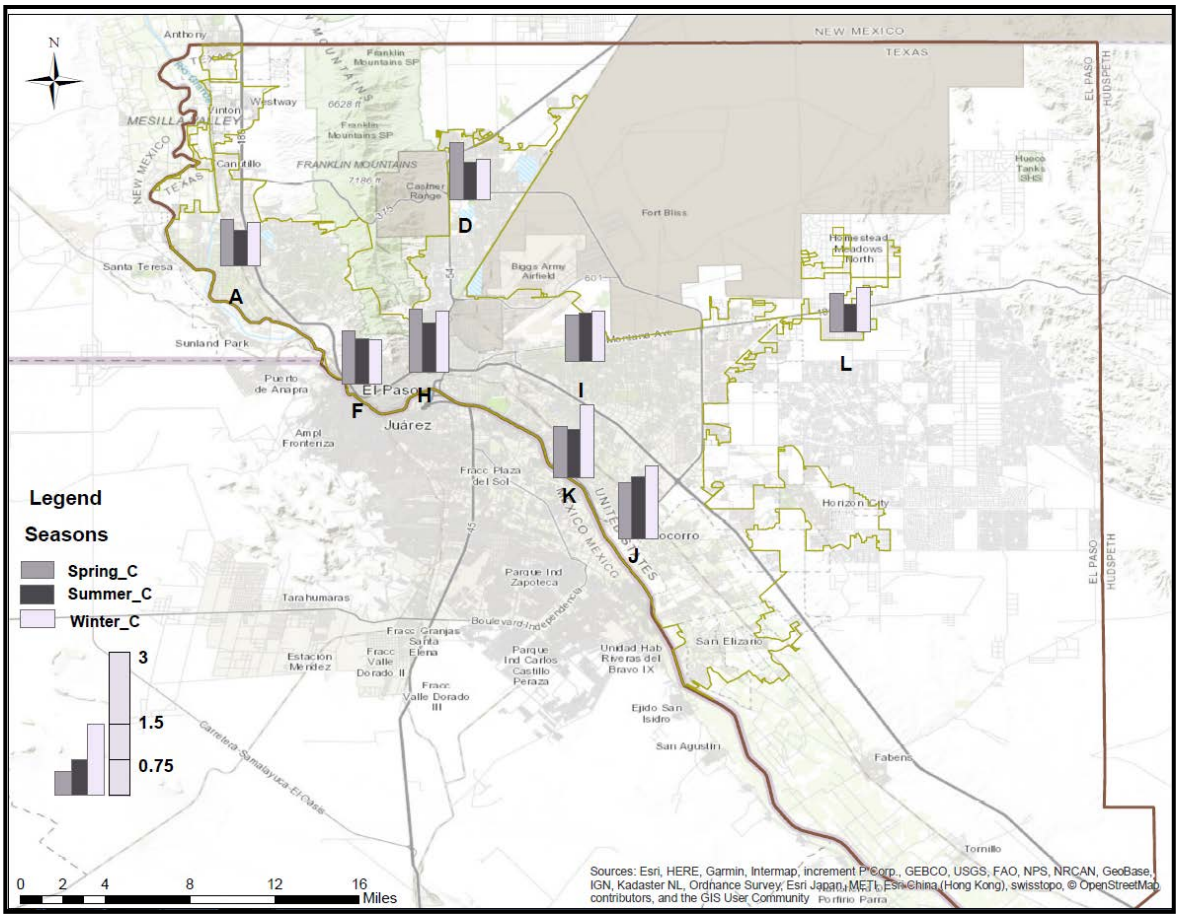

Figure 6. (Color online) Seasonal average of ambient fine cerium in spring, summer and fall recorded at all sites from 2006-2009

