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# Heavy Metal Pollution In The Paso Del Norte Region: Historical Reconstruction And Source Interpretation

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HEAVY METAL POLLUTION IN THE PASO DEL NORTE REGION:  
HISTORICAL RECONSTRUCTION AND  
SOURCE INTERPRETATION

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## **Dedication**

This dissertation is dedicated to the loving memory of my parents  
and to all the citizens of El Paso.

HEAVY METAL POLLUTION IN THE PASO DEL NORTE REGION:  
HISTORICAL RECONSTRUCTION AND  
SOURCE INTERPRETATION

by

EUGENIA SHEKHTER, Master of Engineering

DISSERTATION

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for the Degree of

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## **ABSTRACT**

A unique and complex situation of heavy metal pollution arose in the El Paso del Norte region, one of the largest and oldest metropolitan areas on the US-Mexican border. This region with its complex topography is home to more than 2.2 million people sharing the same environment. Although many studies have been conducted in the region to identify the sources of environmental contamination, the cumulative history of heavy metal pollution is still incomplete.

In order to identify the patterns of heavy metal dispersion and to test the hypothesis that the American Smelting and Refining Company (ASARCO) was a considerable contributor to local heavy metal pollution, we have studied attic dust as a medium of investigation of air pollution history via environmental forensic methods. Undisturbed attic dust provides an integrated history of atmospheric loading of particulates emanating from geological, biological, and anthropogenic sources and helps reconstruct past air pollution events on a local scale.

Ninety-six attic dust samples were collected from surfaces in 15 houses and buildings of varying ages in two neighborhoods, Kern Place and Government Hill areas of El Paso, and from a downtown Ciudad Juarez location (Victoria Theater). Fifty-one combined dust samples and twelve combined samples of unpolluted buried soil horizons were extracted with Aqua Regia and were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP–OES) and Inductively Coupled Plasma Mass Spectrometry (ICP–MS). Concentration values of 17 major and trace elements in the dusts and soil were utilized for calculation of their enrichment factors (EFs). In order to further clarify the sources of heavy metals, the EF data were processed by summary statistics, Pearson correlation analyses, MANCOVA Willk's Lambda test, Cluster and Principal Component (PCA) statistical methods.

All the statistical analyses identified the same group of elements, six heavy metals/metalloids, associated with smelting processes. The mean EFs of Pb (263), As (81), Cd (333), Sb (644), Cu (475) and Zn (376) appeared abnormally high in contrast to other elements' EFs ( $<10$ ) in all locations, suggesting their anthropogenic origin. At the same time the EFs of these elements were much higher in attic dusts collected from Kern Place compared to Government Hill the latter being more distantly located from the ASARCO smelter. Dust from the newest attics and attic surfaces (pipes, ducts, storage containers) post-dating the 2000s showed lower heavy metals EF values than the dust collected on adjacent surfaces that were present during the smelter operation. A fundamental change in the EFs distribution of heavy metals/metalloids occurred after 1966, and it was the year when ASARCO constructed an 828 foot (252.4 m) smokestack. The strongest correlations ( $r > 0.92$ ,  $p < 0.0001$ ) were observed among Pb, As, Cd, Cu and Sb, being the highest from the attic dust sampled in Kern Place area. These metals/metalloids (with minor exceptions) were also grouped together into one cluster and factor, signifying their common source, non-ferrous ore smelting.

Based on the evidence provided by the dust analyses, it is concluded that the identified heavy metals were predominantly emitted from the smelter stack and were preferentially deposited in the surrounding area. The emissions could have followed wind trajectories near the surface along the Rio Grande valley rather than mixing to heights resulting in movement over the Franklin Mountains and deposited on the east side of El Paso.

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# **CHAPTER 1**

## **INTRODUCTION**

In the twenty-first century a deeper understanding of the complexity of environmental problems and the necessity to protect our planet has become one of the most crucial and timely tasks facing mankind. We have to consider the possibility of unpredictable transformations that may be occurring in our environment. Ecological mistakes on the local scale may well develop into a global catastrophe. We currently witness troubling phenomena such as climate change, ozone layer depletion, increasing intensity and frequency of natural disasters, a decrease of biodiversity, deforestation, desertification, progressive soil acidification, salinization and erosion, poor air quality and water pollution. Human social and economic systems may carry the planet into a crisis of no return.

Human beings, in contrast to other species, have altered and strived to control natural processes with the goal to improve their quality of life. This has often led to the opposite effect and resulted in deterioration of human health and disruption of the natural equilibrium. Population growth, changing social structures, enhancement of living standards and improvement of technology for natural resource utilization, may, directly or indirectly, lead to rapid deterioration of the environment.

With the progress of our civilization, especially during the last one hundred years, mankind has increasingly exploited the natural resources of our planet. Most used resources return in the form of waste that can be, in the worst case scenario, hazardous to the environment and all living organisms. Hazardous anthropogenic activities are increasing the pollutant load on the Earth. Large urban areas and megacities, which are constantly growing all over the world, are principally responsible for the enormous release of toxic and hazardous substances into the

environment, in particular, heavy metals/metalloids (Harrison and Laxen 1981; Samuel and Bennett 1983; Forstner 1995; Enger and Smith 2002; Bradl 2005). As more countries have become industrialized and urbanized, heavy metal pollution is reaching disturbing levels. In the past only minimal attention was paid to the prevention of discharges of these materials; however, in recent decades public awareness of heavy metal poisoning is growing even in developing countries.

## **1.1 The Innovative Approach of Biogeochemistry**

An attitudinal change towards the management of our environment is occurring through a more multidisciplinary and holistic approach. One such area is Biogeochemistry.

Biogeochemistry studies the mass exchange of chemical elements between living organisms and the environment, and how biological and geochemical processes affect element cycles in nature, considering space and time (Odum 1971 in Trudinger and Swaine 1979; Shlesinger 1997; Bashkin 2002; Krapivin and Varotsos 2008). In less than one hundred years, Biogeochemistry has become a very productive science with many developing divisions e.g. Evolutionary Biogeochemistry, Regional Biogeochemistry, Environmental Biogeochemistry and Human Biogeochemistry.

The scholar who laid the theoretical foundation of Biogeochemistry was the Russian geochemist Vladimir Vernadsky. Developing the traditions of D. Mendeleev and A. Docuchaev, Vernadsky proposed the revolutionary idea that the Earth and all its processes form a unified system. In his book “The Biosphere” (1926) he defined and described three Earth ‘spheres’ (the Riemann concept of space-phase): the Noosphere (cognitive processes), the Biosphere (the life processes), and the Abiotic Sphere (all non-living energy) (Vernadsky 1926). Each of them

evolved according to its own laws and interacts with the others on the hierarchical principle where the lower spheres, Abiotic and Biosphere, are modified and subordinated by the upper sphere – Noosphere. In contrast to the views of Austrian geologist E. Suess (who proposed a term “Biosphere” in 1875), Vernadsky perceived the notion of Biosphere not only as “the outer sphere of the earth where the living organisms exist”, but as a global system where all forms of life and their metabolites interact with inert matter and are inconceivable without each other, providing Earth’s biogeochemical organization (Vernadsky 1926; Bashkin 2002).

The essence of this interaction is the exchange of chemical elements between living organisms and their environment that is triggered by the living organisms themselves and not by geological factors. In spite of the fact that living matter occupies very little volume on the planet, it plays a principal role in the migration and transformation of chemical elements in various spheres of the Earth (Vernadsky 1926; Krapivin and Varotsos 2008). The migration and transformation of all elements take place not randomly, but in cycles and is determined by the activity of the organisms (Trudinger et al. 1992; Krapivin and Varotsos 2008).

The notion of cycle is a pivotal concept in Biogeochemistry. All known life forms on our planet are subordinated by cycles. The life cycle of the individual organism depends on, and is connected to, universal cycling processes (Degens 1989; Schlesinger 1997). At the same time biogeochemical cycles of all essential elements are interdependent (Trudinger et al. 1992).

Without a biogeochemical approach cycling is difficult to understand. This understanding requires new ways of looking at the complexity of biogeochemical systems, the integration of materials from different disciplines and especially the need for accumulation of information on a local scale (Butcher 1992; Schlesinger 1997; Bashkin 2002).

Biogeochemical cycles in natural conditions always sustain a dynamic equilibrium state - a balance in the cycling of different elements between the main reservoirs; e.g., Atmosphere, Hydrosphere, Lithosphere, Pedosphere (or Rhizosphere). Human intervention into the natural regularity of the biogeochemical cycles of the macro and trace elements has changed the stable chain of global biogeochemical cycles which formed as a result of Biosphere evolution (Krapivin and Varotsos 2008). Industrial and agricultural activities may modify and influence various stages of the cycles of certain elements, increasing or decreasing the amount of the elements at some stages of their cycles (Trudinger et al. 1992).

All the consequences of human activity can be viewed as particular examples of the wide – ranging influences of the Biosphere on the transformations of elements. Environmental pollution from the biogeochemical point of view is a reversible or irreversible alteration into biogeochemical structures within the ecosystem (Trudinger et al. 1992; Bashkin 2002). There are now only a few unpolluted ecosystems in the world. At the present time humans are on the verge of transforming the whole ecosystem structure from a natural to an anthropogenic form (Bashkin 2002).

Very profound deformations of natural biogeochemical cycles and mass exchange processes take place especially on the land because the terrestrial biogeochemical processes are significantly more extensive and the land is the main area of human productive activity (Bashkin 2002). The specific problems of the Earth's terrestrial biogeochemistry have come to the forefront and are severely impacting the sustainable development of mankind. Humans have changed many aspects of the lithosphere's biogeochemistry as well as other spheres, especially the Hydrosphere and Atmosphere (Degens 1989; Schlesinger 1997; Bradl 2005).

Water covers 71% of the global surface, and the water cycle is highly affected by human society (Schlesinger 1997; Krapivin and Varotsos 2008). One of the most crucial problems of water pollution is the waste discharged into waterways (in the form of sewage) that in excessive quantities are very toxic and their indirect (secondary) effects are usually extremely harmful (Moor and Ramamoorthy 1984; Connell 2005).

The atmosphere plays a major role in global processes supporting life. Global change in atmospheric composition is the best evidence that humans alter the environment worldwide. There is a wide concern about the global change of such atmospheric constituents as carbon dioxide, methane, nitrous oxide, as well as the deteriorious effect of anthropogenic pollutants such as  $\text{SO}_2/\text{H}_2\text{SO}_4$  and heavy metals (Degens 1989; Charlson 1992; Lutgens and Tarbuck 2004; Bradl 2005; Connell 2005).

Currently, the biggest challenge for the scientific society is to provide quantitative parameterization of the local, regional, and global change due to natural and anthropogenic transformation. The influences of natural factors versus human activity remain unclear. All current observation of global change must be evaluated in the context of underlying cycles and potentially non-steady state conditions on the Earth systems. All biogeochemical cycles require better scientific and technical understanding (Butcher 1992; Schlesinger 1997; Bashkin 2002).

Our knowledge of many elemental cycles is still incomplete. There are many questions about their driving mechanisms, biogeochemical barriers, quantitative and qualitative aspects of tiny pools, biogeochemical cycles in different ecosystems and regions. The key problem is quantitative predictions of interactions between cycles. To answer these important questions the accumulation of more data is needed regarding cycling of major and trace elements in different media as well as development of methods for processing already existing vast amount of data.

## **1.2 Major and Trace Elements: Cycling**

In the Periodic Table the biologically relevant elements are found at an atomic number less than 54 (I). Elements with an atomic number less than 30 are far more abundant than heavy elements (with 3 exceptions – Li, Be and B). Elements heavier than Fe are no more than trace constituents within living tissues. Ten elements, O, Si, Al, Fe, Ca, Na, K, Mg, Ti and P, are defined as “major” because they encompass nearly 99% of the total elemental content of the earth’s crust (Alloway 1995). Eight elements, O, Si, Al, Fe, Ca, Na, K and Mg, make up close to 99 % of the total elemental mass of living tissue (Butcher 1992; Adriano 2001). According to another classification, C, H, O, N, P and S are considered “major”, because they comprise 95% of the Biosphere and they are the major constituents that living organisms utilize in structural tissues (Degens 1989; Trudinger et al. 1992; Schlesinger 1997). Some scientists also include Ca and Fe as major elements since they are particularly significant for living organisms (Krapivin and Varotsos 2008).

The biogeochemical cycles of the major elements are interconnected and powered by solar energy. The most important and well-known are the cycles of C, N, P, S, and water. The natural biogeochemical turnover of these major elements as well as the water cycle has been altered by human to a significant degree. For example, global warming is attributed to the perturbation of the global carbon cycle and this cycle is now a central focus of Biogeochemistry (Golubic et al. 1979; Holmen 1992; Krapivin and Varotsos 2008). Human perturbation of the global nitrogen cycle is also profound and extensive. Through fertilizer production it has doubled the rate at which N enters the biogeochemical cycle on land (Schlesinger 1997; Krapivin and Varotsos 2008). Mining activity directly enhances the turnover of the global P cycle and in many areas humans have enhanced the availability of P by mining phosphate rocks for fertilizer production

(Kilmer 1979; Pierrou 1979; Young 1992; Schlesinger 1997). As a result of pollution and fertilizer runoff, as well as soil erosion, the flux of P in rivers now is significantly higher than it was in prehistoric times (Bashkin 2002; Krapivin and Varotsos 2008). Recently it was discovered that the cycles of C, N and P are strongly linked and only the right ratio of C: N: P can provide a healthy ecosystem condition (Schlesinger 1997). The S cycle is another very important biogeochemical phenomenon despite the relatively low content of this element in biota, and the fact that S compounds are quantitatively minor (Kilmer 1979; Krouse and McCready 1979; Charlson et al. 1992). Human activity has doubled the flux of oxidized sulfur gases into the atmosphere and has roughly doubled the annual mobilization of S from the crust of the earth (Trudinger 1992; Krapivin and Varotsos 2008). As a result of fossil fuel combustion, areas downwind from industrial regions now may receive massive amounts of acidic deposition from the atmosphere which can lead to changes in rock weathering, forest growth and ocean productivity (Krouse and McCready 1979; Lutgens and Tarbuck 2004).

Many of the trace elements, in spite of being minor in quantitative terms, are important elements in the biogeochemistry of terrestrial and aquatic systems and are essential for the growth and development of living organisms (Davies 1992; Driscoll et al. 1994; Adriano 2001). About twenty trace elements (Na, Mg, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, B, F, Si, Se, Cl, Sn, I, Mo) are considered to be essential to life (Kilmer 1979; Schlesinger 1997; Bashkin 2002; Huang 2008). The number of these elements is constantly growing as we increase our knowledge about them (Davies 1992; Trudinger et al. 1992; Alloway 1995; Krapivin 2001). These metals and non-metals together with the major elements are essential for human nutrition. Particularly important are the relatively abundant minor nutrients such as Zn, Cu, Mo, Se, Mn and B

(Schlesinger 1997), which with Ni, Na and Fe are commonly accepted as micronutrients for higher plants (Lundren and Dean 1979; Davies 1992; Huang 2008).

The definition of heavy metals has been based primarily on the specific gravity of the metals (greater than 4 or 5), location within the periodic table and specific biochemical responses in animals and plants (Preface in Ross 1994; Connell 2005); however, the term is widely used in the literature to describe toxic metals (Ross 1994; Bradl 2005). There is some evidence that non-essential metals such as Hg, Cd and even Pb and As can demonstrate a dual rôle of essentiality and toxicity (Connell 2005); however, the biochemical function of toxic metals is not well understood. Adverse health effects can be observed in both excessive exposure and deficiency syndrome (Davies 1992), depending on the threshold of the element and particularity of the organism (Bashkin 2002). Generally, the following heavy metals and metalloids are the major environmental concerns: Hg, Cd, Pb, Sb, Sn and As (Adriano 2001; Bashkin 2002; Meza-Figueroa 2007). Beside these heavy metals, there is a set of trace metals such as V, Cr, Mn, Co, Ni, Cu, Zn and B, Mo, Se, Ag, which at elevated concentrations or availability may be toxic and their accumulation in biogeochemical cycles leads to acute or chronic poisoning of plant, animal and human organisms (Hutton 1987; Davies 1992; Ross 1994; Bashkin 2002; Krapivin and Varotsos 2008).

### **1.3 Metal Sources in the Environment**

Metals enter into the environment from a variety of sources, both natural and human related. The natural sources are dominated by volcanic activities and chemical weathering of parent rocks and metallic minerals (Alloway 1995; Brown et al.1999; Bradl 2005). The anthropogenic sources are mainly from agricultural activities (fertilizers, animal manures and pesticides, containing heavy metals), metallurgical activities (mining, smelting, and metal processing), fossil

fuel combustion, transportation, industrial processes and industrial products which are deposited as waste (Hart 1987; Alloway 1995; Forstner 1995; Bradl 2005; Wong 2005).

In urban areas the major sources of heavy metal pollution are anthropogenic; whereas in rural areas the sources are a combination of natural and anthropogenic. Historically, the impact of these pollutants is confined mostly to the urban areas; however, the border between urban and rural areas is becoming increasingly blurred (Bradl 2005).

Anthropogenic activity has significantly changed the biogeochemical cycles of many trace elements and increased their bioavailability (Driscoll et al. 1994). In the absence of human activity, elements are released into terrestrial and aquatic environments at the rates corresponding to natural chemical and mechanical erosion. Human activities influence their cycling in two interrelated ways: by altering the rate at which the metals are transported among different reservoirs and by altering the form of the metals from that in which they were originally deposited (Bradl 2005)..

Bruland (1974) concluded that Pb, Cd, Zn, Cu, Ag, Cr, V, and Mo are currently accumulating in the lake sediments at higher rates than a century or more ago. For all of these metals, the anthropogenic component represented at least 1/3 of the natural emission rate, and for Pb, Ag, and Mo the anthropogenic rate exceeded the natural rate (Forstner 1995; Schlesinger 1997). The present rate of the global input of some other metals such as Hg is also in excess of the natural rate of biogeochemical cycling (Forstner 1995). For some metals global contributions from anthropogenic sources may be small compared to natural fluxes; nevertheless, these may cause localized pollution, such as mining waste and leachates (Allen et al. 1993; Connell 2005; Wong 2005).

The total effect of the impact of human activity is uncertain, especially in the long run. Though fluxes of energy and materials through the biosphere are self-regulating, this regulation has limits. Eventually, it is necessary to evaluate the capacity of the biosphere to assimilate anthropogenic metal inputs and to predict the rate and type of changes that will occur as a new steady-state condition is approached. These predictions are limited not only by the level of our understanding of the complex interactions that occur between metals and the environment, but also because the determination of background metal concentrations in uncontaminated environments is difficult to ascertain (Davies 1992). To locate an uncontaminated site is also extremely hard (Kabata-Pendias 2001).

In recent years there have been many efforts to evaluate trace metal concentrations in natural systems and to compare trace metal releases and transport rates from natural and anthropogenic sources. There is no single parameter that can summarize such comparisons. Frequently, in investigating a heavy metal atmospheric deposition, a comparison is made between the composition of atmospheric particles and that of average crustal material to indicate whether certain elements are enriched in the atmospheric particulates (known as the enrichment factor) (Watson and Chow 2007). A second approach is to compare total mining production of a metal to an estimate of its total natural flux, making the assumption that all mined materials will be released to the environment in the near future and comparing it with geologic processes. Some authors have computed metal loading to the environment from specific human activities such as discharges of wastewater, and compare this with a natural release rate. The general observation for many metals is that anthropogenic contributions to metal ion transport rates and environmental burdens are approaching and, in many cases, already exceed natural contributions (Schlesinger 1997).

## 1.4 Metal Transport

Anthropogenically modified heavy metals can be released into the environment in gaseous, particulate, aqueous, or solid form and emanate from both diffuse or point sources (Bradl et al. 2005). For most metals, transport as a gaseous species is of little quantitative importance except in very high-temperature environments. Metals such as Pb, Cu and Zn are only transported as particles, whereas volatile metalloids As, Sb, Se and Hg can be transported both in particles and in gaseous form (Haygarth and Jones 1992; Bradl 2005). Transport of particles suspended in the air is an important process for distributing many metals to regions far from their sources. During transport (in a matter of days or weeks) they can be diluted, precipitated, or transformed by chemical reactions on the way to their emission locations. However, emission calculations can be very uncertain, as many parameters are often not known exactly or vary strongly with time and location (Bradl 2005).

For many trace elements, the atmosphere is an important transport medium (Alloway 1995; Bradl 2005). Atmospheric deposition is a significant source of some trace metals (e.g. Pb, Cd, Cu, Zn) to the total ecosystem input while the other trace metals (Fe, Mn, Al) originate mostly from weathering, mineralization, etc. (Driscoll et al. 1994). The atmosphere is highly conducive to transporting anthropogenic emission compounds across vast areas. Lead and other metals associated with industrial activity are found in remote Arctic and Antarctic ice caps and sediments (Degens 1989; Charlson 1992; Kabata-Pendias 2001).

Atmospheric deposition is a significant source of metals in plants and soil (Haygarth and Jones 1992, Ross 1994; Alloway 1995; Hering 1995). For Pb, more than 90% of the total plant uptake can be attributed to atmospheric deposition (Haygarth and Jones 1992). Metals act upon and are acted upon by biota in important ways and their effect on the chemical environment in

the soils, sediments, or open bodies of water can either stimulate or inhibit biological activity (Kilmer 1979; Moor and Ramamoorthy 1984; Logan and Traina 1993; Turner in Ross 1994; Bradl 2005).

In order to acquire the full picture of a heavy metal air pollution event, it is necessary to analyze a wide spectrum of media (natural and technogenic) such as aerosols, dust, soil, stream and lake sediments, vegetation and water that may reflect the event in different ways (Bradl 2005). Since the degree of uncertainty in heavy metal flux in media is high, the calculation of total atmospheric heavy metal content accumulated in different media requires the monitoring and the acquisition of data on both regional and local scales.

## **CHAPTER 2**

### **HISTORICAL BACKGROUND**

A particularly unique and complex situation relating to heavy metal pollution, especially lead (Pb) and arsenic (As), arose in the El Paso – Juarez metropolis on the US-Mexican border. The situation on this border is critical in a number of environmental parameters which may deteriorate significantly in the future if economic growth, urbanization, industrialization, agricultural development and population continue to increase at the present rate. Among them, air quality is of especial concern for the health and well-being of the border residents.

Almost all binational air basins along the border received non attainment status for ozone (O<sub>3</sub>), carbon monoxide (CO), particulate matters (PM<sub>x</sub>) and sulfur dioxide (SO<sub>2</sub>), exceeding National Ambient Air Quality Standards for all these substances. The Paso del Norte region particularly was classified as non-attainment for three criteria: O<sub>3</sub>, CO and PM<sub>x</sub> (Van Schoik 2003; Currey and Rumfrey 2006). It should be noted that the issues of environmental pollution are more difficult to resolve in border areas because of differences in the regulations, standards and policies of the countries involved. In addition, in this border region urgent problems such as poverty seem to delay of the addressing of the environmental issues to a later date (Parks et al. 2003).

The Paso del Norte region has a long history of air pollution. Many factors such as dusty winds blowing out from the Chihuahua Desert, fugitive dust from unpaved roads, vehicular emissions from heavy traffic, industrial pollution from large and small scale industries, railroads and the combustion of many fuels for heating and cooking contribute to poor air quality in this region (Parks et al 2003). Additionally, one of the largest non-ferrous smelters (primary lead/copper smelter) in the United States, owned by the American Smelting and Refining

Company (ASARCO) since 1889, was functioning in El Paso for more than one hundred years, starting in 1887 (Marcosson 1949; Lee 1950). At the turn of the twentieth century, in El Paso there were two other active smelters, the International and the Federal, but their operations lasted for only a few years (Barnes 1993; Shapleigh 2008). The overall amount of heavy metals emitted into the air from all smelters is still unknown.

The El Paso - Ciudad Juarez twin cities faced the environmental problems common to other twin cities along the border. The environmental health situation in general and air quality in particular was aggravated by the constant and rapid increase of population (now more than two million). Specific unfavorable factors are the intermountain valley topography and extremely dry desert climate (with a severe long windy season) that create complex meteorological phenomena controlling and trapping air pollution (Erickson et al. 2004; Currey and Rumpfey 2006).

Until the 1960s, when the environmental movement around the country started to raise the society's environmental conscience, local communities had no serious concern about people and environmental health. ASARCO, being on the fringe of the small city, was a symbol of prosperity and its industrial activities were considered by many people as a hope for their bright future (Lee 1950). For that time ASARCO was a very progressive facility. Many modern precautionary measures were implemented to protect the health of the ASARCO' workers, but no attention was paid to the health of the residents of Smeltertown (residential area surrounding ASARCO from 1887), and even less for the residents of the region (Landrigan et al. 1975; Samuel 2002). At the same time, some harmful consequences for the local environment were already documented (for instance crop damage in the 1920s) and the City of El Paso several times disputed with ASARCO about some community complaints (Shapleigh 2008).

In April 1970, the City of El Paso sued ASARCO for violating the 1967 Air Safety Code and Texas Clean Air Act based upon complaints about air pollution from the city residents. One month later, the State of Texas joined this suit. In 1971, the El-Paso City-County Health Department (EPCCHD) discovered that 73% of 138 children in Smeltertown had blood-lead level (BLL) that exceeded the initial level of concern which at that time comprised 40 µg/dL (now is 10 µg/dL or in some regions 5 µg/dL); 42% of children had BLL ranging 40-59 µg/dL and 31% of children had BLL over 60 µg/dL. Five children were hospitalized because they needed immediate chelating treatment (Landrigan et al. 1975; Samuel 2002; Dulin 2005).

In early 1972, EPCCHD, ASARCO, and the US Centers for Disease Control and Prevention (CDC) conducted a joint blood lead testing of 1,011 individuals residing in the vicinity of ASARCO. In August of 1972 they repeated this study with 1,369 individuals, 758 of whom were 19 years old or younger. Both studies revealed the same pattern: the closer the children lived to the smelter, the higher was their BLL and this relationship is characterized by a logarithmic dependency. The highest BLL, 83µg/dL, was observed in a two-year-old girl, who lived in Smeltertown (Landrigan et al. 1975; Samuel 2002; ATSDR 2004).

Records show that between 1969 and 1971 the facility emitted approximately 5,000 tons of total particulates from its stacks and this included 1,116 tons of Pb, 560 tons of Zn, 1.2 tons of As, and 12 tons of Cd emitted in the three year period (Garcia et al. 2004; Dulin 2005; Shapleigh 2008). During this period, according to ASARCO statements, the plant was also emitting 230,500 tons of sulfur oxide (SO) per year or 640 tons per day. We do not know the exact quantity of Bi, Mo, Se, Ag, Sb, Bi, In, Te, Ge, Re, Te and Tl contained in stack emissions (Eckel 2000; Drexler 2005) and other by-products of the lead, copper and zinc smelter activities.

From April 1972 until September 1973, the EPCCHD documented violations of permitted levels of pollutants (Pb, Zn, Cd and As), including total particulates. Violations occurred at least twice each month and up to six to seven times per month. Between June and December of 1972 the EPCCHD also collected soil and household dust samples. Elevated levels of Pb, Zn, Cd and As were found in soil and dust samples collected from Smeltertown, Kern Place – Mission Hills neighborhood and University of Texas at El Paso (UTEP). In Smeltertown the maximum concentration of Pb in soil was 11,450 ppm, in dust it was 103,750 ppm; at the Kern Fire Station Pb concentration in soil was 600 ppm, in dust it was 84,000 ppm. Among schools, the highest content of Pb in soil was in Sunset High (1,400 ppm) and in El Paso High Schools (1,200 ppm), with Pb in dust 5,900 ppm and 3,500 ppm respectively (ATSDR 2004; Shapleigh 2008).

House surveys in Smeltertown in 1972 showed that children were being exposed to Pb by many routes. A heavily trafficked highway ran nearby, and in those days gasoline was heavily leaded. Paint inside the houses was considerably leaded as well. Plates, dishes, and pitchers, tested in the houses, showed considerable potential for leaking lead into food and drink stored in them, and the residents of Smeltertown used certain folk medicines that were extremely high in Pb content. However, the massive air-lead levels outside the houses and leaded dust inside the houses were a major factor in children's lead exposure (Landrigan et al. 1975).