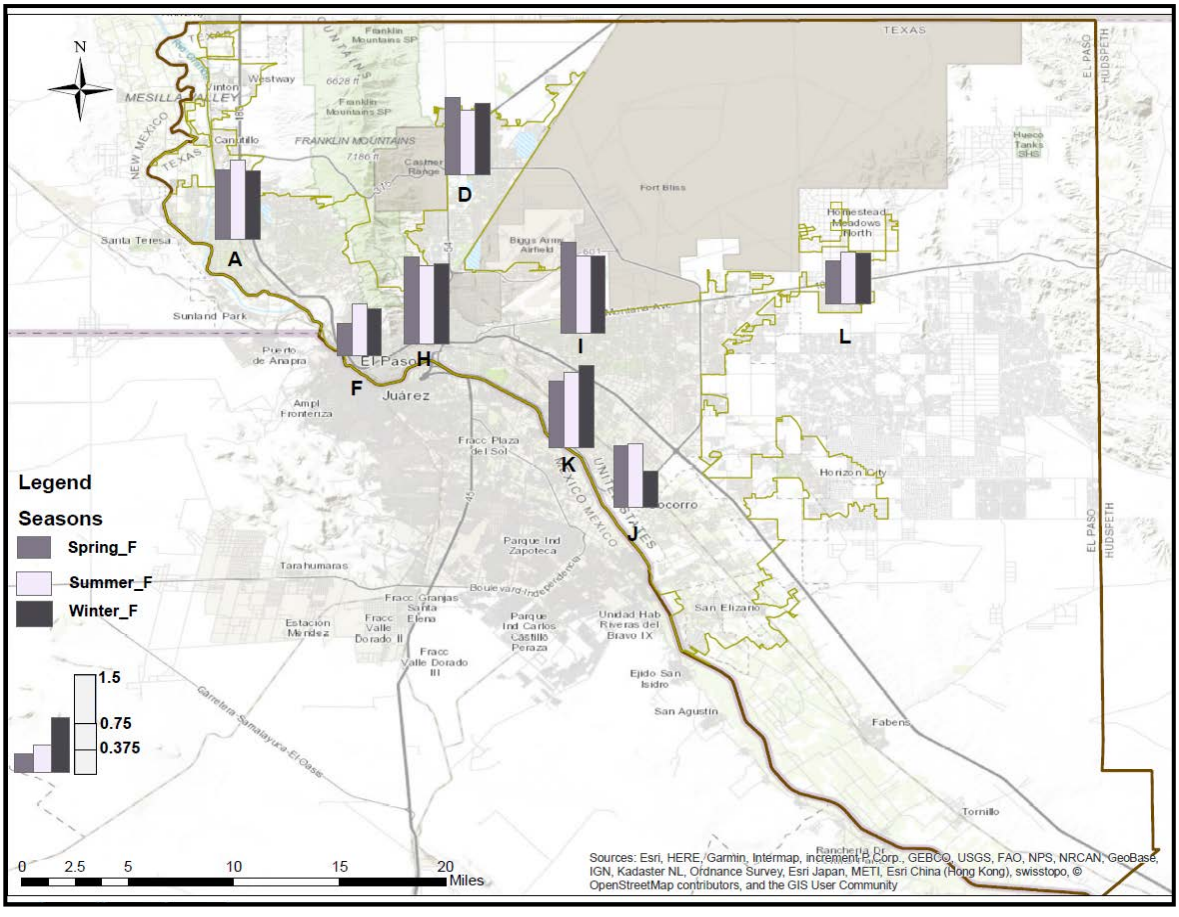

Figure 7. (Color online) Seasonal average of ambient fine cerium in spring, summer and fall recorded at all sites from 2006-2009