On behalf of the general public, the city of El Paso forced ASARCO to take strong measures to control air pollution from its facility. The construction of the 828 feet smokestack (the highest in the USA at that time) in 1966 had not been sufficient. In 1979 ASARCO completed a 90 million dollar renovation to the facility to improve emission quality; however, 96 tons of Pb per year were still emitted until its closure in 1999 (Drexler 2003). Smeltertown was demolished to many residents' regret (Romero 1984; Perales 2003).

Despite the reduction of heavy metal emissions in the environment, the question about their levels in the PdN region has never lost its topicality, and in some quarters, its urgency. Since the 1970s, during the time of ASARCO operations and after it was placed on maintenance status, the citizens of El Paso, TX, have been expressing their concerns about Pb, As, Cd and other heavy metal pollution levels in the soil, particularly in the areas that potentially may be associated with elevated BLL of children. In response to their concerns, from 1997 to 2005, the U.S. Environmental Protection Agency (EPA) Region 6, in cooperation with the Texas Department of Health (TDH), the Agency for Toxic Substances and Disease Registry (ATSDR), the Texas Commission on Environmental Quality (TCEQ), and local city and county officials have been investigating soil contamination in residential yards in El Paso, TX. They have assessed whether the soil lead levels in El Paso are a cause for elevated BLLs in children. On the basis of their assessment, the conclusion was “soil lead probably has a contribution to elevated blood lead levels in this population of children in El Paso, Texas” (ATSDR 2004). Therefore, in 2004 the nation’s first soil-yard-removal project was started in El Paso (Dulin 2005).

In February 2006, there were debates concerning the renewal of ASARCO’s air quality permit and consequently the possibility of reopening the facility. The presence of elevated levels of toxic metals in local soil was not deemed sufficient to deny ASARCO’s request. “No individual, agency or organization has found sufficient evidence to link the company to the pollution” (Ramirez 2006). The commission gave ASARCO an extension to meet air quality requirements. Nevertheless, after persistent efforts by the El Paso community, state and local legislators and officials in 2010 ASARCO was shut down completely.

Several scientific studies have been conducted in the Paso Del Norte region in order to investigate Pb, As, Cd and other heavy metal accumulation in the local environment and the

possible contribution of the ASARCO smelter to the environmental loading of hazardous substances. The majority of researchers used soil as a major media of investigation with some exceptions such as blood (Landrigan et al. 1975; ATSDR 2001; Pingitore et al. 2005), hair (ATSDR 2001), air (Landrigan et al. 1975; Pingitore et al. 2005), dust (Landrigan et al. 1975; ATSDR 2001; Pingitore et al. 2005), seeds and ants (Mackay 1998; Del Toro et al. 2010). Only a few studies were trying to identify possible sources (including ASARCO) of heavy metal pollution in the region (Barnes 1993; Drexler 2003; Garcia et al. 2004; Ketterer 2006). However, the speciation studies were carried out mostly for a few target metals such as Pb and As and a special emphasis was placed on Pb concentration in El Paso soil (Drexler 2003; Walker and Associate Inc. 2003 in Dulin 2005; Garcia et al. 2004; Ketterer 2006). Some of the studies appeared to produce “inconclusive or conflicting results and conclusions” (Dulin 2005).

As part of a broader effort to understand the historical environmental exposure that occurred in the Paso del Norte region, we have performed an investigation of attic dust to provide answers about heavy metal time-space distribution. This medium may help to examine the mechanisms of fate and transport of contaminants in the surrounding environment and to identify their sources.

The objective of this study was to evaluate the historical impact of the smelter activities on the air quality for the last ten decades and to investigate the age, proximity and topography effects on dispersal patterns of heavy metals from ASARCO stack emissions.

The approach was to examine attic dusts from two similar aged neighborhoods in El Paso, TX, one near ASARCO (Kern Place area) and the other on the east side of the Franklin Mountains (Government Hill area). Also, dust was sampled from a location in Juarez, Mexico. In addition to the concentration of heavy metals (expressed as their Enrichment Factors) in the

dust deposited on the original attic surfaces, dust samples from surfaces that post-dated the original construction to determine temporal changes in heavy metal depositions near the end of ASARCO operations and after its closure were of interest.

## **CHAPTER 3**

### **LITERATURE REVIEW**

#### **3.1 Investigation Media for Air Pollution History**

##### **3.1.1 Aerosols**

The chemical and physical composition of the atmosphere plays an important rôle in affecting and controlling the set of processes vital for the life of the planet. The atmosphere consists of stable and unstable components, especially in its lower sphere, the troposphere (80 km or 50 miles from the Earth's surface). The stable components are oxygen, nitrogen and argon, which comprise 99% of the dry atmosphere and the remaining 1% is made up of various gases, vapor, ozone, solid and liquid particles which change in time and space (Enger and Smith 2002; Lutgens and Tarbuck 2004).

Recently, scientists have paid increasing attention to the suspended solid and liquid matter called aerosols. Although aerosols represent a very small percentage of the atmospheric composition, they play a significant rôle in a large number of different atmospheric processes. Aerosols neutralize colloidal acids, scavenge radio nuclides, carry most of the toxic metals in the atmosphere, absorb or reflect solar radiation, facilitate cloud formation, contribute to optical phenomena, reduce the amount of solar energy available to the climate system (having a net cooling effect) and in general greatly affect climate and weather (Pye 1987; Charlson 1992; Cahill 1995; Lutgens and Tarbuck 2004).

The effects of atmospheric aerosols are related to their size distribution. Small particles are much more numerous in the atmosphere and have the greatest influence on global biogeochemical transport of matter through the atmosphere and on the Earth's climate. With increasing altitude, the mass of aerosols declines (Cahill 1995; Schlesinger 1997).

Aerosols that are directly emitted into the atmosphere from the earth's surface - from land (vegetation, forest fires, wind erosion, and industries) or from the ocean (sea spray, surface films, primary productivity, oil platforms) are called primary aerosols (Lutgens and Tarbuck 2004). Secondary aerosols are formed “by chemical reactions in the atmosphere, which involve gases, pre-existing aerosols, and water vapor” (Bradl 2005, p.15).

Atmospheric aerosols are composed of different materials of natural and anthropogenic origins. This composition strongly depends upon the proximity of natural or anthropogenic sources. Under natural conditions the composition of aerosols over the ocean is a mixture of continental silicate minerals and sea salt, while over the land aerosols are dominated by soil minerals (Schlesinger 1997).

Aerosols become pollutants when their concentration in the air is excessive and harmful for people and for the environment. Pollutants also can be classified into primary and secondary categories. The primary air pollutants are emitted directly from identifiable sources which contaminate air at the moment of emission. Some of the primary and major air pollutants such as carbon monoxide (49.1%), sulfur oxides (16.4%), nitrogen oxides (14.8%), volatile organics (13.6%), and particulates (6%) are considered very harmful and were put on the Primary Pollutants list by the US EPA under the Clean Air Act (Lutgens and Tarbuck 2004). Other widespread and very harmful anthropogenic aerosols such as lead particles have declined in global atmospheric abundance over the last 30 years (mainly due to the removal of lead from gasoline) and were eliminated from the Primary Pollutants list. The primary pollutants come mostly from transportation (46.2%), stationary sources of fuel combustion (27.3%), different industrial processes (15%), waste disposal (2.5%), and other sources (9 %) (the percentage calculated on basis of weight: EPA, Lutgens and Tarbuck 2004).

Secondary pollutants are sometimes much more damaging and are the products of a chemical reaction between the primary pollutants in the atmosphere. The most harmful secondary pollutants are sulfuric acid and different types of smog, especially photochemical smog such as ozone and PAHs (Treshow and Anderson 1989; Enger and Smith 2002; Lutgens and Tarbuck 2004). The terrible smog which caused thousands of deaths in London in the winter of 1952 (as well as less severe air pollution episodes in 1953 and 1962) is one of the most striking examples of how dangerous some secondary pollutants can be. The London catastrophes were the catalyst for implementation of modern pollution control in England and in Europe. In the United States the Clean Air Act was implemented at almost the same time because of air pollution events in 1953, 1963, and 1966 in New York (Lutgens and Tarbuck 2004).

In general, the volume of anthropogenic aerosols is steadily increasing, and only current environmental regulations and requirements restrain their critical growth. Even though their anthropogenic sources on a global scale account for only about 10% - 20% of the total (Schlesinger 1997), on a local scale in highly industrialized areas they can cause significant problems (Querol 2002) which can be amplified by local topographic and meteorological factors such as, for example, prolonged and frequent temperature inversion (Enger and Smith 2002; Žibret 2008 ). The quality of air we breathe still remains a serious public health problem. According to the World Health Organization, air pollution leads to the death of about 600,000 people each year (Lutgens and Tarbuck 2004).

The direct measurement of peak concentrations of air contaminants, especially during the past (historic) air contamination events, can rarely be accurately recorded. Dispersion, reaction and deposition of air pollutants can take place over a very short period of time, thereby masking their emission (Ilaqua et al. 2003; Rasmussen et al. 2004). In addition, several sources may

participate in a particular air pollution event in different proportions and their contribution also can change with time (Watson and Chow 2007; Wait and Ramsey 2007).

The difficulties in measuring pollutant concentrations in air in contrast to other media, such as soil, sediments or ground water, make it essential to improve methodology including samplers, sampling materials and sampling collection techniques (Korzhova et al. 2011). Because of significant air heterogeneities in space and time, it is necessary to utilize long-term, continuous samplers for outdoor air pollutants. Indoor air contamination is easier to determine, but indoor samplers require a high sensitivity because of low pollutant concentration. Other parameters such as temperature, pressure, humidity, sampling rate and accessibility to the entire investigated unit also should be considered (Watson and Chow 2007). For these reasons, existing methods of direct measurement of air pollution (especially over a long time) have some limitations, and thus the reconstruction of air pollution history with 100% of accuracy is almost impossible at present.

### **3.1.2 Dusts**

Dust is a type of aerosol that is “related to, but distinct from smokes, mists, fumes and fogs” (Schlesinger 1997, p.1). It is typically composed of particles bigger than 1 micron and smaller than 100 microns, and is always present in a solid form. Dust can also be defined as “a suspension of solid particles in a gas or a deposit of such particles” (Pye 1987, p.1).

Dust has been an integral part of human life throughout history. By the invention of the microscope dust was discovered to contain bacteria, fungi and viruses and to transmit contagious diseases. The realization of this danger was partly the reason for the foundation of hygienic science (Amato 2000).

With the development of industrial society, a larger volume of dangerous dust was formed; there is a definite relation between the words “dust” and “industry” (Amato 2000). In developed countries new types of dust were constantly emitted into the atmosphere from smoke stacks, stockpiles, waste dumps, open - cast mines and quarries, sometimes causing severe air pollution and human health hazard problems not only locally but across a whole region.

Dust released into the atmosphere from industrial plants (especially smelters and refineries) and mines frequently contains large amounts of toxic metals and produces a huge quantity of waste (Gulson et al. 1981; Smith 1987; Young 1992; Gulson et al. 2004; Gosar 2006; Šajn 2006; Tye 2006; Žibret and Šain 2008; Shtiza et al. 2009; Teršik et al. 2009; Balabanova et al. 2011). Mining and smelting operations are also responsible for contributing a wide range of toxic organics, particulates and SO<sub>x</sub> (Lambert and Lane 2004; Savard et al. 2006).

In addition to the mining industry and smelters, other major contributors to the overall amount of dust are cement works, ferrous and non-ferrous industries, petrochemical industries, coal combustion, scrap metal recovery and ceramic industries (Davis and Gulson 2005). Beginning in the twentieth century an unknown amount of radioactive dust has been released into the atmosphere as a result of accidents at nuclear power plants and through nuclear weapon testing (Cidziel and Hodge 1998; Enger and Smith 2002). We cannot fully estimate the consequences of manmade nuclear disasters such as the Chernobyl nuclear reactor accident (1986) and the Fukushima catastrophe (2011) and how it will affect the health of future generations on both local and global scale.

Besides the anthropogenic sources of dust (Pacyna and Pacyna 2001), there are numerous natural sources (These include cosmic dust, volcanic dust, dust generated by forest and brush fires, dust from wind erosion of sediments and soil (mainly from arid and seasonally arid regions

of the world), salt particles from breaking waves and bursting bubbles in the ocean, pollen and spores released by plants (Pye 1987; Bradl 2005).

Dust facilitates the transportation of plant nutrients and trace metals. Brought by wind from continents to oceans, dust supplies iron to phytoplankton; transported from deserts to forests it adds phosphorus to the forest soil. Dust warms the atmosphere over the land and cools the atmosphere over the ocean, helps to stabilize sand dunes and other mobile surfaces, interacts with atmospheric gases and acts as nuclei for the condensation of raindrops (Schlesinger 1997; Goudie 2008).

Currently, all natural dust generating processes are directly or indirectly influenced by humans. For instance, dust storms are becoming more and more frequent and intensive even in areas where they never happened before (Goudie 2009). This increased frequency of dust storm may be caused by anthropogenic modification of desert surfaces and changing climate (Goudie 2008). Dust storms have a very important impact on the environment, particularly on biogeochemical cycling of many elements and climate change. Negative impacts of dust storms are that they can seriously damage engines, interrupt communications systems, lead to transportation incidents, reduce crop production, and most seriously, can transmit diseases and deteriorate human health (Inyang 2006; Van Pelt and Zobeck 2007; Goudie 2009; Okin et al. 2011). Wind erosion events and the loss of fugitive dust during the Dust Bowl of the 1930s in the United States caused irreparable damage to the most fertile agricultural land of the Great Plains and greatly impacted the ecology and the economy of the USA. The economic loss alone was counted in the billions of dollars (Cunningham and Saigo 1999; Inyang 2006).

All human activities that disturb soil surfaces, especially in arid and semi-arid regions, contribute considerably to the large amount of dust naturally generated in such regions and

become the potential source of blowing dust itself (Schlesinger 1997; Rivera Rivera 2009; Okin et al. 2011). These include the intentional burning of land for agricultural purposes, plowing and harrowing of dry soils, construction activities, military maneuvers and traffic on unpaved roads (Groosens and Buck 2011).

Both natural and anthropogenic dust events mostly have a negative influence on the environment and human health. Dust hazards in and around urban areas may be more harmful and dangerous for society (Li et al. 2001; Inyang 2006; Okin et al. 2011). Dust emissions from all kinds of sources can have a global impact because of the immense distance over which dust plume can be transported (Schlesinger 1997).

The records of dust deposition can sometimes provide the most detailed information about past environmental events in going back millions of years which readily facilitate climate change studies and the understanding of biogeochemical cycling in the past. The rôle of dust in biogeochemical cycles and in soil formation is an area of increasing scientific activity (Goudie 2009). With growing environmental concerns, there is a need to accumulate data for modeling the local, regional and global dust cycles.

### **3.1.3 Settled House Dust (SHD)**

#### **3.1.3.1 Advantages of SHD as a Sampling Material over Top Soil in Exposure Studies**

In recent decades new studies demonstrated the strong information potential of settled house dust (SHD), including ceiling and attic dust, for characterization and identification of the sources of environmental hazards. This information is useful not only for a detection of a variety of chemical toxicants, physical toxicants and biotoxins, for providing detailed analyses of

indoor and outdoor air pollutant sources, but also for characterizing residential exposure and for evaluating long term prevention, mitigation and remediation strategies.

From the second part of 19th century, dust was studied in criminal anthropology, legal medicine, forensic chemistry and police technique (Locard 1930). In 1940 dust was analyzed in the USA to determine the microbial level in operating rooms in one hospital and to evaluate the cleanliness of a pharmaceutical manufacturing facility (Lioy et al. 2002).

SHD became a subject of special scientific attention in the 1970s when lead (Pb) was discovered in the household environment. As a result, the necessity to evaluate the lead exposure of residents, especially children, has risen. SHD has become the topic of investigation of experts from different fields such as environmentalists, environmental health specialists, industrial, occupational and environmental hygienists, forensic chemists, toxicologists and microbiologists.

In search of a Total Exposure Assessment Methodology (TEAM), scientists began to concentrate on the measurement of indoor environmental factors with a focus on one or more home microenvironments (Lioy et al. 2002).. Residential soil was steadily losing its predominant role as a sampling media for quantifying the levels of toxicants, for source identification, for estimation of the residents' exposure and especially as a predictor of their blood lead level (BLL). This tendency occurred first because of the results of “Three Urban Soil-Lead Abatement Demonstration (Three Cities Soil) Projects”. The projects were designed to determine the effect on BLL following the removal of lead contaminated soil and showed its negligible impact. In contrast, dust demonstrated a greater importance in affecting the level of toxicants in blood (Gulson et al. 1995).

The subsequent studies clearly defined the soil and dust usage limitations. Soil data can be useful for “profiling the distribution of material to various depths”, “assisting in defining the

period of time when the deposition and/or accumulation of toxicants occurred in the soil”, in the preliminary risk assessments before site cleanup at hazardous waste sites, in arid regions “for detection of reentrainment of desert sand and its redistribution to more than 1000 km away” (Lioy et al. 2002). Since the level of chemical, physical or biological contaminants can represent recently deposited material (Lambert and Lane 2004), for exposure assessment purposes soil data are considered very “crude” and can be used only as supporting data (Lioy et al. 2002). At the same time, the concentrations of especially “urban” elements in house dusts usually are significantly higher than in soil or in street dust (David and Gulson 2005) and have a distinctive multi-element signature from them (Rasmussen et al. 2000). This is why the prediction of indoor dust concentration of hazardous materials based on exterior soil data is “difficult - to impossible” (Riederer et al. 2005). Comparing the relative contribution to heavy metal residential exposure by different media, such as house dust, entryway soil, home-grown vegetables and water, the strongest correlation found was between heavy metal concentration in adult biomarkers and home dust (Riederer et al. 2005; Hogervost et al. 2007).

Šajn, examining mining and metallurgy influences in the Meza Valley (Slovenia), came to a very interesting conclusion: “With respect to geogenic dispersion resulting from an underlying lithological setting (Al-Ce-Co-K-La-Li-Nb-Rb-Sc-Th-Ti-V), the soil has proven to be a better sampling medium than attic-dust. The spatial distribution patterns of chemical elements in topsoil are clearly seen, in contrast to the distribution in attic dust. In the case of the spatial distribution patterns resulting from intense anthropogenic influences (Ag-As-Cd-Mo-Pb-S-Sb-Sn-Zn), the anomalous patterns are shown with more contrast in attic-dust. The advantage of attic-dust over top-soil is evident in the case of less clear anthropogenic anomalous patterns” (Šajn 2006).

Both soil and dust data are essential for periodic heavy metal residential monitoring (Riederer et al. 2005). Yard soil with yard dust in “favorable” conditions can represent an important source of exposure in itself. As noted above, there is a strong positive correlation between, for example, exposure to lead-contaminated soil and blood lead levels (BLL). In general, BLL can increase by to 3-7  $\mu\text{g/DL}$  for each 1,000 ppm increase of Pb concentration in soil (Eckel 2000). Some contaminants such as pesticides from spraying lawn or farms, PAHs, heavy metals, etc. may be transported indoors from outside with dust and dirt by residents or pets and then interact with the home environment (Elles et al. 2007).

Ingestion of contaminated soil and dust is one of the critical pathways of non-occupational exposure to heavy metals, mostly for children with pica behavior (Maertens et al. I 2008). It could be particularly harmful for the residents living near contaminated sites in the countries where remediation efforts are constrained by cost or other factors (Riederer et al. 2005). Populations living in areas historically polluted by Pb, Cd, As, and other heavy metals, may be exposed by consumption of crops or animal produce originating from contaminated soil. Additional sources of exposure in such areas are inhalation of particulate matter (PM) particles, heavy metals in dust and polluted water (Hogervost et al. 2007).

After many decades of research there is still a poor understanding of the sources of heavy metals in soil and dust and their impact on environment and health. There is also a lack of standardized sampling protocols for the heavy metal determination in both soil and dust (Mesa-Figueroa et al. 2007).

### **3.1.3.2 Dust Pathways to the Indoor Environment. Contribution Factors to Total Residential Exposure**

The important factors that influence the quantity and composition of SHD are climate, wind speed and direction, traffic density, industrial activity in surrounding areas, proximity to anthropogenic industrial sources, home age, type of roof construction, presence of leaded paint (before abatement), condition of exterior paint, home location, human activities, cleaning habits, household ventilation, type of air conditioning, coal and central heating or portable units, type of heating fuel (oil, kerosene or natural gas), presence of enclosed garage, type of attic and attic ventilation (Davis and Gulson 2000; Ilaqua 2002; Petosyan et al. 2006; Hogervost et al. 2007; Maertens et al. I 2008; Maertens et al. II 2009).

Usually outdoor dust infiltrates the indoor environment by advection and diffusion through the vents, doors, open windows and other passive ventilation portals (Cizdziel and Hodge 2000; Lioy et al. 2002). Outdoor dust can also accumulate and move to the house from exterior house surfaces (roof, window sills, etc.) and from the attic under certain conditions, particularly if the easiest way for air to enter is from the attic. The presence of “leaky return ducts in the attic or holes between it and the living large space such as unsealed tops of plumbing chase ways” and pressure effect (a negative pressure plays a role of the driving forces caused by leaks of imbalance in the forced air systems) permit attic air to move to the rooms via the heating system and gaps (Katz 2005). “Dust entering the living areas is dependent on micro air currents, eddies, and pressure effects to promote saltation and movement of the particles into living areas” (Davis and Gulson 2005). These attic dust pathways into living areas are considered passive. Good condition attics rarely demonstrate indication of passive attic dust pathways (Davis and Gulson 2005). Active pathways of attic dust are a consequence of natural disaster or home renovation

and are more dangerous for residents who may be exposed to larger volume of dust with high levels of metals and fine particles (Davis and Gulson 2005).

Concern over the potential hazards of attic dust has been a very serious issue in some countries like Australia. The major problem in this country was a type of home roof construction which allows the accumulation of roof dust in the attic. A major hail storm in 1999, which strongly damaged more than 20,000 roofs and attics, resulted in the release of dust into the living areas and exposed the occupants (Davis and Gulson 2005).

Understanding of the nature of each dust pathway, quantitative assessment of its dust conduction and how it potentially contributes to total residential exposure is very important and essential for the development of an effective mitigation strategy (Riederer et al. 2005). “Knowledge of attic (ceiling) dust exposure as well as house dust pathways is an important component of the dust cycle in the urban environment” (Davis and Gulson 2000).

### **3.1.3.3 Indoor Dust Sources. Toxicants in SHD and Their Harmful Effects**

The home environment represents a complex set of passive and active toxicants coming not only from outdoor but also from multiple indoor sources. The indoor air of a modern home is mostly polluted with volatile organic compounds and gases from specific indoor sources such as fabrics, floor covering, dyes, pesticides, refrigerants, heating and cooking fuels, smoking, wood burning and candle burning (Maertens et al. 2008).

Each surface inside the home that is able to accumulate dust can become a source of dust itself. For example, carpets and rugs have been found to be a large reservoir of dust and can act as significant source of heavy metal exposure (Lioy et al. 2002; Petrosyan et al. 2006). Drapes and upholstery, pillows, tops of closets, lamp covers and other surfaces, which are hardly

accessible for cleaning, can be additional sources of home dust accumulation. As a result, SHD may be a significant source of indoor exposure to hazardous substances, particularly harmful for children (Maertens et al. I 2008). House dust is potentially an important and long lived source of exposure to heavy metals especially in areas with contaminated soil and should be incorporated in the assessment of health risks (Cizdziel and Hodge 2000).

SHD is a complex and heterogeneous mixture containing of fungi, microbiological and viable bio particles, asbestos, professional product applications, flame retardants, plasticizers, smoke residues, semivolatile and nonvolatile pesticides, PSB, PANs and heavy metals (Lioy et al. 2002; Maertens et al. I 2008; Maertens et al. II 2009). Researchers established that in a home there might be as many as 100 different substances (Lutgens and Tarbuck 2004), including carcinogenic, neurotoxic or endocrine disrupting toxicants (Lioy et al. 2002).

From the point of view of the health threat the indoor environment in both urban and rural houses may represent in many cases a significant danger. Usually, concentrations of harmful materials is much higher indoors than outdoors. Additionally, home dust particles are finer, and adhere to skin more effectively and more respirable, increasing the potential of exposure (Davis and Gulson 2005; Hogervost et al. 2007). The situation is particularly acute in American homes due to the amount of different hazardous materials used in households. For this reason and because people spend a lot of time inside their homes (from 90% to 98% in winter for children), the risks related to indoor pollution are evident (Cizdziel and Hodge 2000; Lutgens and Tarbuck 2004). According to the conclusions of the EPA, indoor air pollution is one of the eighteen most dangerous sources provoking cancer (Lutgens and Tarbuck 2004).

Many epidemiological and experimental studies have demonstrated that non-occupational exposure to house dust may cause a variety of diseases. Several man-made pollutants in house

dust have been found to promote the development of allergic hypersensitivities and some of them augment allergic risk during the first years of childhood (Ng et al. 2006). Living environments may contain immunodelatory materials and mutagenic substances, which can strongly affect and deteriorate the health of residents of all ages. Asthma related to allergy and allergic respiratory diseases have become more and more typical and are widely spread in developed countries (Ng et al. 2006; Suzuki et al. 2008). Exposure to heavy metals in house dust can lead to neurotoxicity, immunotoxicity, hepatic toxicity, hemotological toxicity, renal toxicity, endocrine disruption, reproductive and developmental defects and a variety of cancer, cardiovascular disease and skin disease (Lanphear et al. 1995; Landrigan et al. 2002; Lambert and Lane 2004; Perzanovski et al. 2006; Hensley 2007).

Understanding hazards posed by the complex matrix of SHD is important for protection of human health and particularly the health of vulnerable individuals. In the case of multiple source signatures, there is a need for their identification and differentiation. Identifying the hazardous component of SHD is a promising area for future research.

There is limited data about distribution of basic major and minor constitutions of house dust in American homes or the homes of other countries. Most studies in dust focus on Pb, Cu, Zn and Hg and little attention is given to other trace elements, such as As, Cd, Sb, Cr, Mn, Ag, etc. (Meza-Figueroa et al. 2007). Clearly, more information is needed to determine present and historic levels of trace metal exposure due to dust, both pedogenic and anthropogenic, in urban and other industrial areas.

### **3.1.4 Attic Dust as a Long-Term Air Pollution Source Identification Medium**

Information extracted from SHD can effectively reflect only the recent air pollution history. Even though the so called “dust follow” (Petri dishes) sampling method offers considerable advantages over, for instance, the vacuum cleaners and surface wipes dust collection techniques (Gulson 1995; Hogervost et al. 2007), this method can collect home dust only for months or, at a maximum, for a number of years. To provide long-term data, some successful attempts were undertaken using materials (dust particles) persisting in surfaces such as rugs, carpet, drapes and upholstery (Lioy et al. 2002; Petrosyan et al. 2005). These surfaces trap the home dust and protect it from removal and degradation; hence, it can be used in historical records, but with some limitations (Cidziel and Hodge 2000). Obtaining dust can help to determine the level of toxicants “that have accumulated from daily living in the home, to discriminate among persistent sources (indoors or outdoors), to specify or document one-time or infrequent events that could lead to acute health outcomes” (Lioy et al. 2002).

To receive records about long-term air pollution history from house dust, it is necessary to have accessibility to locations which have been undisturbed for at least decades or ideally for centuries. Sometimes the relatively undisturbed units like basements, garages, utility sheds, and even stairways (Zheng et al. 2010) and roofs (Meza-Feroguera et al. 2007) can serve for such a purpose.

An attic, compared to other relatively undisturbed home “structures”, has many advantages in respect to collecting and to preserving dust over a long period of time. An attic has more potential to keep dust undisturbed because of more difficult access and attic dust is almost unbiased because of no prior cleaning before sampling. Attics have little or almost no influence from household activities, thus it confirms atmospheric deposition as a sole important source of

impact (Gosar et al. 2006). Attics as archives preserve settled dust and protect it from rain and ultraviolet light (Cidziel and Hodge 2000; Van Pelt and Zobeck 2007).

Attics are selective in particle size, collecting and accumulating only small particles. Attics can collect dust from micro to regional scale particle emission sources (Ilaqua et al. 2003). Attics really may be named the “museums” of dust because therein can be found dust deposited from very short time spans to hundred year time periods and from different sources (Cidziel and Hodge 2000; Davis and Gulson 2005). Furthermore, an attic can substitute for the mathematical model of the fate of hazardous materials over time, and at the same time it may serve better than modeling (Šhajn 2006).