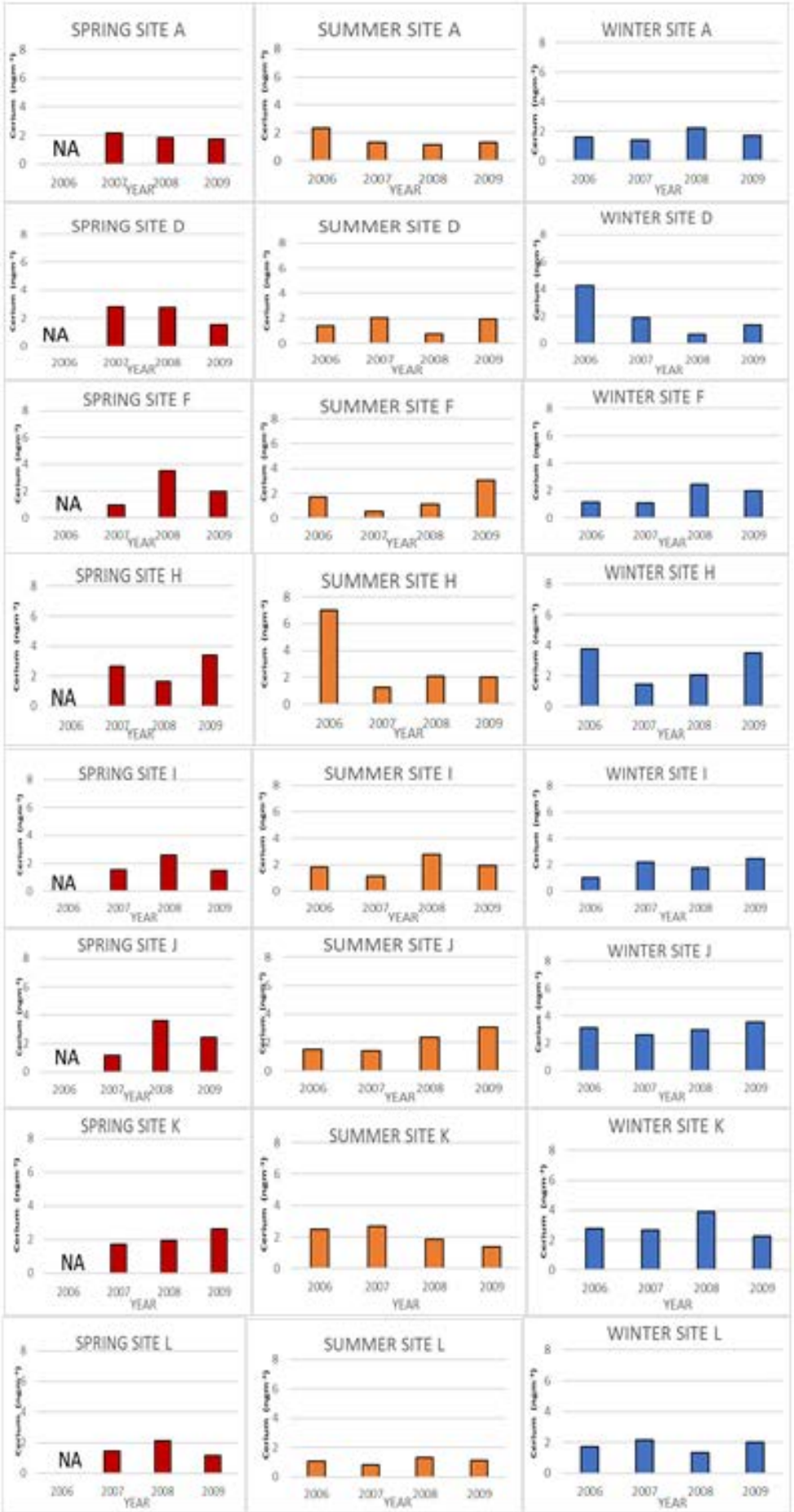

Figure 8. (Color online) Yearly average cerium levels by season in PM_C

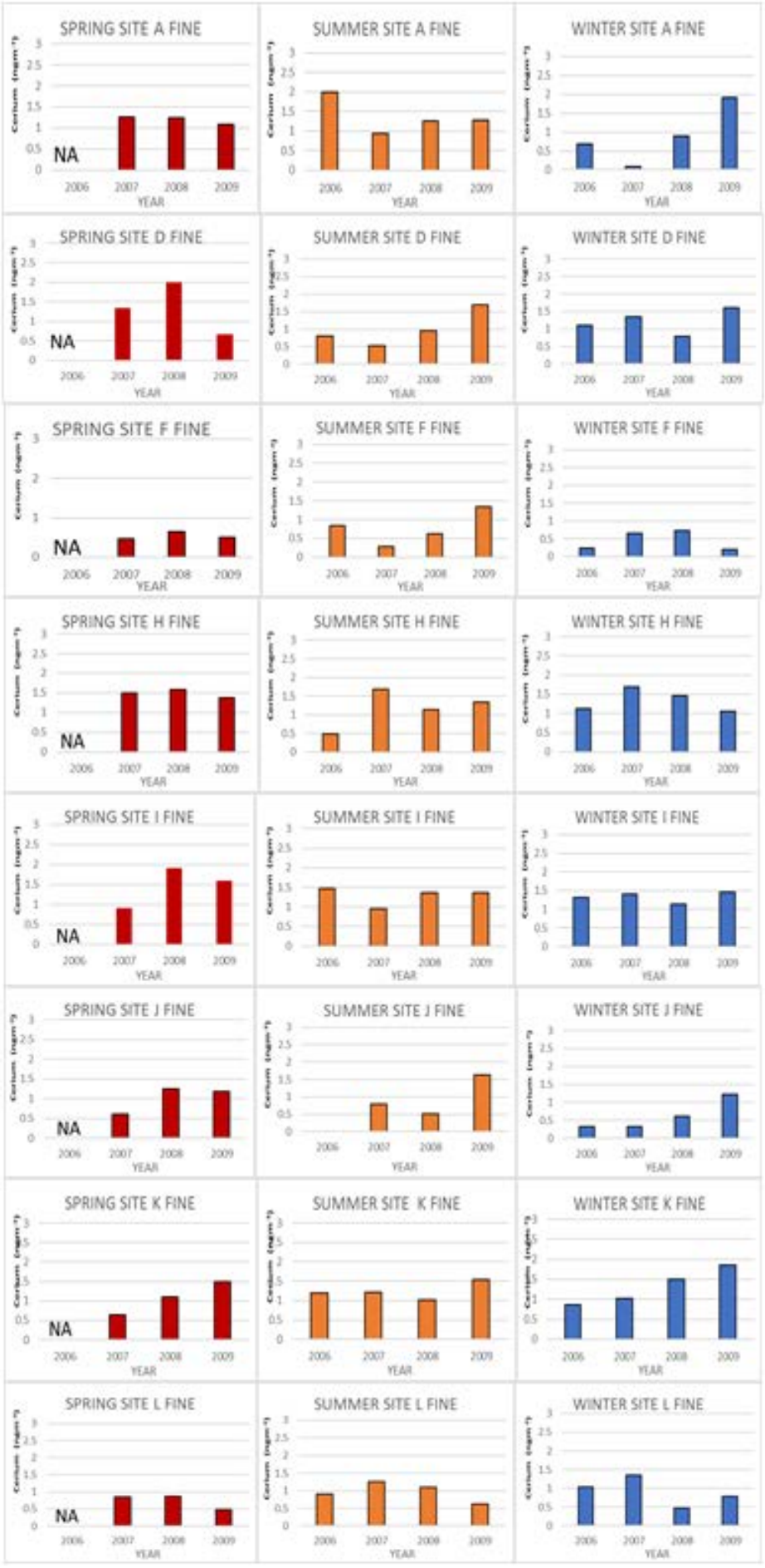

Figure 9. (Color online) Yearly average cerium levels by season in PM_F

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 [7], and cerium that remains in gasoline because of the FCCU crude oil refining process [26]. 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.

Levels of PM_F are generally the same for stations A, D, H, I, and K. Stations F, J, and L cluster at considerably lower cerium levels (Figure 3 and Figure 5). No explanation of this pattern is evident.

The salient feature of the maps (Figure 3, Figure 4 and Figure 5) is the overall concentration of higher cesium 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 [38] 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 [39].

3.7. Seasonal Variation

Figure 6 and Figure 7 are maps showing the average concentrations of coarse and fine cerium in spring, summer and winter, and Figure 8 and 9 are bar graphs permitting comparisons between sites and seasons. Figure 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.

3.8. Public Health Implications

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 [28,38,40]. Based on the higher levels of cerium detected in PM_C, 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 μm) indicates the possible existence of ambient anthropogenic nanoscale (<0.1μm) cerium particles in El Paso. Such n-Ce can reach deeper regions of the respiratory system compared to their microscale counterparts. However, as discussed in 3.4, cerium levels in El Paso are far below the U.S. EPA tentative inhalation reference l concentrations (RfCs) of 200 ng/m^3 and 900 ng/m^3 for micro-sized cerium [27,28].

4. Conclusions

The levels of airborne cerium recorded in El Paso, Texas for this study are higher in coarse particulate matter (overall average ~ 2 ng/m^3) compared to fine particulate matter (~ 1 ng/m^3). However, relative to the total particulate matter concentration for each size fraction, PM_F is richer in cerium than PM_C. Geographical variation indicated that a heavily trafficked urban core location (site H) recorded high levels of airborne cerium, in both PM_C and 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 PM_C, with lower values in the summer. No seasonal variations were apparent in the 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 use in the U.S. Erdakos et al. [1] predicted an average regional contribution of 0.5 ng/m^3 in $PM_{2.5}$ from the potential use of n-Ce, and up to 22 ng/m^3 in urban areas. Given the urban density of El Paso, anticipated increases would be easily detectable relative to current local PM_F levels 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.

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Statement of Competing Interests

NEP serves on the Board of Directors of Texas Mineral Resources Corporation, a publicly traded (stock ticker symbol TMRC) junior miner attempting to develop a rare earth mine in west Texas. Although cerium is present in the deposit, the mining emphasis would be on the more valuable heavy rare earths and other critical elements that characterize the mineralization in the Round Top deposit.

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