Attic dust might be the most suitable material for the research of past anthropogenic emissions in smelting or mining areas and the best indicator for the determination of historical deposition of heavy metals from the atmosphere (Šhajn 2006; Žibret 2008; Žibret and Šhajn 2008; Balabanova et al. 2011). Attic dust can be used for periodical examination of radio nuclide deposition from nuclear fallout and nuclear power plant emissions and for the measurement of toxicants levels that may have been emitted into the ambient air, transported, and then deposited in the attic (Cidziel et al. 1998; Cidziel and Hodge 2000; Liroy et al. 2002; Van Pelt and Zobeck 2007).

In a broader effort to understand potential historic environmental exposure, attics can give supplemental information to other methods such as dendrochronology or glaciology (Ilaqua 2002). Attics may offer a sometimes unique opportunity to measure contaminants which may have infiltrated people's homes years earlier and can be useful for the purpose of reconstructing the pollution history in the areas where the utilization of other media is more difficult or

impossible. Furthermore, attic dust “can provide data for research, regulatory, risk reduction, forensic analyses of population and individual exposure” (Rasmussen 2000) and may help in forensic investigation, related to distribution pathways of contaminants and their deposition (Tye 2007).

It has been suggested that the most distinctive advantage of attic dust is its ability to be used as a surrogate for human exposure to ambient air pollutants that infiltrated the indoor environment as well as the materials that were present outdoors (Ilaqua 2002). The disadvantages of using attic dust are the difficulty of having to find completely undisturbed attics, the limited numbers of such attics in areas of low population density, the absence of old houses, the difficult accessibility to the attics and the specificity to contaminants in the particle phase (Ilaqua et al. 2003).

The method was first applied in Australia at the end of the 1980s to understand the high BLL of children in communities surrounding different smelters and mining areas (Body 1986; Body et al. 1988 in Gulson 1994; Whicker 1997; Chiaradia 1997 in Davis and Gulson 2000). Since 1999 (when a hail storm destroyed tens of thousands of attics in Australia), Australian researchers have mostly dedicated their studies to investigating ceiling and attic dust as a source of environmental hazard to the residents and came to the conclusion that they may expose people, especially children, to elevated levels of metals and fine particles (Davis and Gulson 2000; Davis and Gulson 2005).

As for the United States, the attic dust medium was used for the first time in 1998 to determine the variability of air pollutants and their deposits over time (Cidziel et al. 2000). Prior to this, for less than a decade, American researchers successfully explored only home dust as a media for dust source investigations. For instance, SHD permitted Allot (1990) to show that the

concentration of selected metals in house dust is linked to the distance from major highways; Akhter and Madany (1993) to distinguish the impact of the Gulf War burning of the Kuwaiti oil fields; Hlaway and Nagy (1994) to perform a source apportionment of three industrial emitters; Schneider and Kuhlman (1996) to assign deposited dust particles to fugitive rather than stack emissions from cement kilns and Selim (1998) to measured dust that was settled in barns (Ilaqua 2002).

Cidziel and Hodge (1998, 2000) suggested that an undisturbed attic that captured atmospheric dust might act as a historical repository of all trapped pollutants and should be considered for reconstruction of exposure history because it would reflect past atmospheric events. Since that time attic dust investigations in the US were conducted in a number of different directions. Attic dusts were used to explore of aerosol-born contaminants in a locality (Van Pelt 2002), to determine the level of hazardous material and their sources (Ilaqua et al. 2003), for tracking the sources of human exposure and to estimate a health risk for the residents of communities (Rasmussen et al. 2000; Lioy et al. 2002; Hensley 2007).

This method was specially validated by V. Ilaqua. By using the dust of undisturbed attics, he developed a systematic approach to reconstruct historical atmospheric concentrations of air pollutants. In his research, he proved that attic dust reflects the rise and fall of lead concentrations in the air that correspond to the trend of lead emissions into the air by gasoline consumption. He found that attic microenvironment (attic design, ventilation, air exchange) did not affect particle penetration, velocity, diffusion, deposition and settled dust transformation processes (resuspension, volatilization, degradation, chemical reactions). He concluded that in comparison to other methods (emission inventories, dendrochronology) attic dust analyses may

provide much broader possibilities for understanding air pollution events (Ilaqua 2002, Ilaqua et al. 2003).

A very interesting pattern was found by Van Pelt (2002) while studying dust in only one large attic (built in 1984). Van Pelt determined that particle size analyses, the percentage of organic carbon and total nitrogen,  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  activities and total dust deposition were regressed as a function of distance from the upwind vent (Van Pelt 2002).

Finally, the applicability of attic dust as a strong sampling material for air pollution source investigation has been successfully proven by several European studies. In Europe, where there is a very long history of mining and smelting, attic dust was mainly used to investigate historical emissions from smelters and mining activities (Tye 2006). In the last decade, attic dust was intensively investigated in Eastern Europe and was mainly used to examine mining emissions of metal particulates, to identify the pathways of pollution in the area (Balabanova et al. 2011), to help rule out the level of contamination in the area surrounding the metallurgical complex (Shtiza et al. 2009), and to provide the evidence for forensic investigation of sources, for example, if very high contents of heavy metals in soil was related to smelter deposition.

The usefulness of attic dust and top soil was successfully confirmed in areas historically polluted by heavy metals especially in Slovenia (Žibret and Šajn 2008). Attic dust was used for tracing the mercury halo in Indrija area (Gosar et al. 2006), to distinguish mining and metallurgy influence in the Meza valley (Šajn 2006), for modeling of heavy metals (Zn, Cd) atmospheric dispersion and for recording the processes in the atmosphere during the time of smelting activities in the Celje area (Žibret 2008). During several years of research, all past and present metal mining and smelting sites in Slovenia were assessed through the use of attic dust and

soil sampling media and a detailed summary of their geochemical anomalies was obtained (Žibret and Šain 2008).

### **3.2 Air Pollution Source Identification Methods**

In order to successfully determine sources of environmental pollution it is essential to correctly choose the media of investigation and also the methods of their evaluation. In the investigation of past air pollution events and their sources, it is reasonable to explore the environmental forensic approaches that often deal with historical release of contaminants.

Environmental Forensics usually operates using two types of information: documentaries and sampling data. The sampling data may be evaluated by:

- “1. Tracer techniques based on the presence or absence of a particular chemical;
2. Ratio techniques where the relative amounts of two or more chemical are compared;
3. Trend techniques where the spatial or temporal variation of a concentration or a ratio is of interest;
4. Quantity technique that depend on the integrated concentration over space or time, the mass of the chemical to provide forensic information” (Murphy and Morrison 2007).

Based on data availability and forensic questions of concern, investigators may choose one or more optimal forensic techniques that help to obtain valid results. The best results of forensic investigation rely on a combination of specific methods for each environmental media with universal methods such as, for example, isotope analyses, modeling etc. The necessary requirements and the basis of any source identification method is a high quality analytical chemistry data.

### **3.2.1 Specific Dust Source Evaluation Methods**

#### **3.2.1.1 Particle Pattern Recognition Methods. Particle Size Analysis & Microscopic**

##### **Investigation**

The mechanisms of dust entrainment, dispersion and deposition are very complicated. Dust dispersion (both vertical and horizontal) and deposition depend on many parameters such as particle size, particle compositions, atmospheric stability, air temperature, humidity, the strength and direction of the wind velocity, wind direction and the wind's turbulent structure (Pye 1987). Besides examination of dust chemical composition, researchers often use particle size analysis and microscopic investigation of the particles that to facilitate identification of their sources.

Usually, the average size of the transported dust particles fluctuates from submicron to 100 microns. The smaller particles are more readily held aloft by turbulent motion and often travel very long distances. Those particles that are transported long distances are usually smaller than 10 microns and some even smaller than 2 microns. Research conducted in the Arctic and Antarctic regions showed that the deposited dust in most cases does not exceed 1 micron (Pye 1987).

There is an inverse relation between the size of particles and their persistence in the atmosphere. The small particles (smaller than 20 microns) may remain in suspension for weeks (during which they can be transported great distances) unless washed out by rain, and the larger grains settle back to the surface quickly (depending on the turbulence). Aeolian deposits in the ocean are largely composed of particles finer than 10 microns, consistent with long transport distances, while the particles deposited over land mass are often from 10 to 50 microns (Pye 1987; Liou et al. 2002).

The particle size distribution of the sampled dust may be analyzed by two granulometric classes (coarse, with particle  $D > 2.5$ microns and fine with particle  $D < 2.5$ microns, or by several classes. The shape of the particle size distribution may suggest their atmospheric pollution source (Korzhova et al. 2011). As a rule, the Earth crustal elements Al, Si, Ca, Mg and Fe occur in particles with  $D > 2.5$  microns, whereas the anthropogenic elements such as Pb, Cd, As, Se, Zn, Cu, Sb, Hg, Br, V and Ni are mainly concentrated in particles with  $D < 2.5$  microns, and more than 50 % of these elements have the  $D < 0.5$  micron. In the manufacture of non-ferrous metals, dust containing Pb,Cd, Sb, Cu, Zn, As, Se, V, Cr, Mn, and Ni oxides occurs in particle sizes varying from 0.1 to 1micron (Korzhova et al. 2011).

Often particle size analysis is utilized with morphological and chemical characteristics of airborne particles. Microscopic examination of dust may help to distinguish between sources such as dust combustion material, various lead halides from automobile exhaust, pollen, seeds and plant material (Gulson 2000; Millette and Brown 2007). However, microscopic investigation of dust particles may be useful in its source identification if particles retain the form in which they were emitted. In some cases particles may be transformed from their original emitted condition through chemical reactions or they may undergo transformations that change their chemical and physical characteristics (Millette and Brown 2007). Thus this method needs to be combined with other methods.

### **3.2.1.2 Enrichment Ratio as a Dust Source Indicator**

Analyses of particle sizes together with their chemical composition are very important because this allows not only a better understanding of the dust transport and removal processes but also helps in identification of its sources (Cahill 1995). Dust chemical composition under

natural conditions is expected to reflect elemental composition from the soil of origin and to a certain extent, the parent rocks. Dusts from various locations of the world differ from each other and have a specific “fingerprint” of major and trace elements and their isotopes. Ratios of the elemental or isotopic constituents in analyzed dust may permit the identification of both its geographical origin and the relative contribution of different sources (Pye 1987; Watson and Chow 2007).

To estimate the proportion of natural and anthropogenic sources in analyzed dust, its chemical composition is compared to the corresponding composition of natural materials (Cidziel and Hodge 2000). The calculation of the enrichment ratio (ER) or enrichment factor (EF) is one of the simplest but more effective approaches for achieving this goal. The EF can be estimated relative to the reference values from Taylor and McClennan’s reference book (2002) “Average Continental Crust” or to local background values, obtained from analyses of uncontaminated soil and rocks in the sampling area. The data from local geological sources are considered more reliable (Davis and Gulson 2005).

Chester in 1984 calculated enrichment factors for various elements in suspended dust using the formula:

$$EF_X = (C_{xp} / C_{alp}) / (C_{xc} / C_{alc}),$$

where  $C_{xp}$  and  $C_{alp}$  are the concentrations of an element X and aluminum (al) in aerosol (particle) and  $C_{xc}$  and  $C_{alc}$  are their concentrations in average crustal material (Chester in Pye 1987, p.137).

If the enrichment factor (EF) of the element calculated by this formula is greater than 1, the element is considered to originate not only from soil and rock but also from other sources or

processes (as a result of anthropogenic activities) (Rahn 1976 in Ilaqua 2002). Aluminum was selected, according to the common practice, as one of the most convenient crustal reference element (CRE) (Riemann 1998 in Ilaqua 2002).

Aluminum occurs widely in the environment. In atmospheric particulates aluminum is derived from aluminosilicate minerals (the aluminum cannot be mobilized into biological systems from these insoluble stable complexes), and for that reason it is often used as an indicator of the quantity of CRE in a mixed aerosol. Some elements such as silicon (Si), iron (Fe), barium (Ba), titanium (Ti), zirconium (Zr), manganese (Mn), yttrium (Y), scandium (Sc), and in some cases vanadium (V) may also serve as CREs against which the relative enrichment of other elements in aerosols can be compared (Ilaqua 2002; Watson and Chow 2007).

Other researchers for EF calculation use a more simple equation:

$$EF = [X_{fd}] / [X_{ss}],$$

where  $X_{fd}$  is the concentration of chemical species in fugitive dust (fd) and  $X_{ss}$  is the concentration of the same species in the source soil (ss).

It is commonly concluded that if the EF of elements in analyzed dust calculated by this equation is greater than 10, it suggests their possible anthropogenic source. If the EF of a particular element is much greater than the EF of the mean of CREs, it is almost certainly from anthropogenic sources (Van Pelt and Zobeck 2007).

Heavy metal enrichments usually indicate emission from industrial sources. For instance, lead, copper, zinc, iron and manganese enrichment is attributed to smelting, steel mill or plating. Enriched selenium indicates contribution from coal-fired power stations, and enriched vanadium

and nickel may indicate residual oil combustion or refinery catalytic crackers, etc. (Meza-Figueroa et al. 2006; Korzhova et al. 2011). In each source profile there is a unique chemical component at a fixed ratio (Watson and Chow 2007).

### 3.2.2 Isotope Analysis

One of the most powerful methods widely used in the evaluation of the sources of heavy metal contamination in the environment is isotope analysis. The considering advantage of isotope analysis (radioisotope and stable isotopes) is that it can be applied to a wide spectrum of natural media (rocks, soils, aerosols, dust particles, sediments, water, grasses, tree rings and leaves), as well as to technogenic materials including gasoline, coal, fly ash and fuel oil (Sagden et al. 1993; Dunlap et al. 1999; Gwiazda and Smith 2000; Ketterer et al. 2001; Farmer et al. 2002; Munksgaard et al. 2003; Bacon et al. 2004; Bindler et al. 2004; Duzgoren-Aydin et al. 2004; Bollhover et al. 2006; Margui et al. 2006; Komarek et al. 2008; Bigalke et al. 2010). Isotope analysis can significantly facilitate identification of sources of contaminants from industrial activities because chemical processes are not expected to change the isotopic composition of materials and the analytical technique is sensitive to large isotope variations and compositions (Gulson et al. 1981; Rabinowitz 1995; Bacon et al. 1996; Adgate et al. 1998; Smith 2000; Phillips and Gregg 2003).

Radioisotopes ( $^{137}\text{Cs}$ ,  $^{210}\text{Pb}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{241}\text{Pu}$ ,  $^3\text{H}$ , Uranium - series  $^{238}\text{U}$ ,  $^{234}\text{U}$ ) and their ratios are commonly used in environmental application for dating materials, and are often utilized in various geochemical exploration topics as a natural tracer to study the age and sources of geomaterials (Cizdziel and Hodge; Cizdziel and Hodge 2000; Ilaqua 2003; Cizdziel et al. 2007; Ma et al. 2012). For instance, Van Pelt et al. (2007) used  $^{137}\text{Cs}$  measurement to estimate

rate of soil redistribution by wind. Analysis  $^{137}\text{Cs}$  in wind eroded sediments together with particle size analysis helps to estimate the soil loss (Van Pelt et al. 2002).

Naturally abundant stable isotopes of C, H, N, O, S and Cl (and their ratios) now are routinely used for determining water, nutrient and trace element fluxes and cycling in a variety of ecosystems (Philp and Jarde 2007). The power in the use of heavy metal stable isotopes is their ability to reveal correlations between environmental samples and their sources, particularly ore sources (Rabinowitz and Wetherill 1972; Gulson et al. 1995; Rabinowitz 1995; Phillips and Gregg 2003; Philp and Jarde 2007). Heavy metal stable isotopes (especially four Pb isotopes and more recently Cd, Zn, Cu and Cr isotopes), as related to pyrometallurgical activities of smelters and refineries, were proved to be a sensitive tracers of atmospheric source of them and their transport in soil and other media (Rabinowitz and Wetherill 1972; Eckel et al. 2001; Rabinowitz 2005; Bigalke et al. 2010). One application of this method is to use isotope ratios to quantitatively determine the proportional contribution of several sources and to identify natural versus anthropogenic sources of heavy metals (in particular Pb), not only in, soil, dust, rocks, lake sediments, mosses, peats, bogs, plants (especially trees), but also in human blood, milk, teeth and bones (and even in goose liver) (Ault et al. 1970; Rabinowitz and Wetherill 1972; Gulson et al. 1995, 2004, 2009; Walmought et al. 1995; Bacon et al. 1996; Maddoloni et al. 1998; Dunlap et al. 1999; Gwiazda and Smith 2000; Drexler 2003; Phillips and Gregg 2003; Bindler et al. 2004; Farmer et al. 2004; Rabinowitz 2005; Ketterer 2005; Thapalia et al. 2010).

Lead is probably the only metal that is naturally available for large isotopic tracer experiments. The concept of Pb isotope analysis is based on the principle that lead is composed of four stable isotopes:  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$ . Isotope  $^{204}\text{Pb}$  is named “primeval lead” because it was formed at the time when all of the elements were formed and not as a result of any

radioactive decay process or nuclear reactions. The radiogenic isotopes  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$  originate from the decay of Uranium ( $^{238}\text{U}$ ,  $^{235}\text{U}$ ) and Thorium ( $^{232}\text{Th}$ ), with a half-life of 4.5, 0.7 and 14 billion years respectively (Ault et. al. 1970; Munksgaard 2003; Philp and Jarde 2007). The isotope ratio of common Pb mined today results from addition of radiogenic Pb to primeval Pb the amount of which is constantly increasing at known independent rates throughout the Earth's evolution. Since the formation of the Earth three radiogenic Pb isotopes have exhibited a small increase in abundance with time compared to the nonradiogenic isotope  $^{204}\text{Pb}$ . The relative increase for each radiogenic isotope goes in accord with the rate of radioactive decay of its parent.

Lead ore were formed at different times during the last three billion years; that is why each kind of ore has a unique set of isotopes. In one ore from the same mine the set of isotopes can vary; and isotope ratios in the samples taken at two different locations in the same mine can differ from the mean  $\pm 17\%$ . However, mining, smelting, distributing, stockpiling and compounding cause the mixing and averaging process (Rabinowitz 1995).

Different mining regions are also characterized by different metal isotope ratio. For instance, the lead mines may differ in  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{206}/^{207}\text{Pb}$  ratios. Generally, the  $^{206}/^{204}\text{Pb}$  ratios of Colorado, Utah, and Montana ores fall between 17.5 and 18.5. Mexican ores have somewhat higher ratios. For example, Santa Eulalia ore, used by ASARCO until 1907, has a  $^{206}/^{204}\text{Pb}$  ratio of 18.5 (also known a  $^{206}/^{207}\text{Pb}$  ratio, which is 1.18) (Rabinowitz 2005).

While studying lead isotopes in soil near five historic American smelters and refineries (two of them belonging to ASARCO), Rabinowitz found a match between isotopic patterns of Pb, added decades ago into the undisturbed topsoil, with documented sources of the ores from the smelters' supplies. At the same time, he concluded that "no single number of isotope ratio

can be used to describe fully the ore from the area, rather a range of possible values is appropriate. Even if isotope ratios in all the soils around the factory sites were exactly the same, accurate apportionment among potential sources is not possible. Because of variation of isotope ratios within a single mining district, assigning potential sources of lead ores to smelter soil is necessarily inexact” (Rabinowitz 2005). Nevertheless, the isotope method may be effective in those studies in which a single, well-defined and dominant source of contamination can be identified (Chow and Johnston 1965; Gulson et al. 1981; Rabinowitz 1995; Ketterer et al. 2001; Phillips and Gregg 2003; Gulson et al. 2004).

The isotope ratios of Pb and other heavy metals are significantly different in various environmental media and such differences can be used to distinguish the probable sources of them in these media (Ault et al. 1970; Adgate et al. 1998; Komarek et al. 2008). One of the most successful and significant application of isotope analysis is in distinguishing the sources of pollution in soil and dust, particularly house dust, especially if these sources are related to mining and smelter activities (Gulson et al. 1995; Gwiazda and Smith 2000; Drexler 2003; Rabinowitz 2005). For example, using both major ( $^{206/207}\text{Pb}$ ) and minor ( $^{206/204}\text{Pb}$ ) lead isotope ratios it was possible to differentiate between common Pb sources in SHD and to evaluate their potential contribution to the residents’ BLL (Gulson et al. 1995; Gwiazda and Smith 2000).

The ability to evaluate individual sources of heavy metal hazard and their environmental impact is the most important advantage of Pb and other metal isotope techniques. At the same time the variations in the ratio values constitute the weakness of the isotope analysis method. That is why a measurement of target elemental ratio values in different media is advisable (Ault et al. 1970). In order to successfully exploit stable isotope analysis in heavy metal source identification (and particular of heavy metal emission from smelters), it is necessary to conduct a

preliminary measure the stable isotope ratios of investigating elements in their supply ores. Another important requirement for the environmental application of a wide range of stable isotope analysis is that in most cases they should be used in combination with other methods and techniques (Philp and Jarde 2007).

### **3.2.3 Statistical Methods. Modeling**

Statistical methods are necessary tools for analytical data interpretation in environmental studies and can provide additional and sometimes stronger evidence for distinguishing environmental pollution sources. Various statistical techniques are available for the determination of characteristic ratios between contaminants, for evaluation of trends of pollutant concentration over time and space and for making predictions of their dissemination with a degree of confidence to the results (Gauthier and Hawley 2007).

The application of bivariate statistics (Pearson's product moment correlation coefficient for parametric data; Spearman's rank correlation coefficient for non-parametric data) can show how chemical elements correlate in the content of environmental samples and that may help to distinguish an anthropogenic input in the sampled material. A high correlation among some elements can prove the hypothetical source of their emission. For instance, if V and Ni are highly correlated it can possibly relate to fuel (petroleum) combustion processes (Meza-Figueroa 2007; Watson and Chow 2007), and the strong correlation between Co-Ni and Ti-V potentially reflect their derivation from "metalliferous industries such as foundries, metal fabrication workshops, pigment manufacturers, incineration, and the general degradation of materials" (Davis and Gulson 2005). Cr, Co, Ni, V and W compounds are typically found together in the dust of semi-industrial areas because they originate from different metal processing activities and not from the same geological sources (Davis and Gulson 2005; Korzhova 2011). Mining and smelting

activities are characterized by specific sets of elements such as Pb, Cd, As, Sb, Cu, Zn, Ag, Se, etc. At the same time each mine has its own elemental signature (Šajn 2006; Žibret 2008.). There is summarized information that may help to attribute the specific set of metals and their compounds to their emission sources and correlation analyses may facilitate this attribution (Alloway 1995; Watson and Chow 2007; Korzhova et al. 2011).

Multivariate statistical methods are commonly used in environmental studies to better classify a large amount of data, to analyze the relationship between the elements and thus to provide further understanding of their sources. To reveal associations between the chemical elements, the data matrix can be evaluated by multivariate methods such as different types of ANOVA - MANCOVA (for parametric data), the Wilcoxon's Rank sum test (Mann Whitney U test), the Kruskal-Wallis test (in the case of non-parametric data) (Davis and Gulson 2005), Factor analysis (Reinman et al. 2002; Šajn 2006), Cluster analysis, and Principal Component analysis (PCA) (Tokalioglu and Kartal 2006; Balabanova 2011).

Various exploratory statistical analyses, especially Cluster and PCA, are the most commonly used in environmental studies (Tokalioglu and Kartal 2006). The main function of these analyses is to provide meaningful structure to analyzed data by identifying a smaller number of so-called factors, thus facilitating recognition of common patterns and consequently sources of pollution (Rienmann et al. 2002; Balabanova 2011).

The PCA is usually applied to the grouping of separate statistically significant associations. The numbers of significant factors (and the percent of variance explained by each of them) are calculated by extracting the eigenvectors and eigenvalues from the correlation matrix (Tokalioglu and Kartal 2006). Cluster analysis, in contrast to PCA, takes into account the similarity or distance between clustering variables, minimizing the variability within each cluster

and maximizing the variability between clusters (Ilaqua 2002; Tokalioglu and Kartal 2006; Woocay and Walton 2008).

It should be noted that in analyzing the same environmental data by diverse statistical analyses, slightly different results can be obtained. The main influential factor is the “quality” of analytical data on the basis of which statistical analyses are conducted. These data depend on the analytical method, in particular the instrumentation sensitivity to large spreads (scattering) of analyzed data, how much data of target elements were missed in the analyzed set and if, for instance, of 25% (or more) data below the detection limit were included (Rienmann et al. 2002).

To avoid the deficiency of each statistical analysis, it is advisable to combine the results of several statistical analyses. In order to obtain successful results, particularly in investigating sources of pollution, it is necessary to clearly understand the purpose of every statistical analysis and to take into consideration the media, methods, and analytical techniques used for environmental pollution assessment (Rienmann et al. 2002).

Currently, statistics effectively help to facilitate organization and utilization of different databases and their testing requires model creation, to develop models and to test the significance or validity of the models. Without modeling it is impossible to operate in atmospheric processes studies, in predictions of future atmospheric composition, in atmospheric transport and simulation of hazardous plume movements (Egan and Murphy 2007). Models are being used increasingly around the world to quantify sources, for example greenhouse gases, to examine a wide spectrum of biogeophysical processes, for emission estimation and in emergencies associated with toxic release of harmful materials (such as nuclear disasters) (Gauthier and Hawley 2007; Lin et al 2011).

Modeling can be the most useful method in the case of the uncertainty of the contamination sources, especially when the input of several constituents is changing simultaneously. To develop the spatial and temporal pattern when creating a model for source identification it is very important to accumulate data and organize database for modeling ( Šajn 2006; Egan and Murphy 2007; Lin et 2011).

### **3.2.4 Dendrochemistry: an Emerging Forensic Method**

When listing methods for detection and reconstruction of historical air pollution events, one cannot avoid mentioning the dendrochemical method, a subspecialty of dendroecology. Dendroecology is a temporal study of tree changes in response to different environmental stresses including chemical pollution on local and regional scale (Stokes and Smiley 1996; Balouet et al. 2007). Tree ring reaction to chemical pollution, in particular heavy metals, may induces both physical anomalies and changes to the rings' chemical composition (Balouet et al. 2007).

Dendrochemistry has been an application of dendroecology for contaminant source identification since the early 1990s. Based on dendrochronology (developed by I.E. Douglas in 1929), dendrochemistry identifies and measures the impact of toxic elements in tree rings and their temporal correspondence to pollution events (Sheppard and Funk 1975; Lepp 1975; Bayes III and Ragsdale 1981; Bindler et al. 2004). In favorable circumstances xylem rings are able to provide a record of various absorbed pollutants with a precision of a year or even a season.

Trees have proven to be very effective environmental sensor-monitors of long-term heavy metal pollution (Sheppard and Funk 1975; Hutchinson 1994; Watmough and Hutchinson 1995). Attempts to obtain global historical records of heavy metal pollution have been successfully

carried out using various natural media. Greenland and Antarctic ice and snow strata, lake sediments, mosses, ombrotrophic bogs, lichens, and peat, may allow researchers to create long-term records of heavy metal deposition for hundreds, even thousands of years (Ault et al. 1970; Sheppard and Funk 1975; Bacon et al. 1996; Farmer et al. 2002).

Nonetheless, the utility of these media is limited by geographic location, climate or the possibility of their use in highly polluted areas. Trees are more readily available, and are sometimes the only one applicable medium for an environmental forensic investigation in a given case study, or can be used as a complementary medium (Ilaqua 2002).

The majority of anthropogenic elements in wood are derived from atmospheric pollution either directly through aerial interception, or indirectly through uptake from the soil where they accumulate. However, absorbed metals can diffuse through the xylem due to the porosity of the wood and lead to misleading findings (Hutchinson and Watmough 2002). Unsuccessful results in studies usually occur when heavy metal levels are low or when they are accumulated in tree rings only from soil (Southern 2009). Soil acidity is also an essential variable since its low pH mobilizes metals. Moreover, the choice of tree species is significant due to the dissimilar response of the tree growth to the environmental stress and the tree's sensitivity to particular metal absorption (Baes III and Regsdale 1981; Watmough and Hutchinson 1995). In order to substantiate findings it is also highly advisable to use a series of control trees.

A good test of whether a tree can be an adequate biomonitor of heavy metal pollution is to evaluate trees grown in the area where the type of pollution is understood (Kerstin 2003). Tree rings are excellent media for recording and monitoring environmental pollution in industrial areas. At the same time it is questionable whether urban trees can be used as a bioindicator in assessing the atmospheric pollution impact on urban environments and to what extent. There are

some factors which would lead to erroneous conclusions such as using trees which were transported from other areas or which grow in urban soil treated by fertilizers, and so on. For a correct interpretation of dendrochemical analyses, it is always necessary to acquire additional information from the tree sampling sites as well as modes of trace element deposition in wood (Hofman et al. 1996; Balouet et al. 2007).

Beside the specific requirements for tree sampling, it is very important to select the optimal analytical method of tree core chemical microanalysis. In tree ring analyses a variety of analytical methods, including ion chromatography, electron microscopy and gas chromatography coupled with mass spectrometry are used. The recent more precise methods such as Laser Induced Plasma Spectroscopy (LIPS), Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA ICP-MS), Proton Induce X-ray Emission (PIXE), or Energy Dispersive X-ray Fluorescence (ED XRF) do not destroy tree core samples, and permit dating chemical elements with a precision of within a year and sometimes a season.

In order to trace the source of pollution by LA- ICP-MS, plant materials (tree rings, bark and leaves) may be ablated and analyzed not only for their chemical element content but also for their isotopic composition (Ghazi 2007). Other advantages of these methods are that they analyze several pollutants simultaneously and have low detection limits for all analyzed elements. However, there are some difficulties with regard to standards that need to be further established.

Despite the difficulties, dendrochemistry is a very useful and promising environmental forensic method. In order for dendrochemical methods in pollution source identification to become more effective, one of the requirements is to improve existing non destructive analytical techniques of chemical microanalysis, in particular, lowering detection limit, sensitivity regardless of the atomic number and cost effectiveness.

## CHAPTER 4

### METHODOLOGIES

#### 4.1. Study Area

##### 4.1.1 Geography and Climate

The Paso del Norte (PdN) region is one of the largest and oldest metropolitan areas on the US–Mexican border with a population of over 2.25 million. Three states share a border in this region: Texas, New Mexico and Chihuahua, Mexico. The majority of the population is concentrated in two neighboring cities: El Paso (at the extreme westernmost edge of Texas, pop.649, 121) and Ciudad Juarez (Chihuahua, Mexico, pop.1, 332,131). The population of the USA portion of the PdN region is comprised of 800,647 in El Paso County, Texas and 209,233 citizens in Dona Ana County, NM, including 14,106 citizens in the Municipality of Sunland Park, NM (communities of Sunland Park, Anapra, Meadow Vista, Riverside, Desert View, and parts of Santa Teresa) (U.S. Census Bureau 2010; INEG 2010).

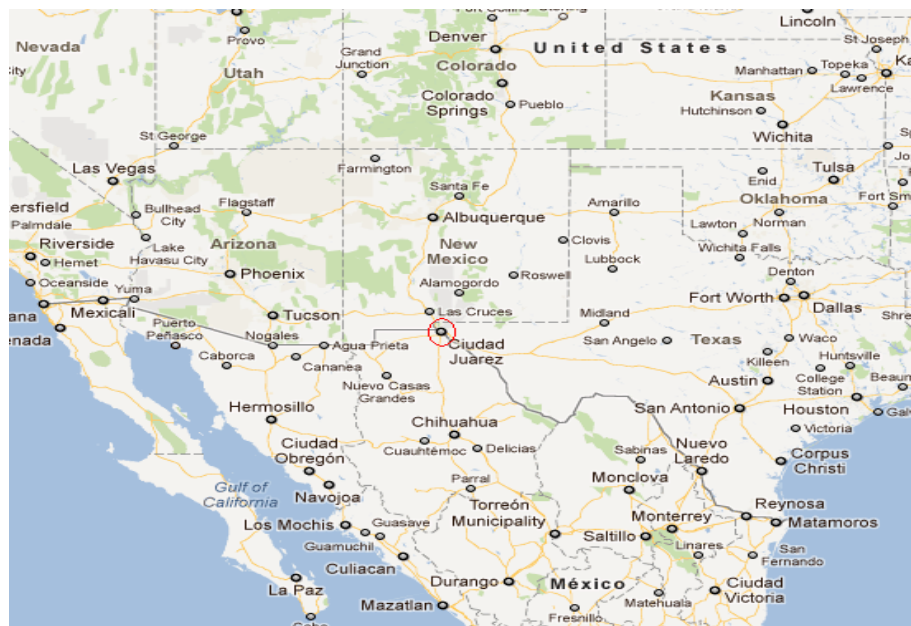


Figure 4.1: Location of Paso del Norte Region (source: Google maps).



Figure 4.2: El Paso-Juarez Area (source: Google maps).

The Rio Grande (Rio Bravo del Norte) River originates in Colorado, flows southward through New Mexico along the Rio Grande rift and then to the Gulf of Mexico. In the PdN region, it determines the border between El Paso, TX and Cd. Juarez, Chihuahua, Mexico.

There are three groups of mountains in the region: Sierra de Juarez on the Mexican side, Mount Cristo Rey on the New Mexico side of the Rio Grande River and the Franklin Mountains on the Texas side which divides El Paso into two sections, western and eastern. Ciudad Juarez is located on the southwestern side of the Mesilla Bolson and occupies the river valley and several terraces leading to the foothill of the Sierra de Juarez Mountain. Small suburbs, colonias and squatter settlements wrap around the northwestern and southeastern end of the Sierra de Juarez.

The complex topography with isolated mountains produces special meteorological conditions, promoting the trapping and transportation of local air pollutants (Rincon et al. 2005). Temperature inversions and reduced wind velocities (low wind events) greatly contribute

(especially in fall and winter) to the trapping and build up of airborne contaminants (Pingitore et al. 2005; Dulin 2005; Grineski et al. 2011).

The region is situated in the Chihuahuan desert within the southern part of the Basin and Range province and is characterized by a warm arid climate. The average annual temperature is 25.1 degrees Celsius (C) and the average minimum temperature is 11.2 degrees C. The warmest month is June with an average temperature of 35.2 degrees C, and the coldest is January with an average temperature of 0.5 degrees C. The region has an average of 302 sunny days per year (Gill 2006).

The rainy season, from July to September, is mostly produced by the North American southwest monsoon accounting for more than half (123 mm) the amount of average annual precipitation. The average annual rainfall amount is 218 mm (Gill 2006). During the monsoon period thunderstorms with flash flooding, hail, high winds and lightning across the region result from the orographic lift from the mountains interacting with strong daytime heating (Gill 2006).

Erosive winds come predominantly from the west and southwest (Drexler 2003). Wind events with sustained velocities of 13.5 m s<sup>-1</sup> (30 mph) with gusts of 35 m s<sup>-1</sup> per hour (75 mph) are common in the winter and spring (Novlan et al. 2007).

The Paso del Norte area is subject to very frequent synoptic-scale and mesoscale dust events (Rivera Rivera et al. 2009). Strong wind and dust storms usually occur in the dry season (December-May), the most intense dust storms starting in February and March and their frequency sometimes lasting until early May (NWS ELP web site).

#### **4.1.2 Geology and Soil**

Several lithologic units cover the PdN region and close surroundings. In El Paso County along the Rio Grande there is Young Quaternary alluvium, Old Quaternary deposits and windblown sand (Garcia et al. 2004). The Franklin Mountains are composed of igneous, metamorphic, metasedimentary and sedimentary rocks whereas Cerro de Cristo Rey consist mostly of igneous rocks (Lovejoy 1980; Cornell 2010). Local geological formations do not appear to be the source of the elevated level of heavy metals (Drexler 2003; Pingitore et al. 2005).

Soil resources of the PdN region are “highly variable, ranging from sand to clay, shallow to deep and nonsaline to saline” (Miyamoto 2000). Usually shallow gravelly or stony soils are found along the foot- hills of the Franklin Mountains and clayey soils in the Upper Valley (Miyamoto 2000). Local soil has been mapped in two main categories named “High intensity surveys” and “Low intensity surveys” (Ndame 1993; Velaverde 2004). High intensity surveys soil are commonly found within the floodplains of the Rio Grande River and Low intensity surveys occur in the foothills and bajadas of the Franklin Mountains (Ndame 1993; Miyamoto 2000).

The soil in the El Paso County can be classified by eight associations. These associations are: Bluepoint - Badland- Pajarito (BBP), DelNorte - Canutillo - Nichel (DCN), Glendayle – Armijo - Harkley (GAH); Harkley – Glendale – Gila (HGG); Hueco - Wink – Bluepoint (HWB); Pintura – Bluepoint - Wink (PBW); Rock Outcrop and Wink – Pintura Complex (WPC) (Barnes 1993; Garcia et al. 2004). In the El Paso study area the soils are mostly DelNorte – Canutillo- Nichel (DCN) and Harkley – Glendale – Gila (HGG). In some areas of the east side of El Paso, surface soil was removed and was replaced by Bluepoint loamy sand for topsoiling and

topdressing (Miyamoto 2000). Even though the soil might have been imported from other local areas for landscaping purposes (or excavated for site grading), the chemical composition of transported soil is still usually similar (Devahalli 1994).

Nevertheless, “there is nothing in the geological record that could account for the elevated heavy metal concentration found in the residential soil” (Drexler 2003). In contrast, the soils in the El Paso area are mostly derived from igneous and limestone parent materials and such soil usually has low levels of heavy metals, particularly As and Pb (Barnes 1993).

#### **4.1.3 Regional Industries: Potential Sources of Heavy Metals**

Today, the region is characterized by several industrial and manufacturing sites, including food, electronics, construction materials, clothing and plastics. Since the 1800s, the Paso del Norte area has been an important trade, transportation and industrial center. In the late 19th century, a mining industry arrived along with railroads for smelting and refining Mexican ores in El Paso. Despite not having substantial local mineral deposits, this industry was concentrated here due to a convenient location, urbanization, workforce population and educational opportunities.

Two smelters were functioning in El Paso for a very short time: the International smelter operated from 1889 to 1894 in the central part of El Paso and the Federal Copper smelter operated from 1901 to 1904 on the east side of El Paso (now Memorial Park). The major non-governmental contributor to the El Paso economy during the whole 20th century was the ASARCO smelter (1899-1999). Originally the plant was built on the edge of the city. Now, because of El Paso's expansion, it is situated in the central part of the West side, close to the University of Texas at El Paso (2.2 km).

The history of ASARCO's industrial activity is complex. Briefly, it was founded in 1887 as a lead smelter by R. Town. In 1889, it became part of American Smelting and Refining Company (ASARCO). It was closed and reopened several times for various reasons, sometimes during the same year. After having been destroyed in 1901 by a large fire, the property was rebuilt and reopened in 1902 with seven new lead furnaces and doubled production. In 1908, due to an economic crisis in Mexico, ASARCO shut down its mines at Santa Eulalia and Santa Barbara in Chihuahua. In 1910, a copper smelter was added to the plant property, receiving ore from the Chino copper mine until 1939. In 1925, ASARCO processed more than 2,000 tons of ore on a daily basis. The ore was transported from mines in Arizona, New Mexico and Northern Mexico (Young 1925 in Dulin 2005; Shapleigh 2008). During a long period of the ASARCO smelting activity, the facility used a large variety of mines from different locations including Mexico and other foreign countries (Marcosson 1949; Lee 1950).

The first important precautionary measure was taken by ASARCO circa 1930 to "abolish smoke". In 1948, slag fuming facilitators were built for recovery of zinc from slag produced by the lead furnaces (Marcosson 1949; Dulin 2008). In 1951, ASARCO constructed a 612 foot (186.6 m) tall smokestack. In 1966, demands for more pollution controls led the company to build an 828 foot (352.4 m) chimney (at the time the world's tallest smokestack) to help alleviate local air pollution (Kohout in Velaverde 2004). In the 1970s, Acid plants (in 1972 and in 1978) and a Sinter plant (in 1979) were installed. In 1979, a 90 million dollar renovation to the facility was implemented. In the 1980s, operations of the zinc smelter (1982) and lead smelter (1985) were suspended. In 1993, continuous top-feed oxygen process technology (CONTOP) was installed (Dulin 2005; Shapleigh 2008). In 1999, ASARCO was placed on care and maintenance

status due to copper prices. In 2000, the plant was completely shut down and in 2011 it was demolished.

A big industrial plant, the Phelps Dodge copper refinery (now Freeport Trowbridge), which has operated in El Paso since the 1920s, may also be considered a potential source of heavy metals in the local environment (Barnes 1993; Pingitore et al. 2005). It receives anodes of copper and electrolytically removes the impurities and the refined metals are then cast into bars

Other potential sources of local air contamination by heavy metals are Fort Bliss, the International Airport, interstate highways (especially during the period when gasoline was leaded), constant traffic on the international bridges and three railroads (Miller in Barnes 1993).

More than 300 maquiladora plants functioning from 1960s in Ciudad Juarez (non Mexican-owned industries located in the free trade zones), including iron foundries and chemical plants, are potentially polluting the air with particulate matter ( $PM_x$ ). However, in terms of emitting heavy metals into the air, these industries are not likely to generate such pollution (Blackman et al. 2003). Mexican-owned small industries, especially brick kilns and also the burning of scrap tires in Cd. Juarez are also significant sources of  $PM_x$ , but not of heavy metals (Blackman and Palma 2002).

## **4.2 Dust Sample Selection Strategy**

### **4.2.1 Site Selection**

In order to assess the impact on the environment of the various contamination sources, in particular ASARCO, and to obtain multiple, spatially distributed dust samples, three research areas were selected – the main area and two control areas. The initial criteria for dust sampling areas were based upon the distance from the ASARCO plant, the prevailing wind direction, the

distances from nearby roads and the age of the houses, which cover a considerable age span. It would have been preferential to investigate attic dusts from the houses built before the ASARCO opening, during its operation and after its closure, representing more than 100 years of smelting activity and influences of the most important facility's "events". However, the investigation included only limited attic dust surfaces ranging from 1916 to 2007.

Given the initial criteria, the Kern Place area (closest and downwind direction from ASARCO), the Government Hill area (beyond the mountain and more distant from ASARCO), both in El Paso, TX and the oldest (central) part in Juarez, Mexico, were chosen.

#### **4.2.2 Buildings, Attics and Attic Surfaces Selection**

Based upon the US Bureau of Census Tract information, the oldest houses in each mentioned location were chosen as a potential for attic sampling. In these locations addresses were selected randomly. Using door-to-door communication, houses were chosen primarily on a volunteer basis. The criteria were the presence of undisturbed and accessible attics and the possibility of sampling of appropriate surfaces. The presence of a sufficient dust loading was another essential requirement.

An oral survey was conducted with the residents who were willing to help in the study to document the house characteristics. Usually all interviewed residents knew the approximate age of their houses, but sometimes were uncertain about details such as installation of items in the attics or previous renovations for which they could only indicate the approximate time (within a decade).

Before sampling, each attic of chosen homes was observed for available locations where dust would be undisturbed and with a minimum of additional materials such as pieces of broken roofing, feathers and other foreign materials.

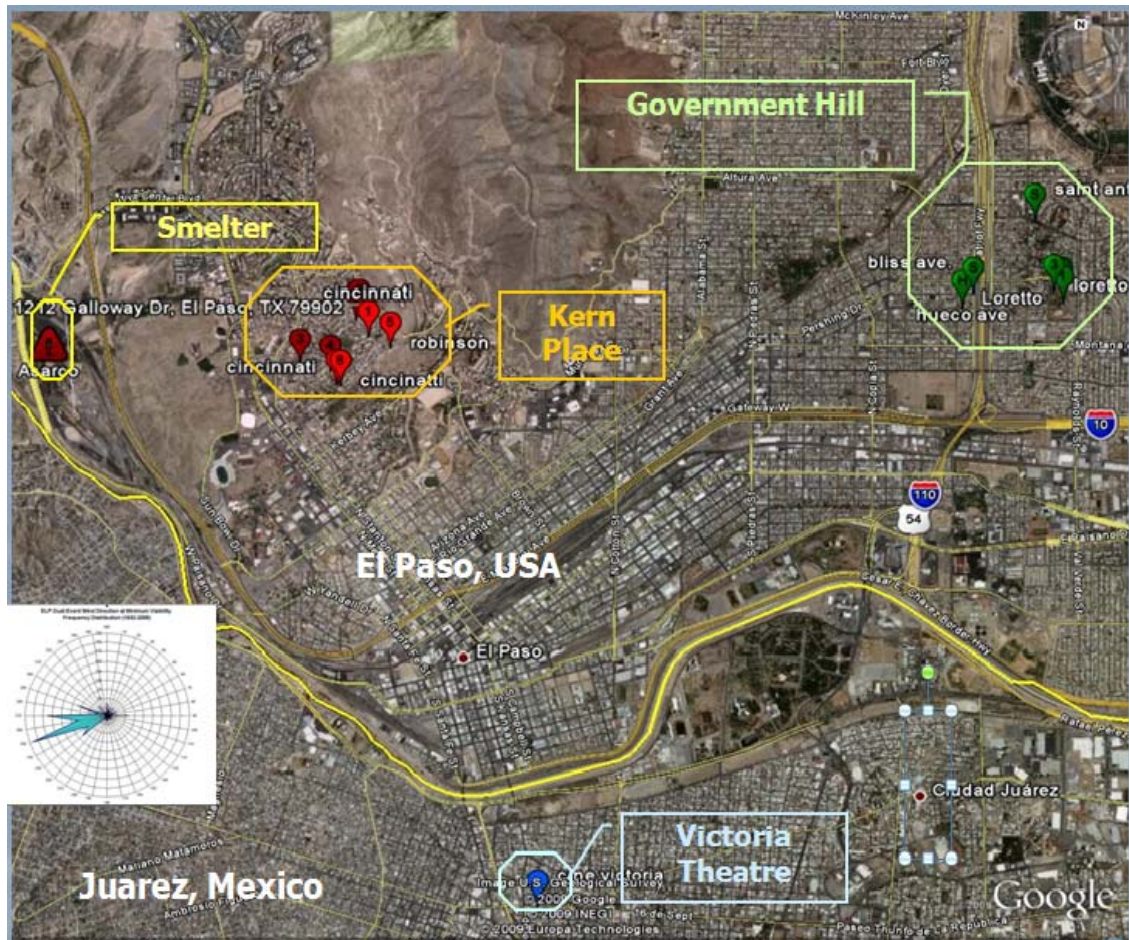


Figure 4.3: Dust sampling sites in El Paso (TX, USA) and Juárez (Chihuahua, Mexico)

(sources: Google Earth and Novlan et al. 2007).

Preferable surfaces were wooden beams with dust potentially deposited over a long period of time and where not affected by routine access. Some newer surfaces (for example electric boxes, pipes, newspapers, etc.) with recent dust deposition were chosen for comparison.

Finally, the dust sampling was applied to eight houses in the Kern Place area (K1-K8) and two houses (LH, LS) and two buildings (one of them with three independent attics L1-L3) from the Government Hill area. The years of their construction range from 1916 to the 1940s and also included some later date surfaces (ranging from 3 to 50 years old). From Juarez, only a single building (including surfaces of varying ages) the Victoria Theater (constructed in 1946), situated at the corner of Av. 16 de September and St. Francisco I. Madero Street, was available for sampling. Dust sampling sites in El Paso, TX and Juarez, Mexico, with the prevailing wind direction are illustrated in Figure 4.3 (p.62).

## **4.3 Sampling Strategy**

### **4.3.1 Attic Dust Sampling**

Attic dust sampling was performed throughout the summer and the beginning of fall (from July to September) 2007. During sample collection some precautionary measures were taken. To prevent inhalation of airborne hazards a filter mask was worn. In some attics two (1 by 10) boards were laid down to form a working platform across ceiling joists. A flashlight and head mounted lamp were always used.

In attics where gable vents were present, the best strategy was to sample in a line between the vents or, in the case of single vent, from the vent to the opposite end of the attic. If the centerline was disturbed or unsuitable, sampling was done beyond the affected distance. Generally, areas with significant amount of disturbance, such as the zone near access ports or stairs, were avoided. In the case of small attics, we sampled some areas away from the centerline.

In buildings with soffet vents, the predominance of the dust mass was near the edge of the attics where access was most difficult. On the center of such attics the deposition depth (and

potentially particle diameters) became progressively smaller. When there was an upward oriented exhaust vent such as a roof turbine or covered fan, samples were taken where it was possible along transects from the soffit vent to the area under the exhaust vent. Where there were no exhaust vents, samplings were performed along multiple transects between soffit vents from upwind to downwind with respect to prevailing winds. Disturbed areas were always avoided.

The surfaces that were available to sample did not vary among attics. Uninsulated sheetrock floor which is considered the ideal surface for sampling dust was found only in the Government Hill area (one attic). In other buildings and houses insulation (to the floor) had often been added. In this case, sampling from below or above insulation was not performed because it may provide a temporal discontinuity. The floored area was not sampled either because of uncertainty about disturbance (except once in Government Hill). Typical chosen surfaces were wooden beams and sometimes wooden corners that were not in immediate contact with the floor or roof tiles in order to avoid collecting particles of construction materials (Figures 4.4a and 4.4b).

The sampling procedure followed the instructions of Dr. Van Pelt and published works of Cidziel (1998) and Ilaqua (2003). Sampling was performed by carefully brushing dust onto a stainless paddle by new poly bristle brushes (for each attic and sometimes for each surface), transferring the dust to labeled polyethylene containers.

In total, 96 samples were taken: 90 from El Paso (56 from Kern Place area, 34 from Government Hill area) and 6 samples from Cd. Juarez (from the Victoria Theater).

The attic descriptions, sketches of their plans and points of sampling are presented in Appendix A1, Figures A1- A11. For the initially sampled four attics from Kern Place area (K1-K4), the big attic from Government Hill (L-1) and the building from Downtown Cd. Juarez (J),

no sketches were made due to the simplicity of these sites or the small amount of samples taken only around the entrance of the attics. Necessary information on each of these sites was transcribed from hand notes.



Fig. 4.4a and 4.4b: Typical attics surfaces for dust sampling: pipe and wooden beams.

#### **4.3.2 Soil Sampling**

Twelve soil samples from several buried soil horizons around El Paso were taken at depths of 5-30 feet, including samples from road cuts in order to access the horizons that would not have been contaminated with particulates from ASARCO. All soil samples were from the Rio

Grande delta and lacustrine sediments similar to the surface soils everywhere in the Paso del Norte region away from the mountains proper.

All dust and soil samples were sent to USDA ARS laboratories (Big Springs, Texas) for further chemical analyses preparation.

## **4.4 Sample Preparation**

### **4.4.1 Dust and soil sample preparation**

In the Big Springs USDA ARS labs, all dust samples were passed through a 100 micron opening nylon mesh to remove gravel, wood chips, insect parts and other foreign particles. Then dust samples were combined by similar surfaces, age and location within a given attic to assure sufficient sample size and then were split using a spinning riffler. Many of the samples were combined because they were not large enough to make extracts after the coarse material > 100 microns was sieved from the samples and they were essentially duplicates from similar sampling surfaces. These composite samples were also more defensible statistically. Thus, a total of 51 dust samples (from the original 96 samples) were created for further analysis. Table B2 with a description of combined dust samples is presented in Appendix B. Due to insufficient amount of dust even in combined samples the particle size distribution analysis was not performed.

The digestion and extraction procedures for dust samples were performed using modified EPA Method 3050B (EPA 1989). The dust aliquots were placed in a 50 ml centrifuge tube and 2 ml of 10% hydrogen peroxide solution was added to each sample to oxidize any organic matter. Samples were allowed to dry and 10 ml distilled water was added. After every 10 samples a blank sample was introduced with all steps alike except the introduction of the dust aliquot. The

mixtures were brought to 100 deg C and placed in an ultrasonic bath for 1 hour. Tubes were centrifuged and the supernatant decanted. Two additional 5 ml aliquots of water were added, heated, sonified, centrifuged, and the supernatant decanted. Aqueous samples were brought to exactly 20 ml by addition of distilled water. For the acid extracts, the dust buttons in the centrifuge tubes were allowed to dry for 48 hours and 10 ml of Aqua Regia (1 M HNO<sub>3</sub> and 2.2 M HCl) was added to each sample and the above procedure repeated to extract the surface coatings of the mineral particles.

The soil samples were processed in the same way as the dust samples, although only acid extraction from soil samples was done. All samples (dust water extractions, dust acid extractions and soil acid extractions) were chilled to 0 C degrees before the transportation to Texas Tech University GeoAnalytical Lab in Lubbock, TX.

## **4.5 Analytical Procedures**

### **4.5.1 Dust and Soil Analyses**

Instrumentation in TTU GeoAnalytical Lab was used to provide quantitative elemental analyses of the attic dust and buried soil samples. ICP-AES analyses were performed for a suite of 14 elements (Fe, Mn, Ba, Zn, Pb, As, Cd, Cu, Al, Ti, Na, Mg, P, and Sr). Additionally, concentrations of 3 elements (V, Se and Sb) were determined by ICP-MS analysis.

#### **4.5.1.1 ICP- AES Analysis**

ICP-AES analyses were performed on a sequential Teledyne Leeman Labs DRE ICP Spectrometer, following the instructions of the modified EPA Method 6010B (EPA, 1996).

Because the elements were analyzed sequentially, the stability of the instrument electronics was monitored every 20 minutes and periodically adjusted by using Hg wavelengths. With an eschelle grating each element wavelength was aligned in an x-y relationship to the Hg wavelength using a 1 ppm single element standard and was periodically checked for alignment. The plasma was aligned (finding the highest concentration of an element in the plasma) by aspirating a 10 ppm Fe standard which is in the same matrix as the samples to be analyzed.

Calibration curves were constructed for each analytical run by analyzing a set of standards in sequence twice. With a sequential instrument it is important to account for both the drift of the instrument over time and the slight variability in the sample introduction system (sample introduction fluctuation) by replicating the conditions expected during the run when building the calibration curves. If the % RSDs are greater than 10 % between the sequential runs of the calibration standards, a third run is performed to verify the accuracy of the calibration. Check standards are used throughout the analytical run to monitor drift over time and evaluate the precision and accuracy of the analysis. For any samples with elemental concentrations above the highest calibration standard there were two choices: 1. rerun the samples with an appropriate set of calibration standards, or 2. dilute the samples to a concentration for the current calibration and rerun (Standard procedure from the TTU GeoAnalytical Lab).

Calibration and check standards were made from a 100 ppm multi-element certified ICP standard (SPEX CertiPrep Instrument Calibration Standard 2) using calibrated pipettes and volumetric flasks. All glassware was cleaned with deionized water, soaked at least 24 hours in a 10% HNO<sub>3</sub> bath, and rinsed thoroughly with deionized water. Standards are matrix matched with the samples. Samples were prepared using the EPA method 3030A for the nitric acid extraction. Final HNO<sub>3</sub> concentration was approximately a 3 % nitric acid. Samples in aqueous

solution and 3% nitric acid solution behave similarly in ICP-AES procedures and thus can be analyzed using standards with a 3% nitric acid solution.

The blank used in the calibration was the acid solution used to make up the standards thus accounting for any possible contamination from deionized water or acids used. In addition, several method blanks were run to document any contamination from the acids and digestion vessels used during sample preparations.

All analytical runs were evaluated for instrument drift that may have occurred due to plasma source and sample introduction fluctuations. The first set of runs had a calibration from blank to 4 ppm; the second run had a calibration from blank to 50 ppm. A 100 ppm sample was run to confirm that the calibration was linear within 10 % so that concentrations between 50 ppm and 100 ppm were valid.

The consistency of sample preparation was checked by analysis of method blanks with each batch of samples. Approximately after every ten analyses and at the end of the sample run the calibration blank and calibration standards were analyzed to verify the accuracy and precision of the analytical run. A 180 second wash of 3% v/v HNO<sub>3</sub> was run between each sample analysis.

Analyses of all analytes were within  $\pm 10\%$  of the highest concentration value in the calibration. The samples having concentrations higher than the established quadratic dynamic range were diluted and reanalyzed or run with a different calibration that met the goal of being within 10% of the highest concentration value in the calibration. Lower Limit of Quantification (LLQ) was approximately 0.01 ppm for all elements. Detection Limit (DL) was 0.03 ppm (DL = 3LLQ). The sensitivity of the lower limit of detection was adequate for the elements determined. Most elements did not drift more than 15% from the check standard values. All samples

including dust in aqueous solution, dust in acidic solution and buried soil in acidic solution were analyzed under the same conditions described above.

#### **4.5.1.2 ICP-MS Analysis**

Target elements not detectable by ICP-AES in dust and soil acidic solutions were analyzed by ICP- MS using the same solutions. Sb, V and Se were analyzed following a modified EPA Method 200.8 and using an Agilent 7500cs Inductively Coupled Plasma Mass Spectrometer. A tuning solution was prepared from scandium, yttrium, indium, terbium and bismuth stock standards. An internal standard containing Be, Sc, In and Tb was used to correct for instrument drift. The internal standard was added by mixing with the solution prior to nebulization using a third channel on the peristaltic pump and a mixing coil.

The calibration standards were made up from the same certified standard as used for the ICP- AES analyses (SPEX CertiPrep Instrument Calibration Standard 2). All standards were made up in a 2% nitric acid solution using trace metal nitric acid and 18 mega ohm water. Standards of the following concentrations (blank, 200 ppb, 40 ppb, 8 ppb, 1.6 ppb and 0.32 ppb) were used to build the calibration curve. The same calibration solutions were used to both build the calibration and check consistency throughout the analytical runs. Standard ICP-MS instrument procedures were followed for tuning and method development. After every ten analyses and at the end of the sample run the calibration blank and calibration standards were used to document the stability of the analytical run. For all elements the calibration was linear.

Each sample was aspirated into the instrument at a rapid speed for 45 sec and then allowed to settle for 60 sec before beginning the analysis. The resulting analysis was an average of three readings. The rinse solution used was a 5 % v/v HNO<sub>3</sub> solution to reduce any memory effects (McGinnis et al. 1997). The goodness of the rinsing program and condition of carry over effect

were checked by running the first rinse as a sample after the 1000 ppb (1 ppm) standard. Data is reported in µg/L or ppb.

## **4.6 Data Processing**

The analytical data set was processed to acquire the EF of each from investigating 17 major and trace elements. For this purpose, the actual elemental concentrations in the dust and soil samples were calculated. Then, based on actual elemental concentration values in dust and soil, the enrichment factor EF of each investigated element was computed. The obtained EFs values were processed in subsequent statistical analyses in order to clarify possible sources, in particular heavy metals found in attic dusts.

### **4.6.1 Calculation of Actual Elemental Concentration in Attic Dust and Soil.**

The actual elemental concentrations in dust aqueous and then in acid solutions were calculated using the following formula:

$$C_x = \frac{(C_d - C_{db})}{W_s / 20},$$

where  $C_x$  is the concentration of an element X in the dust sample in ppm (µg/g),  $C_d$  is the element concentration in the analyzed digest,  $C_{db}$  is the mean blank subtraction (the element concentrations in the water or acid blank for the digestion batch to which the sample belonged),  $W_s$  is weight of the sample, and 20 is the dilution factor conversion (Ilaqua 2002).

The actual concentrations of all investigating elements acquired from attic dust aqueous and acidic solutions were summarized. Using the same equation, the actual concentrations of the same chemical elements were computed in acidic soil solutions.

#### 4.6.2 Enrichment Factors Calculation

In order to investigate the presence of anthropogenic “anomalies” in the natural distribution of major and minor elements, the EF was calculated for each of 17 elements using the equation:

$$EF = [X_d] / [X_s],$$

where  $X_d$  is the concentration of chemical species in dust (d), and  $X_s$  is the concentration of the same species in the soil (s) (Van Pelt and Zobeck 2007).

In our case, the EF is the concentration of an element in dust (from each of the 51 dust samples) divided by the same element's concentration in soil (the mean value of 12 soil samples from uncontaminated buried soil horizons).

Before carrying out the statistical procedures, the EFs data set was tested for normality. If variables didn't show the normal distribution, they were transformed by natural log e (ln) transformation. Since EF data demonstrated normal distribution, parametric statistical methods were used. Statistical runs were performed using a software package, e. g. SPSS version 9.2.

#### 4.6.3 STATISTICAL ANALYSES

Summary statistics and then bivariate (Pierson correlation analysis) and multivariate statistical methods (Multivariate Analyses of Covariance, Cluster analysis and Principal Component analysis) were applied sequentially to the EF data set. These statistical methods were used to examine the relationships among elements found in attic dust and their patterns of accumulation with respect to time and location.

In all statistical analyses the term “age” indicates approximate time of dust accumulation on the attics’ various surfaces. Each age value was obtained by subtracting the age of the house, where the attic dust was sampled, or the known age of the attic’s surface from 2007 (the year of the sampling). For all figures involving the MANCOVA tests, the Y axis indicates the EF of the element and the X axis the age of dust (Age to 2007) accumulated on different surfaces, not the date. Namely, “0” corresponds to the year 2007 when all dust was collected, and “90” corresponds to 1916, the age of the oldest house. This resulted in a backward or “mirror” appearance of the distribution of elemental EF values in relation to time. When the MANCOVA results are applied to two time periods, the number “50” designates 1966 (1966 minus 1916). Therefore the time period before 1966 is located on the right side of the figures, and the period after 1966 is represented on left half of the figures.

The locations of the attic dust sampling, i.e. the “Kern Place”, “Government Hill” and “Juarez” were considered “groups”.

#### **4.6.3.1 Summary Statistics**

Summary statistics (Mean, Standard Deviation, Standard Error, Minimum and Maximum) were applied in order to determine the EFs of all investigated chemical elements separately in each group/location.

#### **4.6.3.2 Bivariate analysis. Calculation of Pearson Product Correlation Coefficient**

The Pearson Product Correlation Coefficient was calculated to assess the relationship between the pairs of the elemental EFs (and thus their concentrations) including the age of accumulated dust. The bivariate Pearson correlation (first row) analysis with the corresponding

p-values for the two-tailed t-tests (second row) for the 17 elements' EFs and age of dust was applied using data from 51 samples (all groups/locations together). Additionally, the same Pearson correlation analyses were computed separately for the same elements from the group "Kern Place" (28 attic dust samples) and the group "Government Hill" (19 dust samples).

#### **4.6.3.3 Multivariate Analyses of Covariance (MANCOVA)**

The MANCOVA statistical method (Willk's Lambda Test) was used for the determination of all investigated elements' EF fluctuations depending on location of attics and age of sampled attic dusts. For comparison "Kern Place" and "Government Hill" groups were chosen. Group "Juarez" was excluded due to a limited dust sample size (four combined samples). The comparisons between the EFs of 17 chemical elements analyzed in attic dusts samples from Kern Place versus Government Hill were computed using the MANCOVA Wilks' Lambda tests with Age to 2007 as covariate. The MANCOVA analyses examined the significance of Group Effect (the influence of the dust sampling locations on the elemental EFs), Age Effect (the influence of the dust age on the elemental EFs) and Age by Group Interaction (both dust age and sampling location influences simultaneously).

For each investigated element (either its EF original units or ln transformed for normality) the procedures were the following:

Step1. The factor "Age by Group Interaction" was tested for significance (by ANCOVA).

Step2a. If the interaction was significant, the factor "Age Effect" could not be used as a covariate. In this case, the elemental EF values from the "Kern Place" and the "Government Hill" groups were compared by using the F-test (equivalent to the t-test, ANOVA).

Step2b. If the interaction was not significant, the factor “Age Effect” was used as a covariate. Then the Covariance analysis with factor “Group Effect” and covariate factor “Age Effect” was proceeded to. If the covariate Age Effect was not significant, the EF of each element in the indicated two groups was compared, using the F-test for group effect.

To test the hypothesis that the distribution of heavy metals/metalloids changed after 1966 (when ASARCO built a new 828-foot smokestack), the same ANCOVA for their EFs was additionally provided with a cut off of 50 years, i.e. separately for two time periods: before 1966 (from 1916 to 1966) and after this time (from 1966 to 2007).

To obtain supplementary information that could further clarify the sources of investigated elements, the exploratory Cluster analysis and Principal Component analysis were also performed.

#### **4.6.3.4 Cluster Analysis**

The hierarchical Cluster analysis was applied to all investigated elements in order to reveal the associations among them and to sort these elements into clusters according to their commonality. Each cluster may unify the elements of common origin and therefore may help to identify their source.

Using the EFs of elements obtained from the combined 51 dust samples (for all three locations together) Cluster analysis was performed with squared Euclidean distance method and Ward’s minimum variance linkage type.

#### **4.6.3.5 Principal Component analysis**

A different type of clustering, Principal Component analysis (PCA) was used in order to distinguish principal components in the EF data set in order to additionally ascertain the common origin of investigated elements and thereby indicate the pollution sources of heavy metals (Reimann et al. 2002; Tokalioglu and Kartal 2006; Šajn 2006). Using the EFs of 17 elements from the 51 samples, PCA with varimax rotation was conducted to organize them into principal components or factors. The choice of the number of factors was based on the Scree plot.

## **CHAPTER 5**

### **RESULTS**

#### **5.1 ICP-AES & ICP-MS Elemental Analyses Results**

As detailed in Methodology (Chapter 4, section 4.5), the investigation was initiated by analyzing the elemental concentration in 12 soil samples and 51 combined attic dust samples from three locations (Kern Place and Government Hill in El Paso and downtown Juarez). Concentrations of Pb, As, Cd, Cu, Zn, Fe, Mn, Ba, Al, Ti, Na, Mg, Ca and K (14 elements) were analyzed in dust (aqueous and acidic extracts) and soil (only acidic extracts) sample solutions by ICP–AES analytical technique. The results of the analyses of the indicated elements in aqueous and acidic attic dust solutions by ICP-AES are presented in Table C2 and Table C3 (respectively) in Appendix C. In Tables C1a - C1c are presented check standard data for ICP-AES analytical runs. The elemental concentrations of the same elements in soil acid solution analyzed by ICP-AES and check standards are presented in Tables C4a and C4b (Appendix C). Summarized data of ICP-AES elemental analyses (17 elements) of acid digestion buried soil samples is presented in Table C5. All data are reported in mg/L or ppm.

Additionally, concentrations of V, Se and Sb (not detectable by ICP–AES) were determined by ICP-MS technique from the same solutions. Concentrations of these three elements determined by ICP-MS from attic dust solutions are presented in Tables C6a - C6c in the Appendix C. Elemental data obtained from the acidic soil samples solution analyzed by ICP-MS are presented in the same Tables C6a - C6c. Data are reported in  $\mu\text{g/L}$  or ppb.

The elemental concentrations of investigated elements in both media, dusts and soil, were used only to compute the EFs of 17 elements in the 51 attic dust samples based on the formula

outlined in the Methodology chapter section 4.6.2. The further statistical analyses were applied to the obtained elemental EF data set.

## 5.2 EF Calculation

Based upon the actual elemental concentrations, the calculated EFs of the targeted elements are given in Table C7 (full table) in Appendix C and those EF values of the specific toxicants of interest are presented in Table 5.1 (p.79). In this table “Decades” indicate approximately the years when the houses were built or the year when new surfaces were added (and therefore started to accumulate dusts that were used for sampling).

Visual inspection of this table pinpoints to a considerable difference in EF values among chemical elements studied. Very high EFs (sometimes more than 600) were observed for the heavy metals/ metalloids (Pb, As, Cd, Sb, Cu, Zn) compared to low EF values (less than 10) of other elements hypothetically of crustal origin (Na, Mg, Mn, Ba, K, etc.).

A large variation was also noted between the EFs of the same anthropogenic elements found in attic dusts from different locations but of similar “age” as well as between EFs of the same anthropogenic element accumulated during different time periods in the same attic. For instance, dust collected from one of the oldest attics (91 year old house, decade 1910s) from the Kern Place area shows  $EF_{Pb} = 698$  and  $EF_{As} = 220$  (sample K7 w. beam), whereas dust from an almost similarly aged attic (83 year old house, decade 1920s) from the Government Hill area (sample L1 a+b+c) shows significantly smaller enrichment factors of  $EF_{Pb} = 157$  and  $EF_{As} = 35$ . Related collaborating data comes from the dusts taken from later installed surfaces in the indicated attics (sample K7 Res. Light, decade 2000s and sample L1 E Kneeler, decade 1990s). The EF values of Pb and As are much smaller in “new” dusts from both locations:  $EF_{Pb} = 71$

Table 5.1: Enrichment Factors of 9 Elements of Interest.

Sample	Decades	Fe	Mn	Ba	Zn	Pb	As	Cd	Cu	Sb
<i>K1 new</i>	1960 s	1.64	1.33	2.87	84.33	79.24	13.31	67.45	84.70	157.65
<i>K1 old</i>	1920 s	2.24	1.32	1.02	65.64	90.01	27.13	92.08	74.50	135.56
<i>K2 new roof</i>	1970 s	5.33	3.88	3.82	146.19	111.03	37.81	139.95	504.30	429.68
<i>K2 old attic</i>	1940s	4.81	4.07	4.30	175.02	146.56	56.83	211.10	460.69	509.83
<i>K3 wood</i>	1920s	5.53	3.05	4.24	966.48	177.99	44.98	183.01	429.55	447.83
<i>K3 galv</i>	1920s	7.16	2.57	2.57	3632.41	175.59	41.20	197.79	327.98	525.19
<i>K3 scuttle</i>	1990s	2.69	3.38	3.70	169.43	52.90	19.01	82.86	237.27	234.68
<i>K4 post 89</i>	1980s	3.17	3.37	4.85	261.51	109.80	33.82	168.50	409.14	554.60
<i>K4 b. beam</i>	1940s	3.49	3.79	6.14	213.02	345.19	119.36	565.22	493.07	864.39
<i>K4 transect</i>	1940s	3.62	3.08	4.29	139.44	342.98	72.43	276.71	588.46	621.42
<i>K5 n.vent</i>	1930s	3.34	2.69	3.45	149.31	384.46	91.47	346.77	784.63	679.73
<i>K5 side</i>	1930s	3.98	4.67	4.96	1792.19	316.47	137.04	430.94	662.28	1811.44
<i>K5 f.vent</i>	1930s	2.88	5.57	6.39	478.77	328.80	144.46	659.04	478.23	805.10
<i>K6 R beam</i>	1930s	2.29	2.48	2.39	154.10	172.83	64.38	224.97	370.49	428.65
<i>K6 n.attic</i>	1950s	2.08	3.35	3.55	103.20	130.43	60.02	208.68	272.17	387.11
<i>K6 M1&amp;2</i>	1930s	3.43	3.37	3.76	110.81	238.23	56.03	296.13	492.44	687.35
<i>K6 4-8</i>	1930s	2.59	2.48	3.75	150.06	147.18	45.91	243.46	246.03	458.68
<i>K7 1</i>	1910s	2.38	2.62	4.00	92.33	253.66	94.74	315.06	390.89	565.35
<i>K7 w.beam</i>	1910s	4.41	3.94	5.10	255.25	697.64	219.83	782.19	1048.70	1343.09
<i>K7 Beam 2</i>	1910s	4.09	3.66	5.68	157.55	328.50	132.62	423.91	450.94	646.10
<i>K7 e.beam</i>	1910s	2.32	3.45	4.05	84.49	222.22	82.77	369.41	409.15	545.95
<i>K7 3 wool</i>	1990s	3.16	4.45	5.36	223.25	67.84	29.96	133.42	168.81	288.28
<i>K7 Res.Light</i>	2000s	2.66	4.52	4.69	170.25	70.85	34.92	124.03	166.07	345.42
<i>K8 left corner</i>	1920s	3.09	3.47	4.37	162.64	381.77	142.98	521.83	568.00	722.55
<i>K8 c.r.window</i>	1920s	2.90	3.05	3.72	147.34	498.58	98.32	522.73	783.61	712.37
<i>K8 w. &amp; c.left</i>	1920s	2.47	3.34	3.32	123.80	399.47	104.85	555.00	639.72	843.79
<i>K8 c.left 2</i>	1920s	2.88	3.37	3.45	153.46	555.47	143.72	664.12	835.37	1084.30
<i>K8 f.left 1</i>	1920s	6.40	3.12	4.66	155.72	547.32	107.19	529.87	916.60	1196.50
<i>L1 a+b+c</i>	1920s	5.79	2.34	6.97	102.18	156.92	45.35	130.13	196.53	259.59
<i>L1 E keytop</i>	1980s	6.33	2.54	4.37	53.46	35.08	20.70	48.06	100.55	107.31
<i>L1 E Kneeler</i>	1990s	7.07	3.63	4.65	49.69	27.22	18.68	35.70	110.03	99.85
<i>L2 attic bag</i>	1960s	5.39	3.94	4.68	83.11	33.55	9.72	101.44	115.35	196.91
<i>L2 Beam</i>	1920s	5.65	3.73	5.76	126.54	117.28	29.86	114.29	159.69	255.13
<i>L2 attic pipe</i>	1990s	6.23	2.11	5.69	1712.57	166.14	36.62	81.27	172.74	290.33
<i>L2 attic airc.</i>	2000s	5.17	2.92	5.06	146.25	42.76	17.27	27.30	104.63	101.17
<i>L3 attic door</i>	1990s	5.17	2.53	4.93	132.62	49.03	10.22	30.03	277.41	276.96
<i>S1 window</i>	1920s	4.99	2.21	4.35	32.29	72.07	14.43	61.20	139.89	146.79
<i>S2 window</i>	1920s	5.39	2.88	5.06	40.21	95.83	24.46	95.16	168.74	177.58
<i>S3 c. &amp; side</i>	1920s	4.50	2.84	3.81	29.07	39.67	15.06	39.69	106.48	73.94
<i>J V1 + V2</i>	1980s	5.28	3.23	8.99	363.87	104.03	34.76	94.37	118.06	429.04
<i>J V3 seats</i>	1980s	4.39	3.62	6.53	95.57	99.50	26.72	110.41	139.98	276.75
<i>J V4 + V5</i>	1940s	46.47	4.12	6.49	185.95	148.10	37.08	217.60	412.76	296.44
<i>J V6 gl.bulb</i>	1990s	5.57	3.54	8.32	52.85	30.05	22.18	46.82	196.79	192.34
<i>LH N1</i>	1910s	5.93	3.89	8.18	77.41	92.27	25.62	90.89	258.27	282.60
<i>LH N2</i>	1910s	3.06	1.99	3.43	24.10	24.38	6.31	16.74	53.69	71.97
<i>LH N3</i>	1910s	5.64	3.25	5.38	56.36	40.28	18.05	39.30	120.72	142.35
<i>LH bN4+N5</i>	1910s	3.98	1.83	4.78	34.24	50.60	12.16	29.27	75.00	124.46
<i>LS N1 + N2</i>	1930s	8.93	4.44	7.46	355.59	72.12	25.26	81.95	213.09	186.64

and  $EF_{As} = 35$  from the Kern Place attic, and  $EF_{Pb} = 27$  and  $EF_{As} = 19$  from the Government Hill attic respectively. The same tendency can be observed for all heavy metals, providing clear evidence for their significantly higher elemental EF values in attic dusts from older houses in the Kern Place area, which is closer to the ASARCO smelter.

The statistical significance of the divergence in EFs values determined for 17 chemical elements in attic dusts of different ages and from different locations was checked first by summary statistics and then by bivariate and multivariate statistical methods.

## **5.3 Statistical Results**

### **5.3.1 Summary Statistics Results**

The results of summary statistics calculated for the EFs of the 17 elements analyzed in attic dust sampled in the mentioned three locations are presented in Tables 5.2, 5.3 and 5.4 below. In these tables N indicates the number of combined samples and variable “Age to 2007” indicates the age of dust accumulated on surfaces of various ages up to the year 2007, when dusts were collected.

The Table 5.2 shows that dust samples from Juarez were mostly enriched in Sb (mean EF = 299), Cu (mean EF = 217), Zn (mean EF = 175), Cd (mean EF = 117), Pb (mean EF = 95), and As (mean EF = 30). Very high enrichment levels of these elements indicate their anthropogenic sources. For other elements, excluding Fe (mean 15), EFs do not exceed 10, therefore their presence in dust may be explained by mainly crustal contributions.

Table 5.2: Summary Statistics for the EFs of 17 Elements: Juarez Group  
(4 combined samples).

Variable	N	Mean	Std Dev	Std Error	Minimum	Maximum
Fe	4	15.43	20.70	10.35	4.39	46.47
Mn	4	3.63	0.37	0.18	3.23	4.12
Ba	4	7.59	1.27	0.64	6.49	8.99
Zn	4	174.56	137.87	68.93	52.85	363.87
Pb	4	95.42	48.78	24.39	30.05	148.10
As	4	30.18	6.94	3.47	22.18	37.08
Cd	4	117.30	72.11	36.06	46.82	217.60
Cu	4	216.90	134.73	67.36	118.06	412.76
Al	4	3.35	0.27	0.13	3.08	3.62
Ti	4	6.16	1.03	0.52	5.11	7.46
Sr	4	2.90	0.63	0.32	2.34	3.53
K	4	6.04	1.40	0.70	4.66	7.53
Na	4	4.49	1.52	0.76	3.02	6.55
Mg	4	1.32	0.14	0.07	1.16	1.44
Age_to_2007_	4	24.25	15.54	7.77	12.00	47.00
V	4	8.33	1.44	0.72	7.39	10.45
Se	4	4.69	0.59	0.30	4.01	5.30
Sb	4	298.64	97.96	48.98	192.34	429.04

The Kern Place attic dusts (Table 5.3) are more enriched than Juarez dusts by the same anthropogenic elements such as Sb, Cu, Zn, Pb, Cd and As: mean  $EF_{Sb} = 644$ ; mean  $EF_{Cu} = 475$ ; mean  $EF_{Zn} = 376$ ; mean  $EF_{Pb} = 263$ ; mean  $EF_{Cd} = 333$ ; and mean  $EF_{As} = 81$ . Other elements have mean EFs values of less than 6.

Table 5.3: Summary Statistics for the EFs of 17 Elements: Kern Place Group (28 combined samples).

Variable	N	Mean	Std Dev	Std Error	Minimum	Maximum
Fe	28	3.47	1.34	0.25	1.64	7.16
Mn	28	3.34	0.91	0.17	1.32	5.57
Ba	28	4.09	1.14	0.22	1.02	6.39
Zn	28	375.64	726.00	137.20	65.64	3632.41
Pb	28	263.32	170.21	32.17	52.90	697.64
As	28	80.61	49.61	9.38	13.31	219.83
Cd	28	333.44	200.49	37.89	67.45	782.19
Cu	28	474.78	245.97	46.48	74.50	1048.70
Al	28	1.95	0.62	0.12	1.16	4.45
Ti	28	5.43	3.68	0.70	2.69	18.07
Sr	28	2.55	2.48	0.47	1.32	12.20
K	28	3.16	0.93	0.18	0.83	4.69
Na	28	4.21	3.69	0.70	-0.27	18.95
Mg	28	1.50	0.26	0.05	0.90	1.92
Age_to_2007_	28	64.64	26.70	5.05	3.00	91.00
V	28	4.39	1.29	0.24	2.21	8.09
Se	28	5.76	2.30	0.43	2.59	10.54
Sb	28	644.02	367.43	69.44	135.56	1811.44

The Government Hill location EF data exhibits a similar pattern. Mean EF values of “anthropogenic” elements are high: for Sb =171, for Zn = 173, for Cu = 145, for Cd = 63, for Pb = 70 and for As = 20, whereas the other elements show mean EF values of less than 10.

Table 5.4: Summary Statistics for the EFs of 17 Elements: Government Hill Group (19 combined samples).

Variable	N	Mean	Std Dev	Std Error	Minimum	Maximum
Fe	19	5.52	1.21	0.28	3.06	8.93
Mn	19	3.02	0.79	0.18	1.83	4.44
Ba	19	5.31	1.19	0.27	3.43	8.18
Zn	19	172.99	380.16	87.21	24.10	1712.57
Pb	19	70.23	41.73	9.57	24.38	166.14
As	19	20.46	9.54	2.19	6.31	45.35
Cd	19	62.30	32.65	7.49	16.74	130.13
Cu	19	145.05	58.50	13.42	53.69	277.41
Al	19	4.47	1.01	0.23	2.08	6.75
Ti	19	7.78	1.78	0.41	4.38	10.23
Sr	19	2.01	0.41	0.09	1.47	3.40
K	19	4.69	1.22	0.28	3.15	8.13
Na	19	3.58	1.95	0.45	1.32	10.33
Mg	19	2.21	0.33	0.08	1.79	3.09
Age_to_2007_	19	60.84	30.75	7.06	7.00	88.00
V	19	8.04	1.69	0.39	5.81	12.01
Se	19	3.91	1.32	0.30	2.56	8.20
Sb	19	171.18	72.06	16.53	71.97	290.33

In concluding the results of summary statistics, it is essential to underline that the same pattern is observed for all groups (locations): the very high levels of mean EFs were observed predominantly for Sb, Cd, Pb, Cu, As and Zn and the low levels of mean EFs for the rest of the investigated elements. The highest enrichments of “anthropogenic” elements are found in attic dusts from the Kern Place location. The lowest enrichment contents in dust samples were found for Sr and Mg in all locations.

These results justified further investigation of the influences of the dusts’ sampling locations and age on the EFs of the investigated elements, particularly heavy metals/metalloids, by multivariate statistical analyses.

The test for normality of the elemental EF data set demonstrated that the data were normally distributed. For the 8 elements (Pb, As, Al, Mn, Ba, K, Mg, V), the normality was assumed for its natural EF values. Log<sub>e</sub> transformation was employed for the EFs of the rest of the elements (Cd, Sb, Fe, Zn, Cu, Se, Ti, Sr, and Na) and the normality was implicit on the basis of the natural logarithms e (ln) of their content.

### 5.3.2 MANCOVA Analyses Results

An overall MANCOVA Willk's Lambda test (described in Methodology, section 4.6.3.3), was applied to check the elements' EFs fluctuation in time and space. Comparisons of 17 elemental EFs were only computed for the two groups "Kern Place" and "Government Hill".

Of primary interest was testing the "Age by Group Interaction" (ANCOVA test), and significant interactions were found for EF<sub>Pb</sub> (p = 0.0027), EF<sub>As</sub> (p = 0.0039), lnEF<sub>Cd</sub> (p = 0.0386), lnEF<sub>Cu</sub> (p = 0.0487), EF<sub>Al</sub> (p = 0.0324) and lnEF<sub>Se</sub> (p = 0.0281). Therefore, Age Effect as a covariate was not used for those elements. The F-test (ANOVA) was applied comparing their EF between "Kern Place" and "Government Hill" groups. The differences were detected for EF<sub>Pb</sub> (p< 0.0001), EF<sub>As</sub> (p< 0.0001), ln EF<sub>Cd</sub> (p<0.0001), ln EF<sub>Cu</sub> (p<0.0001), EF<sub>Al</sub> (p<0.0001), and ln EF<sub>Se</sub> (p = 0.0016). Using the Bonferroni correction for multiple comparisons with  $\alpha = 0.00290$  (0.05/17), significance was found for the EF of all the above mentioned elements except for EF of Se.

The results of the ANCOVA "Age by Group Interaction" test for EF<sub>Pb</sub>, ln EF<sub>Cd</sub> and EF<sub>Al</sub> as illustrative of the elements showing significance in this test are presented in Tables 5.5 - 5.10 and Figures 5.1-5.6 (pages 86-91). The results of the ANCOVA analyses for other elements

showing this interaction, i.e.  $EF_{As}$ ,  $\ln EF_{Cu}$ , and  $\ln EF_{Se}$  are presented in the Appendix D, Tables D 5, D 8, D21 and Figures D5, D8 and D21 respectively.

All these Figures show that the EFs of Pb, Cd, As, Cu and Se underwent the same influence of time on the elements' accumulation (concentration) in attic dusts in both locations. However, the age of sampled dust produced a different effect upon accumulation of these elements in the Kern Place and Government Hill locations. In attic dust samples from the Kern Place area, the EFs (and hence, concentrations) of Pb, Cd, As, Cu and Se gradually increased with the age of dust accumulated. No such trend was observed in the Government Hill location. This observation was confirmed by an F-test analysis that demonstrated a significant group effect for the above-mentioned elements.

The EF of Al, in contrast to heavy metals, has higher values in attic dusts from the Government Hill location than from the Kern Place. At the same time the highest concentration of Al occurs in the dusts from newest surfaces in the attics of this location. We can see from Figure 5.5 (p.90) that the EFs values of this element are decreased with dust age in the Government Hill group while they increased slightly in the Kern Place group. Accordingly, the F-test demonstrated a significant group effect ( $p < 0.0001$ ), i.e. significant difference in EFs of Al between the two locations with the higher value in Government Hill.

Table 5.5: Results of the ANCOVA “Age by Group Interaction” test for  $EF_{Pb}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	707849.754	235949.918	19.36	<.0001
Error	41	499640.181	12186.346		
Corrected Total	44	1207489.936			

R-Square	Coeff Var	Root MSE	Pb Mean
0.586216	60.33173	110.3918	182.9747

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	4391.3270	4391.3270	0.36	0.5516
Age_to_2007_	1	150017.9961	150017.9961	12.31	0.0011
Age_to_2007_*Group	1	123872.1071	123872.1071	10.16	<b>0.0027 *</b>

\* = significant interaction so cannot use Age as covariate

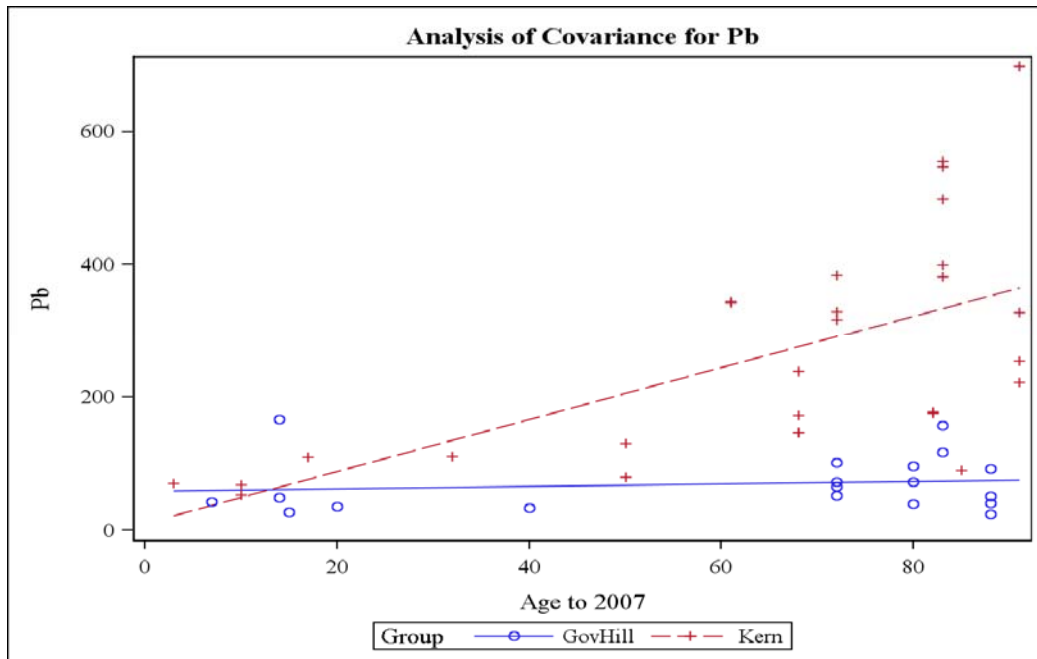


Figure 5.1: The  $EF_{Pb}$  distribution with age of dust in 2 groups (locations of El Paso). The regression lines are fitted according to “Age by Group Interaction” test.

Table 5.6: Results of the ANOVA “Group effect” test for  $EF_{Pb}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	422042.578	422042.578	23.34	<.0001
Error	45	813562.865	18079.175		
Corrected Total	46	1235605.443			

R-Square	Coeff Var	Root MSE	Pb Mean
0.341567	72.57805	134.4588	185.2610

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	422042.5776	422042.5776	23.34	<.0001 *

**\* = significant Group effect at the 0.05 alpha level**

Means with the same letter are not significantly different.			
t Grouping	Mean	N	Group
A	263.32	28	Kern
B	70.23	19	GovHill

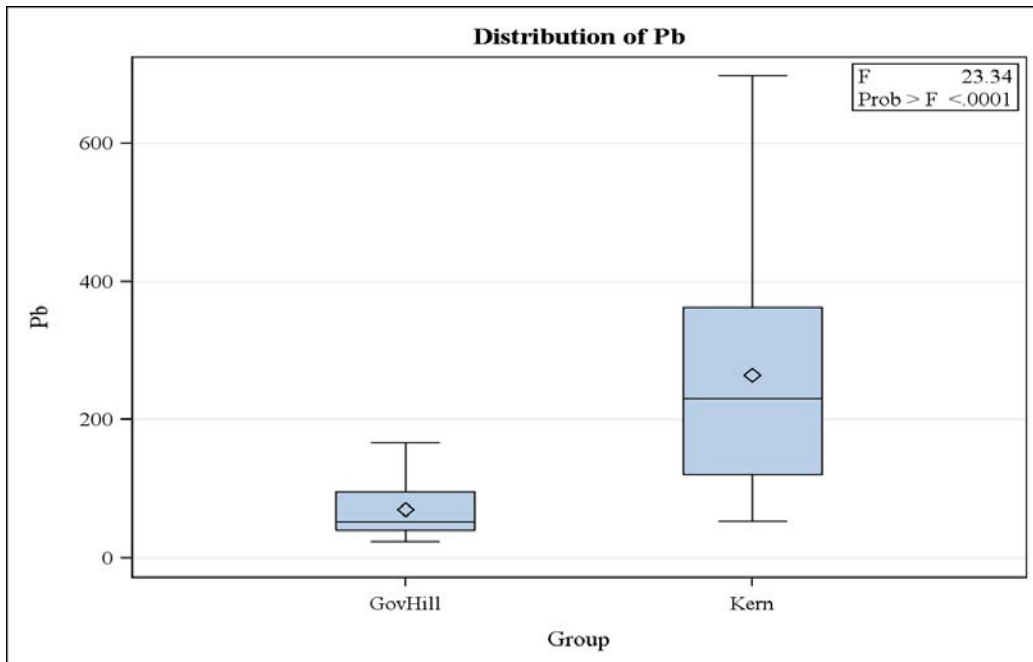


Figure 5.2: Box plots of the  $EF_{Pb}$  distribution in 2 groups (locations of El Paso).

Table 5.7: Results of the ANCOVA “Age by Group Interaction” test for  $\ln EF_{Cd}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	34.25621765	11.41873922	36.59	<.0001
Error	41	12.79552474	0.31208597		
Corrected Total	44	47.05174238			

R-Square	Coeff Var	Root MSE	logCd Mean
0.728054	11.32607	0.558647	4.932397

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	1.16497834	1.16497834	3.73	0.0603
Age_to_2007_	1	3.48778341	3.48778341	11.18	0.0018
Age_to_2007_*Group	1	1.42610802	1.42610802	4.57	<b>0.0386 *</b>

**\* = significant interaction so cannot use Age as covariate**

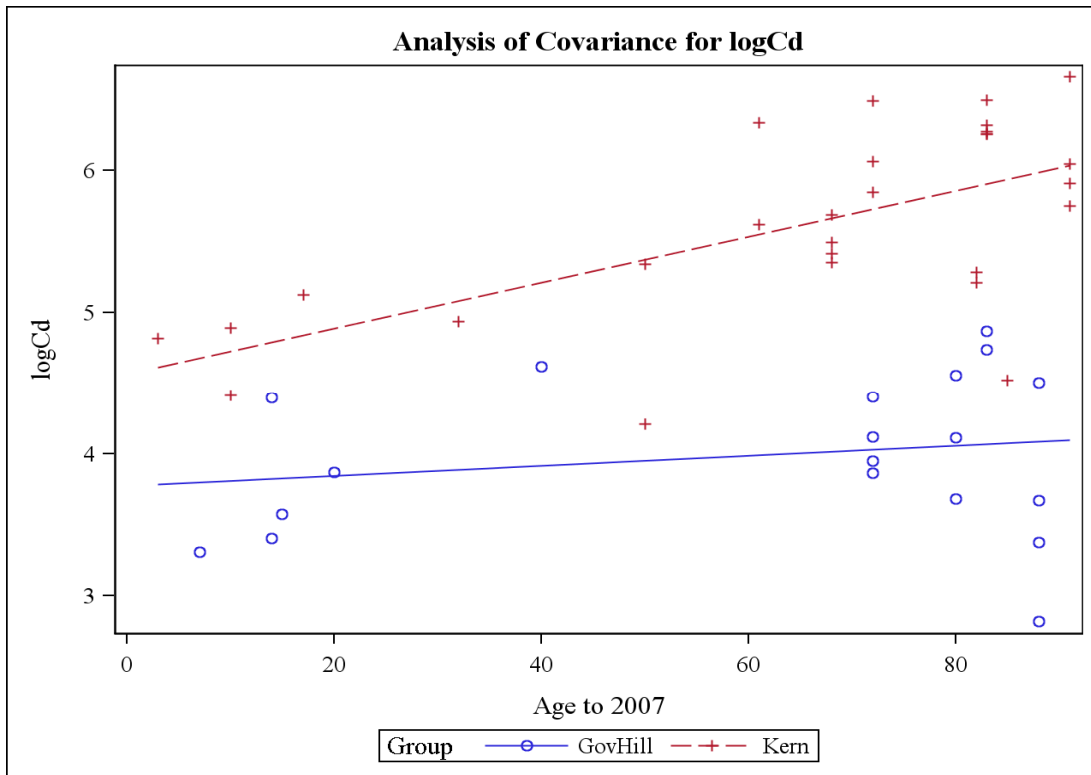


Figure 5.3: The  $\ln EF_{Cd}$  distribution with dust age in 2 groups (locations of El Paso). The regression lines are fitted according to the test “Age by Group Interaction”.

Table 5.8: Results of the ANOVA test “Group effect” for  $\ln EF_{Cd}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	29.62352316	29.62352316	73.87	<.0001
Error	45	18.04621727	0.40102705		
Corrected Total	46	47.66974044			

R-Square	Coeff Var	Root MSE	logCd Mean
0.621432	12.77835	0.633267	4.955779

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	29.62352316	29.62352316	73.87	<.0001 *

\* = significant Group effect at the 0.05 alpha level

Means with the same letter are not significantly different.			
t Grouping	Mean	N	Group
A	5.6098	28	Kern
B	3.9920	19	GovHill

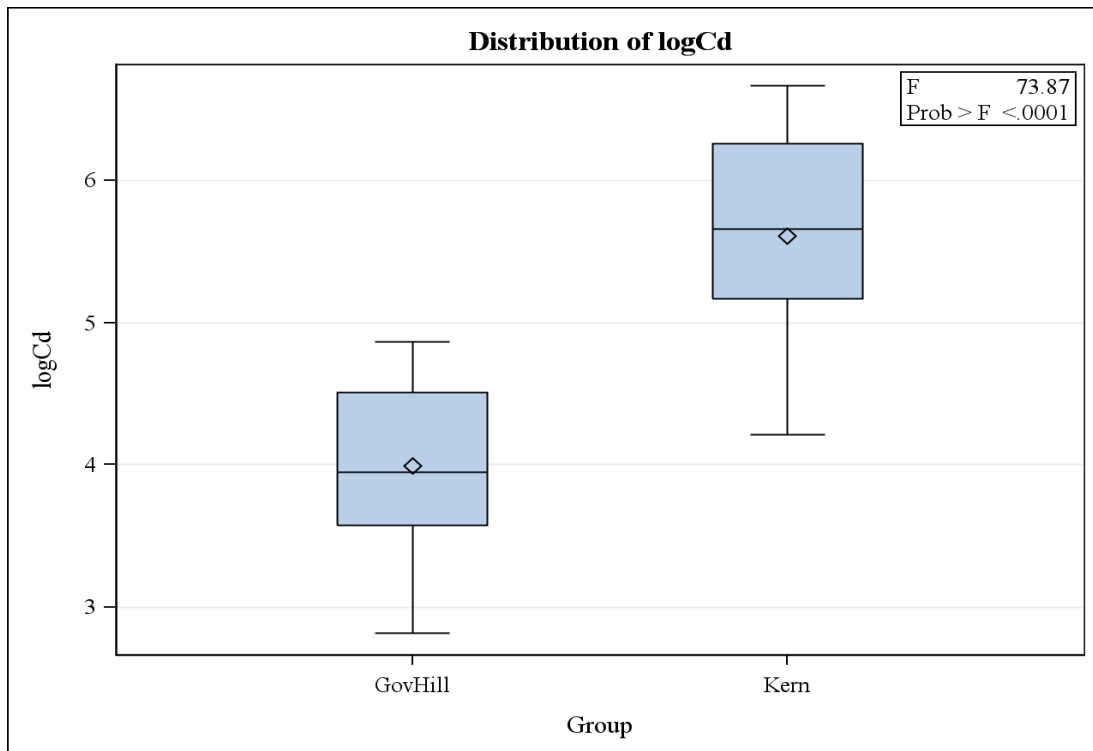


Figure 5.4: Box plots of the  $\ln EF_{Cd}$  distribution in 2 groups (locations of El Paso).

Table 5.9: Results of the ANCOVA test “Age by Group Interaction” for  $EF_{AI}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	71.16284626	23.72094875	39.36	<.0001
Error	41	24.71059565	0.60269745		
Corrected Total	44	95.87344191			

R-Square	Coeff Var	Root MSE	AI Mean
0.742258	25.56760	0.776336	3.036406

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	24.44039689	24.44039689	40.55	<.0001
Age_to_2007_	1	0.61491609	0.61491609	1.02	0.3184
Age_to_2007_*Group	1	2.95555959	2.95555959	4.90	<b>0.0324 *</b>

**\* = significant interaction so cannot use Age as covariate**

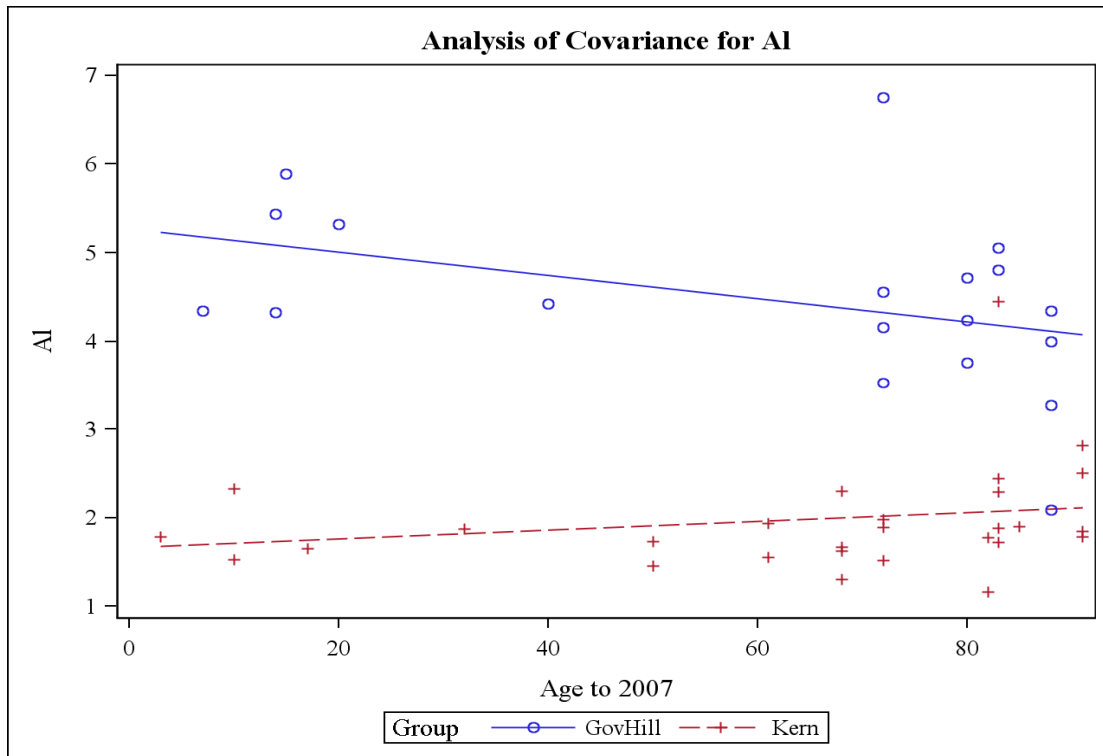


Figure 5.5: The  $\ln EF_{AI}$  distribution with dust age in 2 groups (locations of El Paso). The regression lines are fitted according to the “Age by Group Interaction” test.

Table 5.10: Results of the ANOVA “Group effect” test for  $\ln EF_{AI}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	71.7924692	71.7924692	113.03	<.0001
Error	45	28.5823043	0.6351623		
Corrected Total	46	100.3747735			

R-Square	Coeff Var	Root MSE	AI Mean
0.715244	26.82318	0.796971	2.971202

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	71.79246915	71.79246915	113.03	<.0001 *

\* = significant Group effect at the 0.05 alpha level

Means with the same letter are not significantly different.			
t Grouping	Mean	N	Group
A	4.4716	19	GovHill
B	1.9531	28	Kern

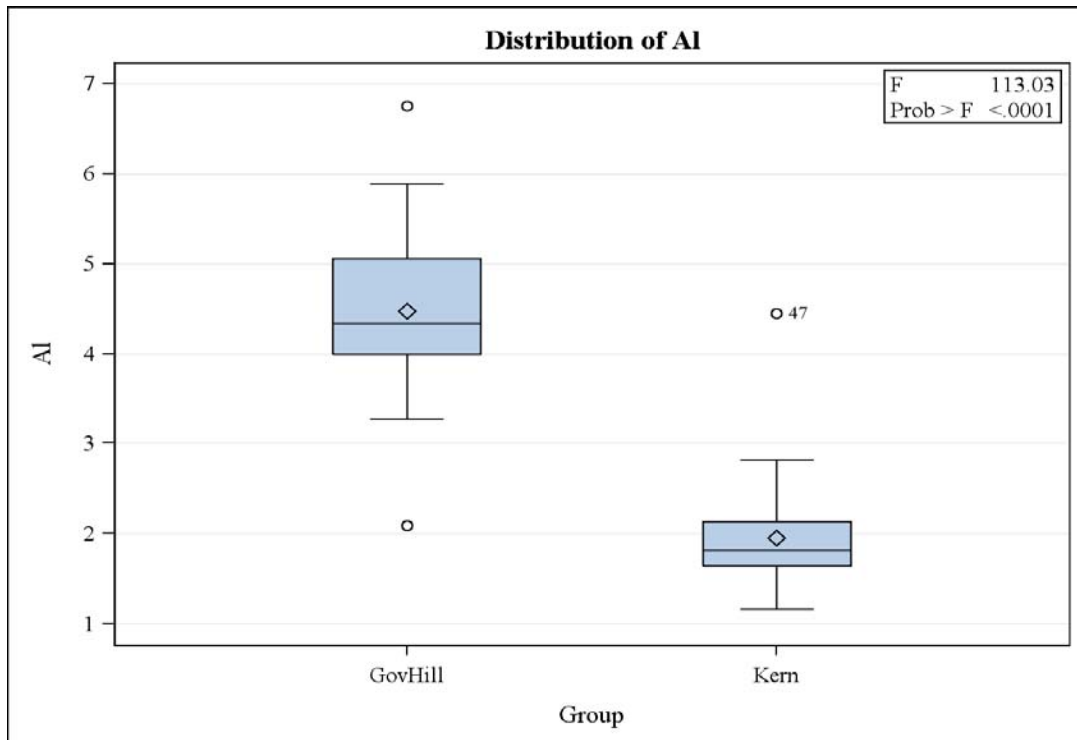


Figure 5.6: Box plots of the  $EF_{AI}$  distribution in 2 groups (locations of El Paso).

For the remainder of the elemental EFs, i.e. of Fe, Mn, Ba, Zn, Ti, Sr, K, Na, Mg, V and Sb, the Age by Group Interaction effect was not significant. For these elements an “Age Effect” was used as a covariate. However, the Age Effect was not significant for any of them. With the analyses of covariance, the significance of the Group Effect for those elements was tested through the F-test. The significance was found for  $\ln EF_{Fe}$  ( $p < 0.0001$ ),  $EF_{Mn}$  ( $p = 0.2091$ ),  $EF_{Ba}$  ( $p = 0.0011$ ),  $\ln EF_{Zn}$  ( $p = 0.0021$ ),  $\ln EF_{Ti}$  ( $p = 0.0004$ ),  $\ln EF_{Sr}$  ( $p = 0.5602$ ),  $EF_K$  ( $p < 0.0001$ ),  $\ln EF_{Na}$  ( $p = 0.9441$ ),  $EF_{Mg}$  ( $p < 0.0001$ ),  $EF_V$  ( $p < 0.0001$ ), and  $\ln EF_{Sb}$  ( $p < 0.0001$ ). Using the Bonferroni correction with  $\alpha = 0.0029$ , a significant Group effect was obtained for  $\ln EF_{Fe}$ ,  $EF_{Ba}$ ,  $\ln EF_{Zn}$ ,  $\ln EF_{Ti}$ ,  $EF_K$ ,  $EF_{Mg}$ ,  $EF_V$  and  $\ln EF_{Sb}$ .

The results of the MANCOVA analyses for  $\ln EF_{Fe}$ ,  $EF_{Mn}$ ,  $\ln EF_{Ti}$ ,  $\ln EF_{Sr}$ ,  $EF_K$ ,  $\ln EF_{Na}$ ,  $EF_{Mg}$ ,  $EF_V$ , and  $\ln EF_{Se}$  are presented in Tables D1+D2, D3+D4, D9+D10, D11+D12, D13+D14, D15+D16, D17+D18, D19+D20, D21+D22 and Figures D1+D2, D3+D4, D9+D10, D11+D12, D13+D14, D15+D16, D17+D18, D19+D20 and D21+D22 respectively in Appendix D. The results of the MANCOVA tests for  $EF_{Ba}$ ,  $\ln EF_{Zn}$ , and  $\ln EF_{Sb}$  as illustrative of this data set are presented in Tables 5.11- 5.16 and Figures 5.7-5.12 (pages 93-98).

Table 5.11: Results of the ANCOVA test “Age by Group Interaction” for  $EF_{Ba}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	17.87756711	5.95918904	4.17	0.0115
Error	41	58.58699489	1.42895109		
Corrected Total	44	76.46456201			

R-Square	Coeff Var	Root MSE	Ba Mean
0.233802	25.93394	1.195387	4.609355

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	0.15859397	0.15859397	0.11	0.7407
Age_to_2007_	1	0.00822946	0.00822946	0.01	0.9399
Age_to_2007_*Group	1	1.90019474	1.90019474	1.33	<b>0.2555 ns</b>

**ns = no significant interaction so can use Age as covariate**

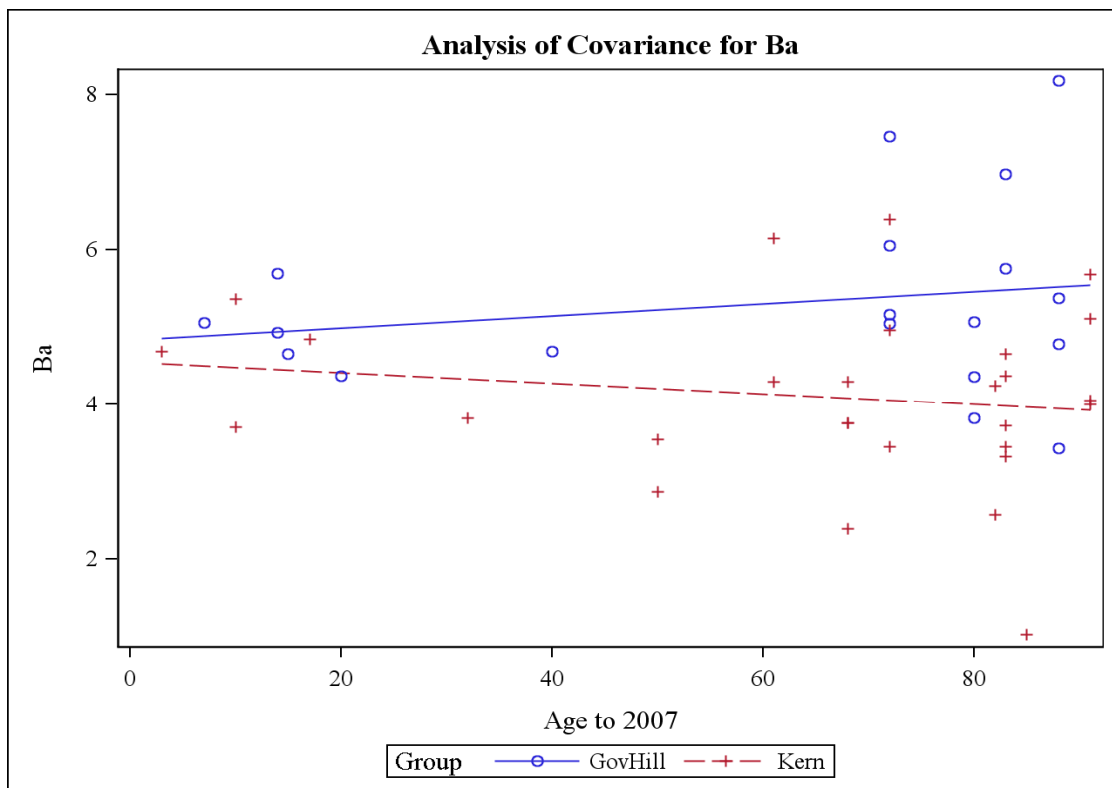


Figure 5.7: The  $EF_{Ba}$  distribution with dust age in 2 groups (locations of El Paso). The regression lines are fitted according to the test “Age by Group Interaction”.

Table 5.12: Results of the ANCOVA “Group effect” and “Age effect” tests for  $EF_{Ba}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	16.83297910	8.41648955	6.09	0.0046
Error	44	60.82279038	1.38233615		
Corrected Total	46	77.65576948			

R-Square	Coeff Var	Root MSE	Ba Mean
0.216764	25.67118	1.175728	4.579953

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	16.78398176	16.78398176	12.14	<b>0.0011 *</b>
Age_to_2007_	1	0.00287179	0.00287179	0.00	0.9639

**\* = significant Group effect at the 0.05 alpha level**

Group	Ba LSMEAN	H0:LSMean1=LSMean2 Pr >  t
GovHill	5.30702501	0.0011
Kern	4.08658263	

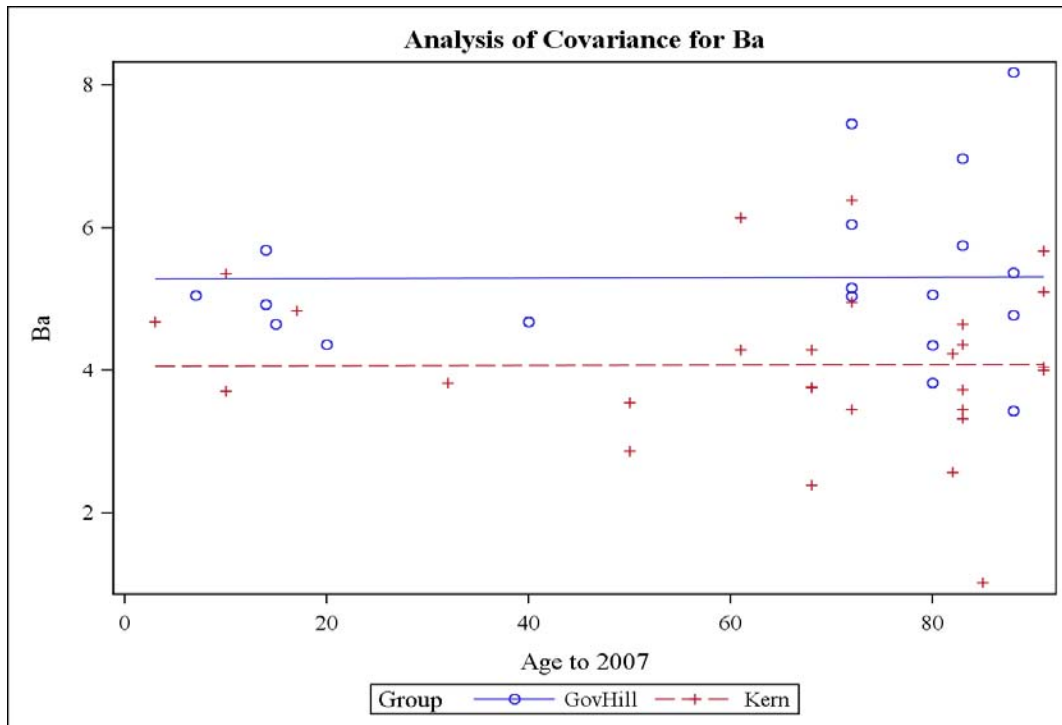


Figure 5.8: The  $EF_{Ba}$  distribution with dust age in 2 groups (locations of El Paso). The fitted regression (parallel) lines illustrate “Group effect”.

Table 5.13: Results of the ANCOVA “Age by Group Interaction” test for  $\ln EF_{Zn}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	13.03913886	4.34637962	5.06	0.0045
Error	41	35.22069192	0.85904127		
Corrected Total	44	48.25983078			

R-Square	Coeff Var	Root MSE	logZn Mean
0.270186	18.78834	0.926845	4.933084

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	0.00290280	0.00290280	0.00	0.9539
Age_to_2007_	1	1.60249716	1.60249716	1.87	0.1794
Age_to_2007_*Group	1	2.23277446	2.23277446	2.60	<b>0.1146 ns</b>

**ns = no significant interaction so can use Age as covariate**

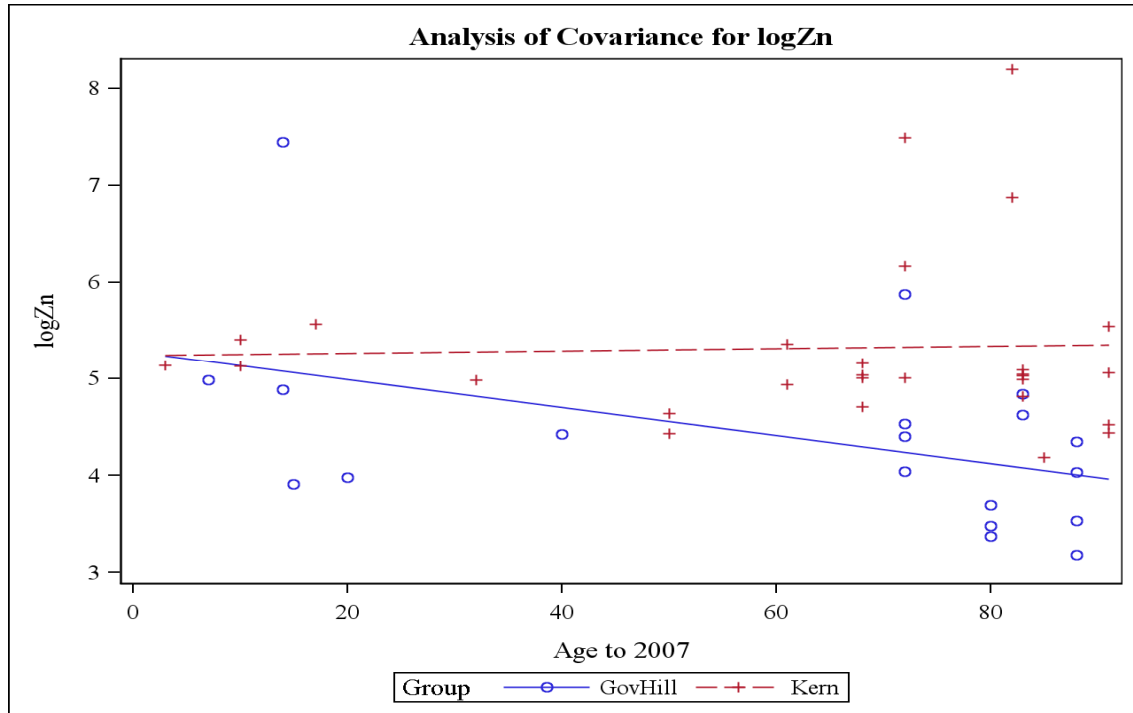


Figure 5.9: The  $\ln EF_{Zn}$  distribution with dust age in 2 groups (locations of El Paso). The regression lines are fitted according to the test “Age by Group Interaction”.

Table 5.14: Results of the ANCOVA “Age effect” and “Group effect” tests for  $\ln EF_{Zn}$

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	10.16428303	5.08214152	5.86	0.0056
Error	44	38.18163435	0.86776442		
Corrected Total	46	48.34591738			

R-Square	Coeff Var	Root MSE	logZn Mean
0.210241	18.90730	0.931539	4.926874

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	9.32030855	9.32030855	10.74	<b>0.0021 *</b>
Age_to_2007_	1	1.25693550	1.25693550	1.45	0.2352

**\* = significant Group effect at the 0.05 alpha level**

Group	logZn LSMEAN	H0:LSMean1=LSMean2 Pr >  t
GovHill	4.38506656	0.0021
Kern	5.29452934	

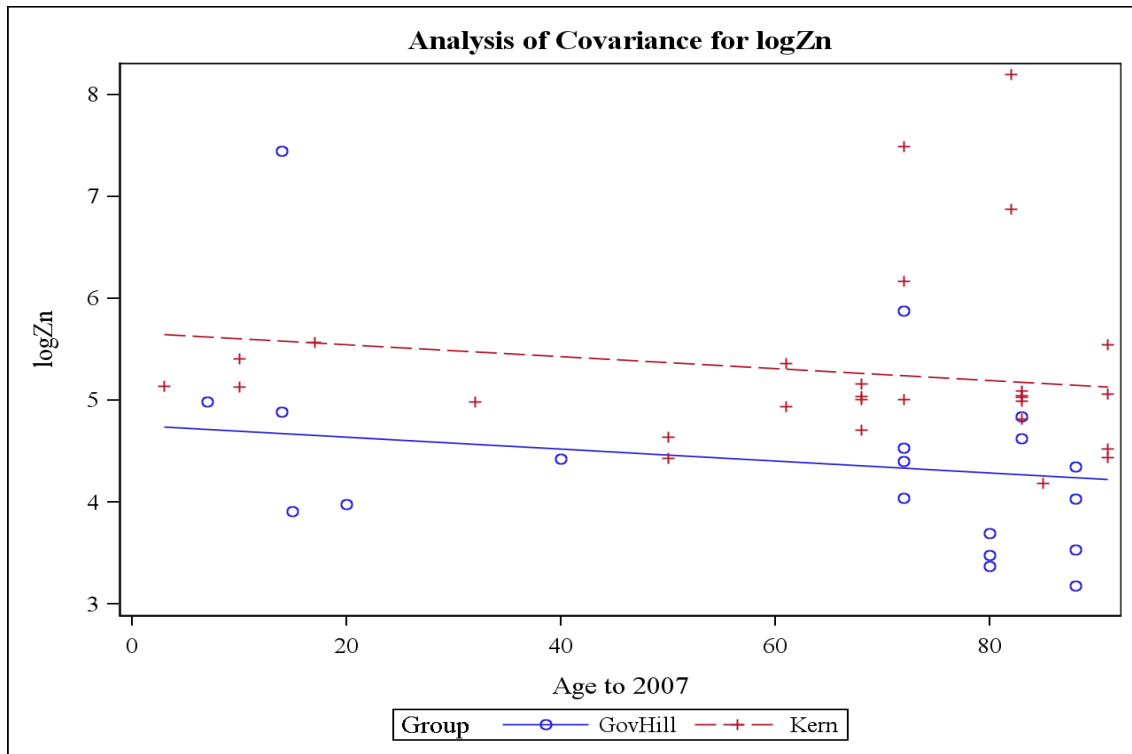


Figure 5.10: The  $\ln EF_{Zn}$  distribution with age of dust in 2 groups (locations of El Paso). The regression lines illustrate the “Group effect”.

Table 5.15: Results of the ANCOVA “Age by Group Interaction” test for  $\ln EF_{Sb}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	19.50454458	6.50151486	24.62	<.0001
Error	41	10.82862538	0.26411281		
Corrected Total	44	30.33316997			

R-Square	Coeff Var	Root MSE	logSb Mean
0.643010	8.880175	0.513919	5.787263

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	0.69573537	0.69573537	2.63	0.1122
Age_to_2007_	1	0.81184535	0.81184535	3.07	0.0870
Age_to_2007_*Group	1	0.91922267	0.91922267	3.48	<b>0.0693 ns</b>

**ns = no significant interaction so can use Age as covariate**

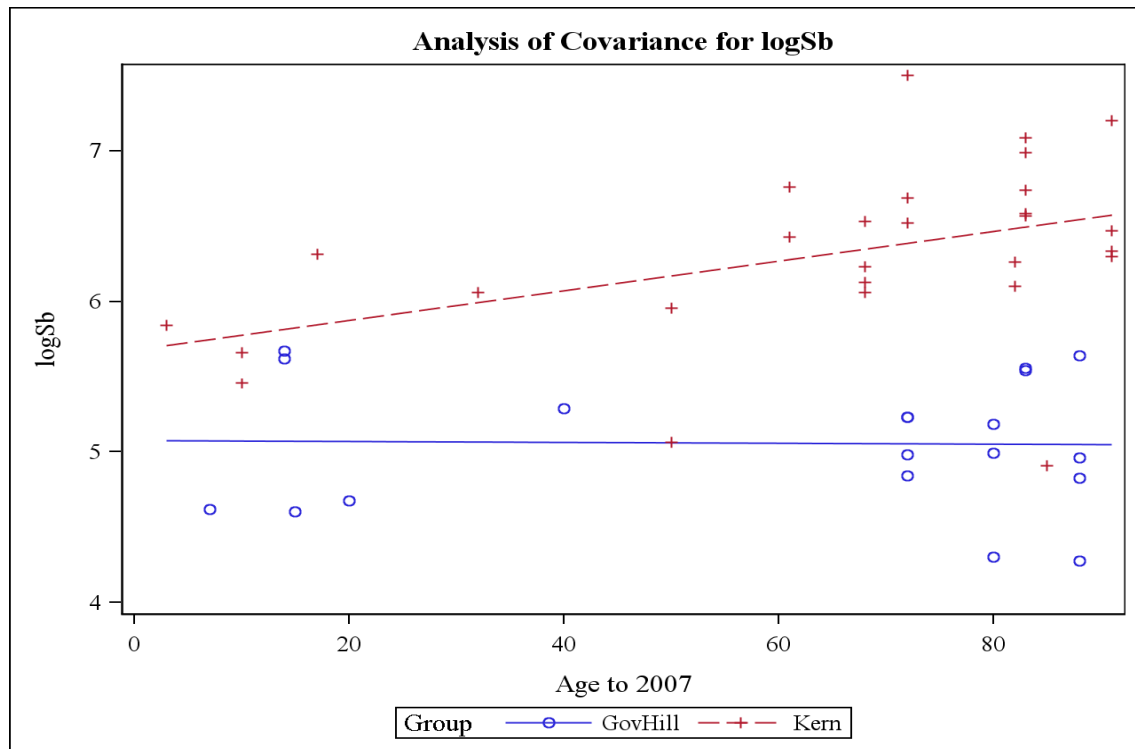


Figure 5.11: The  $\ln EF_{Sb}$  distribution with age of dust in 2 groups (locations of El Paso). The regression lines are fitted according to the test “Age by Group Interaction”.

Table 5.16: Results of ANCOVA “Age effect” and “Group effect” tests for  $\ln EF_{Sb}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	18.91795525	9.45897762	35.13	<.0001
Error	44	11.84612423	0.26923010		
Corrected Total	46	30.76407948			

R-Square	Coeff Var	Root MSE	logSb Mean
0.614936	8.938968	0.518874	5.804628

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	17.33081348	17.33081348	64.37	<.0001 *
Age_to_2007_	1	0.95669513	0.95669513	3.55	0.0660

\* = significant Group effect at the 0.05 alpha level

Group	logs LSMEAN	H0:LSMean1=LSMean2 Pr >  t
GovHill	5.06580695	<.0001
Kern	6.30597134	

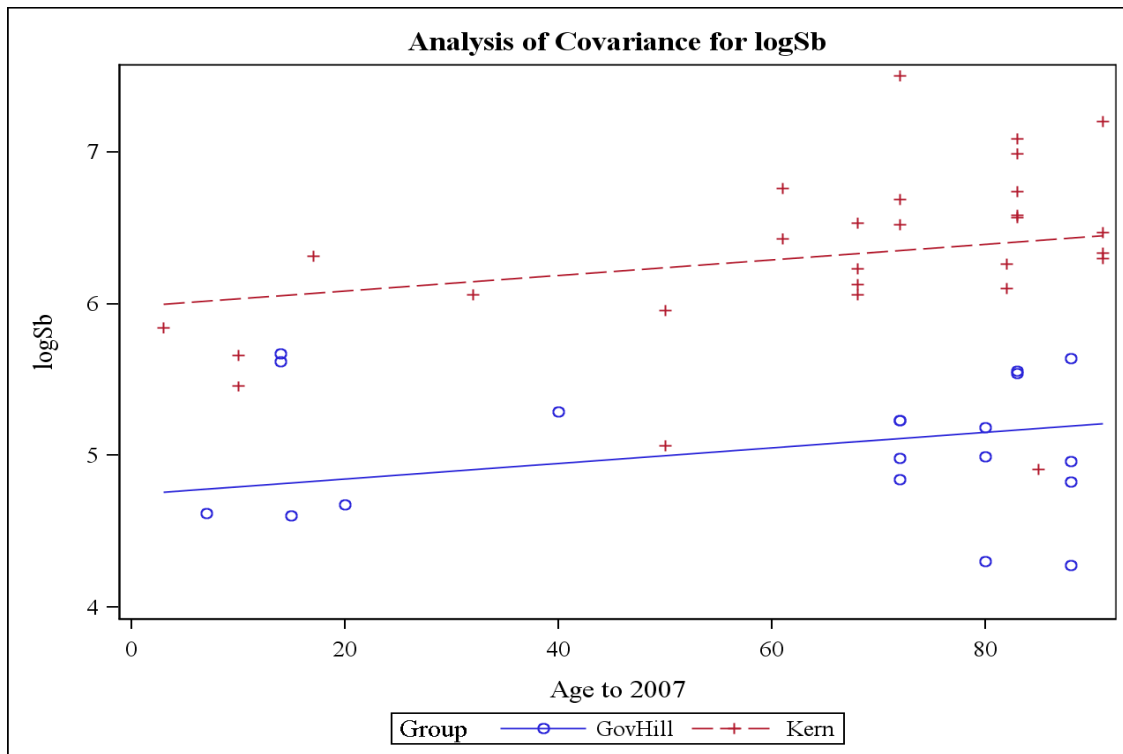


Figure 5.12 : The  $\ln EF_{Sb}$  distribution with dust age in 2 groups (locations of El Paso). The regression (parallel) lines illustrate the “Group effect”.

All these Figures clearly demonstrate that the EFs of the elements in this subset did not substantially increase with the age of dust in either of the two groups/locations despite having significantly different EF values. These results suggest that the accumulation of these chemical elements occurred at the same rate, independent of dust sampling locations and dust age. The EFs of Fe, Ba, Ti, K, Mg and V practically did not change with time (age of dust), but their content was much higher in the Government Hill location. Sr and Na did not show any spatial or temporal variation of their EFs. The EFs of Zn and Sb exhibited similarity to the other heavy metal distribution trend: in the Kern Place group the EFs of these trace elements (and therefore their concentrations) were gradually increasing with the age of dust accumulation.

However, in contrast to the EFs distribution of Pb, As, Cd, Cu and Se, the EFs of Zn and Sb steadily increased also in dusts from Government Hill location. The increasing rate of their EFs is approximately the same in both groups/locations.

The ANCOVA “Age by Group Interaction” test was applied separately to two time periods - before and after 1966 (this year corresponding to 50 years of dust age) for the EFs of the six elements (Pb, As, Cd, Cu, Sb and Se) and showed the similar trends. The results of these analyses are presented in Tables D 23 – D 34 and Figures D 23 – D 34 in Appendix D. To simplify comparison of the EFs distribution pre and post 1966, the combined results (the regression lines) for each mentioned element on the same figure are presented separately below in pages 100-102 (Figures 5.13-5.18).

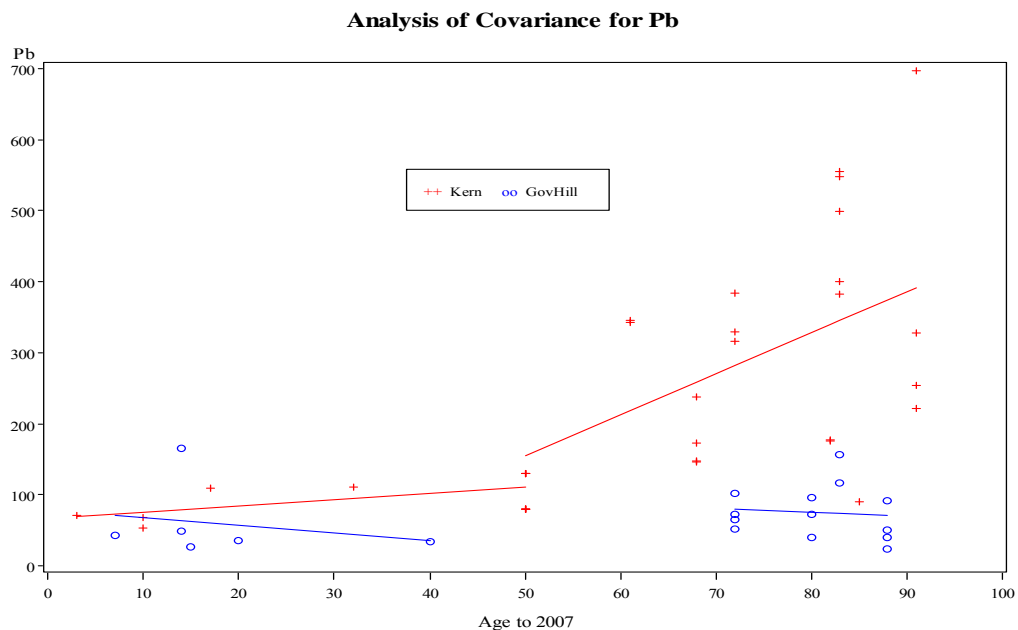


Figure 5.13: The  $EF_{Pb}$  distribution with age of dust post 1966 (0-50 years of dust age) and pre 1966 (50-90 years) in 2 groups /locations of El Paso.

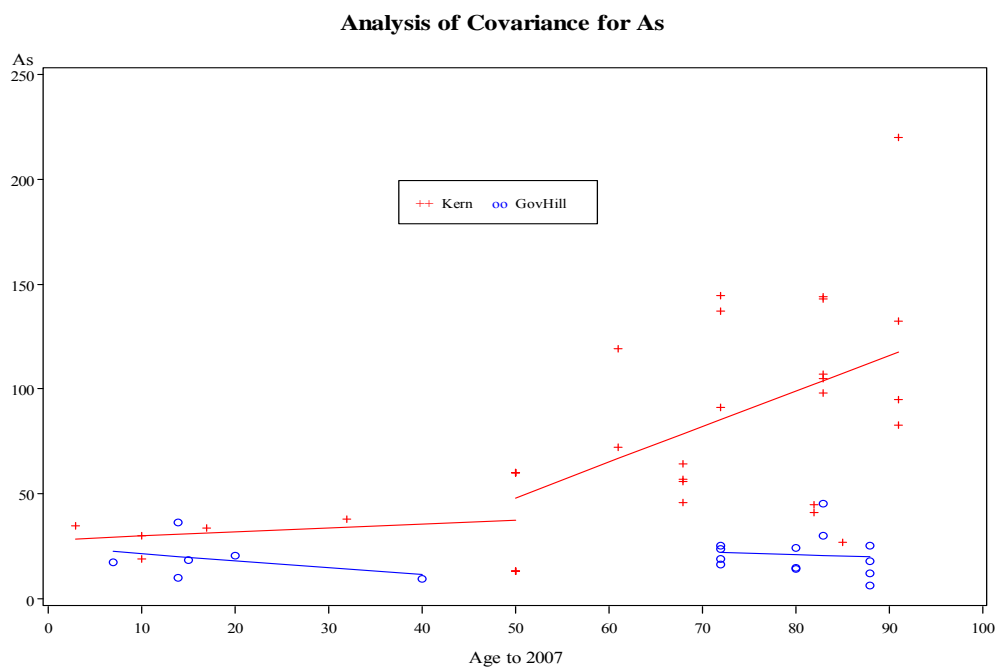


Figure 5.14: The  $EF_{As}$  distribution with age of dust post 1966 (0-50 years) and pre 1966 (50-90 years) in 2 groups /locations of El Paso.

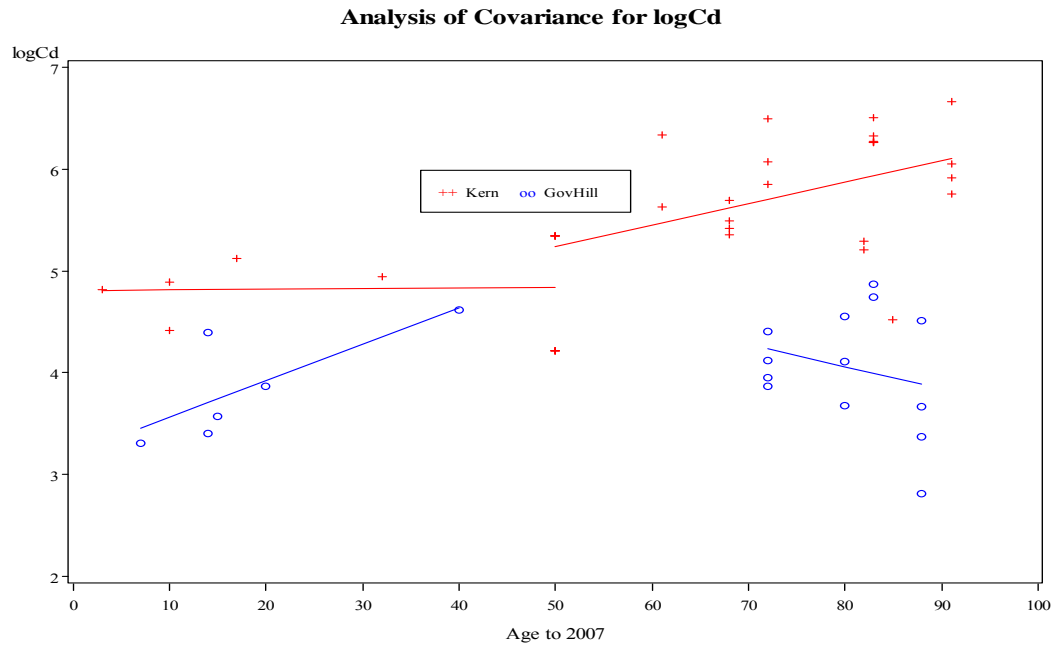


Figure 5.15: The  $\ln EF_{Cd}$  distribution with dust age post 1966 (0-50 years) and pre 1966 (50-90 years) in 2 groups /locations of El Paso.

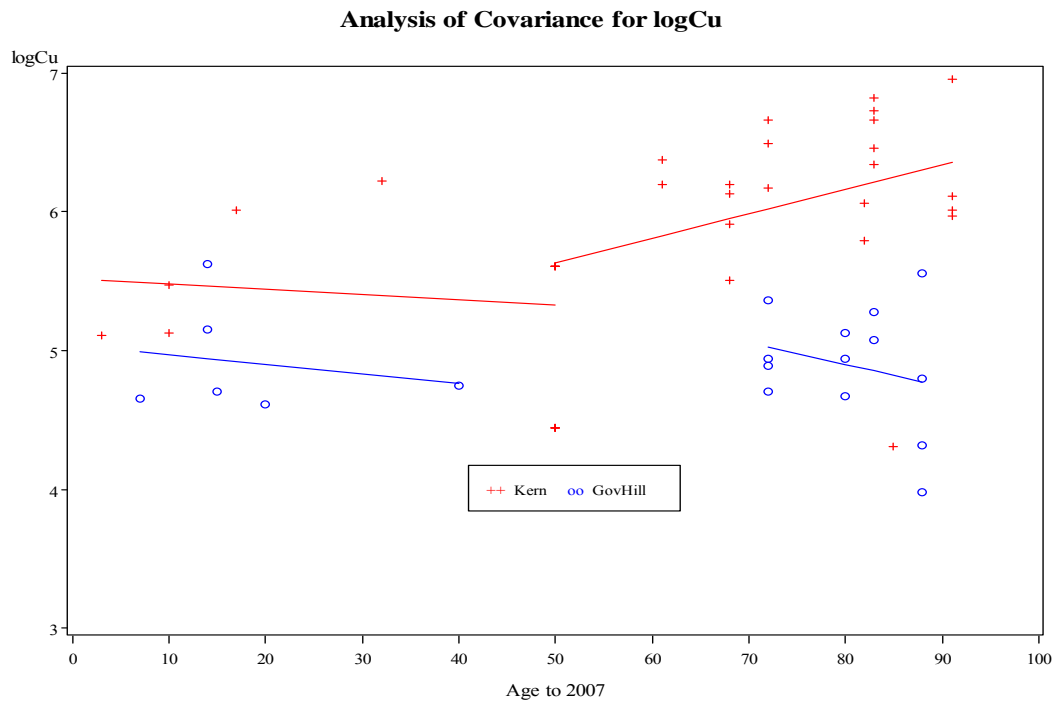


Figure 5.16: The  $\ln EF_{Cu}$  distribution with dust age post 1966 (0-50 years) and pre 1966 (50-90 years) in 2 groups /locations of El Paso.

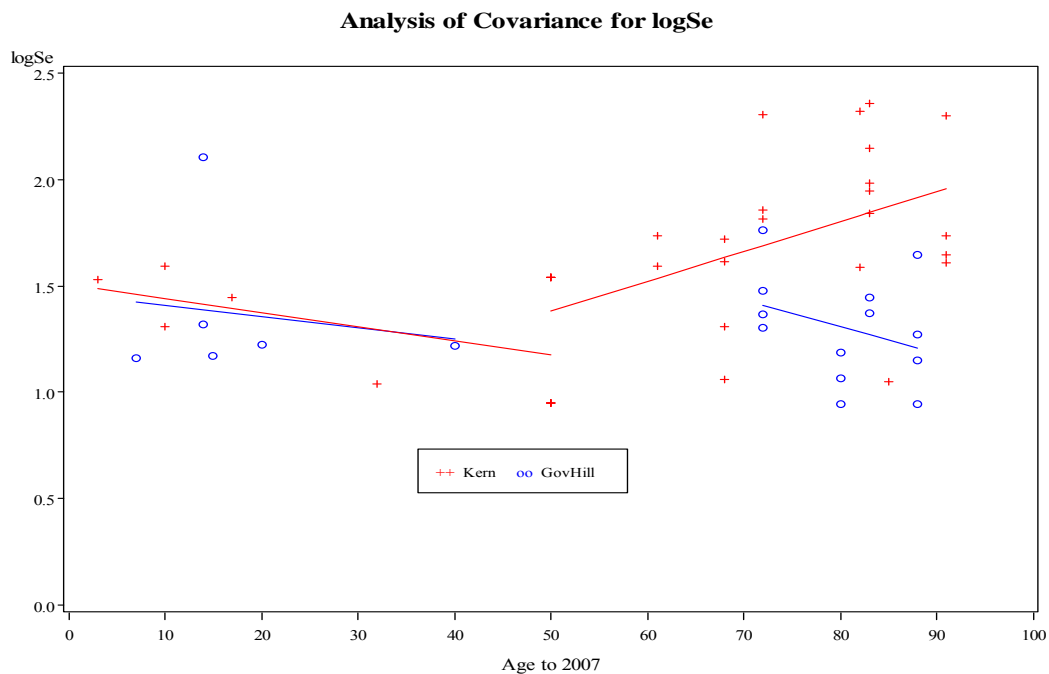


Figure 5.17: The  $\ln EF_{Se}$  distribution with dust age post 1966 (0-50 years) and pre 1966 (50-90 years) in 2 groups /locations of El Paso.

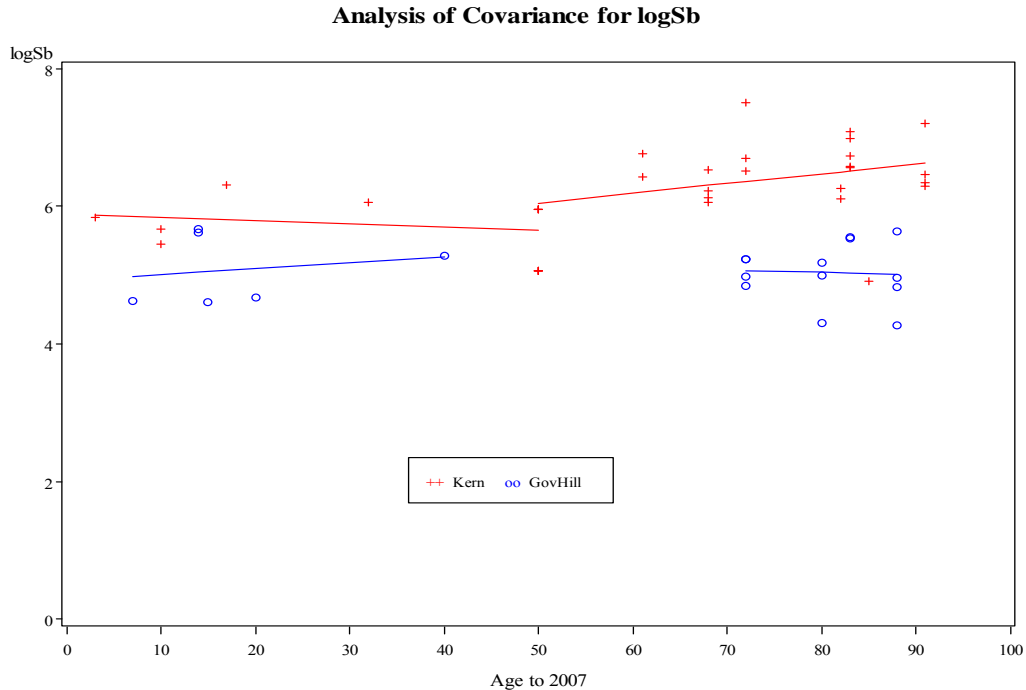


Figure 5.18: The  $\ln EF_{Sb}$  distribution with age of dust post 1966 (0-50 years) and pre 1966 (50-90 years) in 2 groups /location of El Paso.

All heavy metals/metalloids demonstrate very similar distribution patterns in their EFs before 1966. Clearly, the EFs of the elements Pb, As, Cd, Cu, Sb and Se show the same steeply increasing slope relative to the time of dust accumulation for the Kern Place group before 1966. The EFs of the elements in the Government Hill group slightly decrease with dust age. After 1966 this pattern completely changes for all of these elements in both locations. In the Kern Place group the slope becomes almost a straight line, signifying no change, i.e., stability, in elemental accumulation with time. Although there are a few minor patterns to be discerned in the Government Hill group, these are not significant enough to be usable for source identification assessment. Interestingly, the Pb and As have almost similar EFs distribution patterns in both locations and at both periods of time.

Such results lead to the conclusion that some sources of the above-mentioned heavy metals/metalloids had a very strong stabilizing influence on the elements' deposition and accumulation in the attic dusts from the Kern Place area, starting in 1966. The most likely reason was the installation by ASARCO in this year of a new smokestack to alleviate local pollution.

Again, the MANCOVA results allow one to distinguish a subset of the elements characterized by similar patterns, namely the dependence of the element's concentration associated with the age of sampled dust and location where attic dusts were sampled. This subset includes Pb, As, Cd, Cu, and Sb and Se (to some degree). However, Zn was excluded from this set, even though it has high EF values. The distinction of this subset of elements was additionally verified with by the exploration of Correlation analysis, Cluster and PCA analysis.

### 5.3.3 Correlation Analyses Results

As described in the Methodology chapter, the Bivariate Pierson correlations were computed for each pair of the 17 elements EF values from three groups /locations together (51 samples total) plus for the EFs of each element and dust age. Then, the same Correlation analyses were applied separately for the Kern Place (28 samples) and the Government Hill (19 samples) groups. The results of the first row and the corresponding p-values for the two-tailed t-tests (second row) for the 17 elements and the age in three locations together are given in Tables 5.17a and b (pages 106-107). The results of the correlation analysis for the Kern Place group are presented in Tables 5.18a and b, and for the Government Hill group in Tables 5.19a and b (pages 108-111).

The strong association between variables is considered if the absolute values of Pierson coefficient are  $r > 0.50$  and  $p < 0.05$ . Using this criterion the strongest correlations were detected among Pb, As, Cd, Cu, Sb and Se in all groups. At the same time, the correlations between those elements were slightly higher in the Kern Place group than in the Government Hill group with the exception of the pair Pb and As whose correlation coefficients were equal ( $r = 0.88$ ,  $p < 0.0001$ ) in both groups. For instance, the Pierson correlation coefficient for pair Pb - Cd was  $r = 0.92$ ,  $p < 0.0001$  in the Kern Place group and  $r = 0.73$ ,  $p < 0.0004$  in the Government Hill group; for the pair Pb – Sb  $r = 0.77$ ,  $p < 0.0001$  in the Kern Place group and  $r = 0.74$ ,  $p < 0.0003$  in the Government Hill group; for the Pb - Cu the  $r$  is  $0.92$ ,  $p < 0.0001$  in the Kern Place group, and  $r$  is  $0.48$ ,  $p < 0.03$  in the Government Hill group; and for the pair Pb – Se  $r = 0.74$ ,  $p < 0.0001$  in the Kern Place group and  $r = 0.68$ ,  $p < 0.0013$  in the Government Hill group. The same high values of the correlation coefficients ranging from  $0.65 < r < 0.94$  ( $p < 0.0001$ ) were observed between

other heavy metals/metalloids, with higher correlation coefficients for all of them in the Kern place group.

Only this set of elements shows significant correlation with age of accumulated dust and only in the Kern Place group. The high correlations with age of dust were demonstrated by Pb ( $r = 0.62$ ,  $p < 0.0005$ ), As ( $r = 0.59$ ,  $p < 0.001$ ), Cd ( $r = 0.58$ ,  $p < 0.0011$ ), and lower correlations were revealed by Cu ( $r = 0.48$ ,  $p < 0.009$ ), Se ( $r = 0.45$ ,  $p < 0.01$ ), and Sb ( $r = 0.43$ ,  $p < 0.02$ ). Zn shows positive correlation only with Se; the correlation between these elements were unexpectedly high in the Government Hill group ( $r = 0.86$ ,  $p < 0.0001$ ).

The other elements show positive correlation with at least one other element, with the exception of Fe and Mn that demonstrate negative or very weak positive correlation with other elements ( $0.006 < r < 0.447$ ). In observing the results of other elements Pierson correlation analyses, high correlations were found between Ti and Sr (they correlated only to each other with  $r = 0.725$ ,  $p < 0.0001$ ); between Zn, Se and Na (Zn correlated with Se ( $r = 0.57$ ,  $p < 0.0001$ ) and Na ( $r = 0.62$ ,  $p < 0.0001$ ); between Ba, V, K and Al (Ba correlated with Al ( $r = 0.52$ ,  $p < 0.0001$ ), K ( $r = 0.565$ ,  $p < 0.0001$ ), and V ( $r = 0.684$ ,  $p < 0.0001$ )).

Table 5.17a: Results of Pearson Correlation Analyses for all Groups Combined (EFs of 17 elements, 51 dust samples).

Pearson Correlation Coefficients, N = 51 Prob >  r  under H0: Rho=0										
	Fe	Mn	Ba	Zn	Pb	As	Cd	Cu	Al	Ti
<b>Fe</b> Fe	1.00000 0.2241	0.17323 0.0460	0.28071 0.0460	0.04939 0.7307	-0.09331 0.5149	-0.13262 0.3535	-0.09324 0.5152	-0.01087 0.9397	0.26306 0.0622	0.00643 0.9643
<b>Mn</b> Mn	0.17323 0.2241	1.00000 0.0010	0.44679 0.0010	0.00363 0.9798	0.17689 0.2143	0.33631 0.0158	0.34146 0.0142	0.27526 0.0506	0.00169 0.9906	-0.32983 0.0181
<b>Ba</b> Ba	0.28071 0.0460	0.44679 0.0010	1.00000 0.0010	-0.09951 0.4872	-0.14816 0.2995	-0.07446 0.6036	-0.12631 0.3771	-0.17074 0.2309	0.52030 <.0001	0.01455 0.9193
<b>Zn</b> Zn	0.04939 0.7307	0.00363 0.9798	-0.09951 0.4872	1.00000 0.0010	0.09278 0.5173	0.10395 0.4679	0.07625 0.5948	0.10198 0.4764	-0.15072 0.2911	-0.16992 0.2332
<b>Pb</b> Pb	-0.09331 0.5149	0.17689 0.2143	-0.14816 0.2995	0.09278 0.5173	1.00000 0.0010	0.92297 <.0001	0.94259 <.0001	0.93434 <.0001	-0.35335 0.0110	-0.27536 0.0505
<b>As</b> As	-0.13262 0.3535	0.33631 0.0158	-0.07446 0.6036	0.10395 0.4679	0.92297 <.0001	1.00000 0.0010	0.96085 <.0001	0.85494 <.0001	-0.39631 0.0040	-0.33414 0.0166
<b>Cd</b> Cd	-0.09324 0.5152	0.34146 0.0142	-0.12631 0.3771	0.07625 0.5948	0.94259 <.0001	0.96085 <.0001	1.00000 0.0010	0.88221 <.0001	-0.43875 0.0013	-0.34647 0.0128
<b>Cu</b> Cu	-0.01087 0.9397	0.27526 0.0506	-0.17074 0.2309	0.10198 0.4764	0.93434 <.0001	0.85494 <.0001	0.88221 <.0001	1.00000 0.0010	-0.41541 0.0024	-0.39580 0.0040
<b>Al</b> Al	0.26306 0.0622	0.00169 0.9906	0.52030 <.0001	-0.15072 0.2911	-0.35335 0.0110	-0.39631 0.0040	-0.43875 0.0013	-0.41541 0.0024	1.00000 0.0010	0.49433 0.0002
<b>Ti</b> Ti	0.00643 0.9643	-0.32983 0.0181	0.01455 0.9193	-0.16992 0.2332	-0.27536 0.0505	-0.33414 0.0166	-0.34647 0.0128	-0.39580 0.0040	0.49433 0.0002	1.00000 0.0010
<b>Sr</b> Sr	-0.05992 0.6762	-0.33176 0.0174	-0.17846 0.2102	-0.10305 0.4718	-0.17380 0.2226	-0.17778 0.2120	-0.17409 0.2218	-0.25688 0.0688	-0.08264 0.5643	0.72459 <.0001
<b>K</b> K	0.47134 0.0005	0.19903 0.1615	0.56497 <.0001	-0.16195 0.2562	-0.27537 0.0505	-0.25741 0.0682	-0.25570 0.0701	-0.28220 0.0448	0.59214 <.0001	0.18097 0.2038
<b>Na</b> Na	0.18578 0.1918	-0.00528 0.9707	-0.06938 0.6285	0.61634 <.0001	-0.09444 0.5098	-0.11129 0.4369	-0.06356 0.6577	-0.02574 0.8577	-0.14869 0.2977	-0.13864 0.3319
<b>Mg</b> Mg	-0.00650 0.9639	0.09127 0.5242	0.38382 0.0054	-0.11255 0.4317	-0.30345 0.0304	-0.29234 0.0374	-0.34273 0.0138	-0.34598 0.0129	0.76924 <.0001	0.22816 0.1073
<b>V_51</b> V/51	0.25916 0.0663	0.15002 0.2934	0.68426 <.0001	-0.12067 0.3989	-0.27819 0.0481	-0.31454 0.0246	-0.35400 0.0108	-0.33129 0.0176	0.81764 <.0001	0.40557 0.0032
<b>Se_82</b> Se/82	-0.04754 0.7404	0.25016 0.0767	0.03896 0.7861	0.56738 <.0001	0.76037 <.0001	0.70301 <.0001	0.70634 <.0001	0.71630 <.0001	-0.18504 0.1936	-0.21648 0.1271
<b>Sb_121</b> Sb/121	-0.11827 0.4085	0.35456 0.0107	-0.08447 0.5556	0.27904 0.0474	0.85122 <.0001	0.87572 <.0001	0.86292 <.0001	0.87110 <.0001	-0.42788 0.0017	-0.33473 0.0164
<b>Age_to_2007_</b> Age to 2007	-0.08566 0.5501	-0.14175 0.3211	-0.22969 0.1049	0.02537 0.8597	0.43796 0.0013	0.40370 0.0033	0.40695 0.0030	0.33746 0.0154	-0.13306 0.3519	-0.08664 0.5455

Table 5.17b: (Cont) Results of the Pearson Correlation Analyses for all Groups Combined (EFs of 17 elements, 51 dust samples).

Pearson Correlation Coefficients, N = 51 Prob >  r  under H0: Rho=0								
	Sr	K	Na	Mg	V	Se	Sb	Age_to_2007_
<b>Fe</b> Fe	-0.05992 0.6762	0.47134 0.0005	0.18578 0.1918	-0.00650 0.9639	0.25916 0.0663	-0.04754 0.7404	-0.11827 0.4085	-0.08566 0.5501
<b>Mn</b> Mn	-0.33176 0.0174	0.19903 0.1615	-0.00528 0.9707	0.09127 0.5242	0.15002 0.2934	0.25016 0.0767	0.35456 0.0107	-0.14175 0.3211
<b>Ba</b> Ba	-0.17846 0.2102	0.56497 <.0001	-0.06938 0.6285	0.38382 0.0054	0.68426 <.0001	0.03896 0.7861	-0.08447 0.5556	-0.22969 0.1049
<b>Zn</b> Zn	-0.10305 0.4718	-0.16195 0.2562	0.61634 <.0001	-0.11255 0.4317	-0.12067 0.3989	0.56738 <.0001	0.27904 0.0474	0.02537 0.8597
<b>Pb</b> Pb	-0.17380 0.2226	-0.27537 0.0505	-0.09444 0.5098	-0.30345 0.0304	-0.27819 0.0481	0.76037 <.0001	0.85122 <.0001	0.43796 0.0013
<b>As</b> As	-0.17778 0.2120	-0.25741 0.0682	-0.11129 0.4369	-0.29234 0.0374	-0.31454 0.0246	0.70301 <.0001	0.87572 <.0001	0.40370 0.0033
<b>Cd</b> Cd	-0.17409 0.2218	-0.25570 0.0701	-0.06356 0.6577	-0.34273 0.0138	-0.35400 0.0108	0.70634 <.0001	0.86292 <.0001	0.40695 0.0030
<b>Cu</b> Cu	-0.25688 0.0688	-0.28220 0.0448	-0.02574 0.8577	-0.34598 0.0129	-0.33129 0.0176	0.71630 <.0001	0.87110 <.0001	0.33746 0.0154
<b>Al</b> Al	-0.08264 0.5643	0.59214 <.0001	-0.14869 0.2977	0.76924 <.0001	0.81764 <.0001	-0.18504 0.1936	-0.42788 0.0017	-0.13306 0.3519
<b>Ti</b> Ti	0.72459 <.0001	0.18097 0.2038	-0.13864 0.3319	0.22816 0.1073	0.40557 0.0032	-0.21648 0.1271	-0.33473 0.0164	-0.08664 0.5455
<b>Sr</b> Sr	1.00000	-0.07479 0.6019	-0.00215 0.9881	-0.23942 0.0906	-0.03730 0.7950	-0.23088 0.1031	-0.19340 0.1739	-0.05418 0.7057
<b>K</b> K	-0.07479 0.6019	1.00000	0.29963 0.0327	0.51309 0.0001	0.58958 <.0001	-0.19263 0.1756	-0.31461 0.0245	-0.07264 0.6125
<b>Na</b> Na	-0.00215 0.9881	0.29963 0.0327	1.00000	-0.03844 0.7888	-0.12119 0.3969	0.14901 0.2967	-0.05020 0.7265	0.09721 0.4974
<b>Mg</b> Mg	-0.23942 0.0906	0.51309 0.0001	-0.03844 0.7888	1.00000	0.67223 <.0001	-0.16747 0.2401	-0.31901 0.0225	0.11903 0.4054
<b>V</b> V	-0.03730 0.7950	0.58958 <.0001	-0.12119 0.3969	0.67223 <.0001	1.00000	-0.05254 0.7142	-0.30148 0.0316	-0.04684 0.7441
<b>Se</b> Se	-0.23088 0.1031	-0.19263 0.1756	0.14901 0.2967	-0.16747 0.2401	-0.05254 0.7142	1.00000	0.80409 <.0001	0.23493 0.0970
<b>Sb</b> Sb	-0.19340 0.1739	-0.31461 0.0245	-0.05020 0.7265	-0.31901 0.0225	-0.30148 0.0316	0.80409 <.0001	1.00000	0.29407 0.0362
<b>Age_to_2007_</b> Age to 2007	-0.05418 0.7057	-0.07264 0.6125	0.09721 0.4974	0.11903 0.4054	-0.04684 0.7441	0.23493 0.0970	0.29407 0.0362	1.00000

Table 5.18a: Results of the Pearson Correlation Analyses for Kern Place Group  
(EFs of 17 elements, 28 dust samples).

Pearson Correlation Coefficients, N = 28 Prob >  r  under H0: Rho=0										
	Fe	Mn	Ba	Zn	Pb	As	Cd	Cu	Al	Ti
<b>Fe</b> Fe	1.00000 0.4030	0.16446 0.4030	0.16982 0.3876	0.59883 0.0008	0.20637 0.2921	0.09479 0.6314	0.08231 0.6771	0.36332 0.0574	0.36731 0.0545	-0.17719 0.3671
<b>Mn</b> Mn	0.16446 0.4030	1.00000 <.0001	0.79870 <.0001	0.03192 0.8719	0.16659 0.3968	0.40370 0.0331	0.38197 0.0449	0.25757 0.1858	0.18953 0.3341	-0.50272 0.0064
<b>Ba</b> Ba	0.16982 0.3876	0.79870 <.0001	1.00000 <.0001	-0.09488 0.6310	0.27276 0.1602	0.46929 0.0118	0.44637 0.0173	0.28029 0.1485	0.38701 0.0419	-0.37272 0.0508
<b>Zn</b> Zn	0.59883 0.0008	0.03192 0.8719	-0.09488 0.6310	1.00000 <.0001	-0.06623 0.7377	-0.03729 0.8506	-0.06811 0.7306	-0.02977 0.8805	-0.23531 0.2281	-0.18743 0.3395
<b>Pb</b> Pb	0.20637 0.2921	0.16659 0.3968	0.27276 0.1602	-0.06623 0.7377	1.00000 <.0001	0.87993 <.0001	0.91819 <.0001	0.92298 <.0001	0.48074 0.0096	-0.12231 0.5352
<b>As</b> As	0.09479 0.6314	0.40370 0.0331	0.46929 0.0118	-0.03729 0.8506	0.87993 <.0001	1.00000 <.0001	0.94340 <.0001	0.77654 <.0001	0.39038 0.0400	-0.20677 0.2911
<b>Cd</b> Cd	0.08231 0.6771	0.38197 0.0449	0.44637 0.0173	-0.06811 0.7306	0.91819 <.0001	0.94340 <.0001	1.00000 <.0001	0.80384 <.0001	0.40893 0.0307	-0.19768 0.3133
<b>Cu</b> Cu	0.36332 0.0574	0.25757 0.1858	0.28029 0.1485	-0.02977 0.8805	0.92298 <.0001	0.77654 <.0001	0.80384 <.0001	1.00000 <.0001	0.44223 0.0185	-0.28993 0.1345
<b>Al</b> Al	0.36731 0.0545	0.18953 0.3341	0.38701 0.0419	-0.23531 0.2281	0.48074 0.0096	0.39038 0.0400	0.40893 0.0307	0.44223 0.0185	1.00000 <.0001	0.31289 0.1050
<b>Ti</b> Ti	-0.17719 0.3671	-0.50272 0.0064	-0.37272 0.0508	-0.18743 0.3395	-0.12231 0.5352	-0.20677 0.2911	-0.19768 0.3133	-0.28993 0.1345	0.31289 0.1050	1.00000 <.0001
<b>Sr</b> Sr	-0.34771 0.0698	-0.53580 0.0033	-0.42342 0.0248	-0.14137 0.4730	-0.31428 0.1034	-0.33780 0.0787	-0.35114 0.0669	-0.47187 0.0112	-0.02890 0.8839	0.89408 <.0001
<b>K</b> K	0.18823 0.3374	0.19913 0.3097	0.30998 0.1084	-0.04428 0.8230	0.19000 0.3328	0.26806 0.1678	0.29809 0.1234	0.16297 0.4073	0.48048 0.0097	0.00946 0.9619
<b>Na</b> Na	0.56400 0.0018	-0.16075 0.4138	-0.19239 0.3267	0.76243 <.0001	-0.21614 0.2693	-0.24845 0.2024	-0.21061 0.2820	-0.17325 0.3780	-0.19071 0.3310	-0.10960 0.5788
<b>Mg</b> Mg	0.35000 0.0679	0.45294 0.0155	0.50110 0.0066	-0.04120 0.8351	0.23140 0.2361	0.31231 0.1057	0.30288 0.1172	0.26925 0.1659	0.50258 0.0064	-0.19332 0.3243
<b>V_51</b> V_51	0.33282 0.0835	0.33013 0.0862	0.46167 0.0134	-0.10549 0.5932	0.59103 0.0009	0.53878 0.0031	0.56951 0.0016	0.54753 0.0026	0.83376 <.0001	0.24919 0.2010
<b>Se_82</b> Se_82	0.46018 0.0137	0.24409 0.2107	0.22124 0.2579	0.49882 0.0069	0.73834 <.0001	0.65475 0.0002	0.69066 <.0001	0.69937 <.0001	0.36205 0.0583	-0.18381 0.3491
<b>Sb_121</b> Sb_121	0.30181 0.1186	0.42740 0.0233	0.41909 0.0264	0.21198 0.2789	0.76627 <.0001	0.80046 <.0001	0.77132 <.0001	0.79805 <.0001	0.38270 0.0444	-0.19516 0.3196
<b>Age to 2007_</b> Age to 2007	0.17579 0.3709	-0.25246 0.1949	-0.14773 0.4531	0.14695 0.4556	0.61805 0.0005	0.58776 0.0010	0.58302 0.0011	0.48431 0.0090	0.23269 0.2334	0.08111 0.6816

Table 5.18b: cont. Results of the Pearson Correlation Analyses for Kern Place Group  
(EFs of 17 elements, 28 dust samples).

Pearson Correlation Coefficients, N = 28 Prob >  r  under H0: Rho=0								
	Sr	K	Na	Mg	V_51	Se_82	Sb_121	Age_to_2007_
<b>Fe</b> Fe	-0.34771 0.0698	0.18823 0.3374	0.56400 0.0018	0.35000 0.0679	0.33282 0.0835	0.46018 0.0137	0.30181 0.1186	0.17579 0.3709
<b>Mn</b> Mn	-0.53580 0.0033	0.19913 0.3097	-0.16075 0.4138	0.45294 0.0155	0.33013 0.0862	0.24409 0.2107	0.42740 0.0233	-0.25246 0.1949
<b>Ba</b> Ba	-0.42342 0.0248	0.30998 0.1084	-0.19239 0.3267	0.50110 0.0066	0.46167 0.0134	0.22124 0.2579	0.41909 0.0264	-0.14773 0.4531
<b>Zn</b> Zn	-0.14137 0.4730	-0.04428 0.8230	0.76243 <.0001	-0.04120 0.8351	-0.10549 0.5932	0.49882 0.0069	0.21198 0.2789	0.14695 0.4556
<b>Pb</b> Pb	-0.31428 0.1034	0.19000 0.3328	-0.21614 0.2693	0.23140 0.2361	0.59103 0.0009	0.73834 <.0001	0.76627 <.0001	0.61805 0.0005
<b>As</b> As	-0.33780 0.0787	0.26806 0.1678	-0.24845 0.2024	0.31231 0.1057	0.53878 0.0031	0.65475 0.0002	0.80046 <.0001	0.58776 0.0010
<b>Cd</b> Cd	-0.35114 0.0669	0.29809 0.1234	-0.21061 0.2820	0.30288 0.1172	0.56951 0.0016	0.69066 <.0001	0.77132 <.0001	0.58302 0.0011
<b>Cu</b> Cu	-0.47187 0.0112	0.16297 0.4073	-0.17325 0.3780	0.26925 0.1659	0.54753 0.0026	0.69937 <.0001	0.79805 <.0001	0.48431 0.0090
<b>Al</b> Al	-0.02890 0.8839	0.48048 0.0097	-0.19071 0.3310	0.50258 0.0064	0.83376 <.0001	0.36205 0.0583	0.38270 0.0444	0.23269 0.2334
<b>Ti</b> Ti	0.89408 <.0001	0.00946 0.9619	-0.10960 0.5788	-0.19332 0.3243	0.24919 0.2010	-0.18381 0.3491	-0.19516 0.3196	0.08111 0.6816
<b>Sr</b> Sr	1.00000	-0.09690 0.6237	-0.02399 0.9036	-0.37242 0.0510	-0.00260 0.9895	-0.39142 0.0394	-0.37476 0.0494	-0.04378 0.8249
<b>K</b> K	-0.09690 0.6237	1.00000	0.31655 0.1008	0.72467 <.0001	0.39315 0.0385	0.12163 0.5375	0.15759 0.4232	0.14157 0.4724
<b>Na</b> Na	-0.02399 0.9036	0.31655 0.1008	1.00000	0.06239 0.7525	-0.18109 0.3564	0.14987 0.4465	-0.16424 0.4036	0.11716 0.5527
<b>Mg</b> Mg	-0.37242 0.0510	0.72467 <.0001	0.06239 0.7525	1.00000	0.47133 0.0113	0.22691 0.2456	0.35001 0.0679	0.10760 0.5857
<b>V_51</b> V/51	-0.00260 0.9895	0.39315 0.0385	-0.18109 0.3564	0.47133 0.0113	1.00000	0.46662 0.0123	0.61398 0.0005	0.31675 0.1005
<b>Se_82</b> Se/82	-0.39142 0.0394	0.12163 0.5375	0.14987 0.4465	0.22691 0.2456	0.46662 0.0123	1.00000	0.81123 <.0001	0.45615 0.0147
<b>Sb_121</b> Sb/121	-0.37476 0.0494	0.15759 0.4232	-0.16424 0.4036	0.35001 0.0679	0.61398 0.0005	0.81123 <.0001	1.00000	0.42512 0.0241
<b>Age_to_2007_</b> Age to 2007	-0.04378 0.8249	0.14157 0.4724	0.11716 0.5527	0.10760 0.5857	0.31675 0.1005	0.45615 0.0147	0.42512 0.0241	1.00000

Table 5.19a: Results of the Pearson Correlation Analyses for Government Hill Group  
(EFs of 17 elements, 19 samples).

Pearson Correlation Coefficients, N = 19 Prob >  r  under H0: Rho=0										
	Fe	Mn	Ba	Zn	Pb	As	Cd	Cu	Al	Ti
Fe Fe	1.00000 0.0188	0.53289 0.0188	0.60125 0.0065	0.27550 0.2536	0.23285 0.3374	0.48449 0.0355	0.38465 0.1039	0.46805 0.0433	0.94676 <.0001	0.70334 0.0008
Mn Mn	0.53289 0.0188	1.00000	0.42248 0.0715	-0.17775 0.4666	-0.13586 0.5792	0.02656 0.9140	0.29192 0.2252	0.23215 0.3389	0.38524 0.1034	0.43563 0.0623
Ba Ba	0.60125 0.0065	0.42248 0.0715	1.00000	0.18745 0.4422	0.58905 0.0080	0.66729 0.0018	0.61091 0.0055	0.70778 0.0007	0.45343 0.0512	0.38517 0.1034
Zn Zn	0.27550 0.2536	-0.17775 0.4666	0.18745 0.4422	1.00000	0.57913 0.0094	0.45329 0.0513	0.18900 0.4384	0.20459 0.4008	0.34374 0.1496	0.28151 0.2430
Pb Pb	0.23285 0.3374	-0.13586 0.5792	0.58905 0.0080	0.57913 0.0094	1.00000	0.88300 <.0001	0.73060 0.0004	0.48168 0.0368	0.31318 0.1917	0.30487 0.2044
As As	0.48449 0.0355	0.02656 0.9140	0.66729 0.0018	0.45329 0.0513	0.88300 <.0001	1.00000	0.72957 0.0004	0.43076 0.0656	0.53515 0.0182	0.49060 0.0329
Cd Cd	0.38465 0.1039	0.29192 0.2252	0.61091 0.0055	0.18900 0.4384	0.73060 0.0004	0.72957 0.0004	1.00000	0.46912 0.0427	0.42233 0.0717	0.41359 0.0784
Cu Cu	0.46805 0.0433	0.23215 0.3389	0.70778 0.0007	0.20459 0.4008	0.48168 0.0368	0.43076 0.0656	0.46912 0.0427	1.00000	0.40480 0.0856	0.37556 0.1131
Al Al	0.94676 <.0001	0.38524 0.1034	0.45343 0.0512	0.34374 0.1496	0.31318 0.1917	0.53515 0.0182	0.42233 0.0717	0.40480 0.0856	1.00000	0.76449 0.0001
Ti Ti	0.70334 0.0008	0.43563 0.0623	0.38517 0.1034	0.28151 0.2430	0.30487 0.2044	0.49060 0.0329	0.41359 0.0784	0.37556 0.1131	0.76449 0.0001	1.00000
Sr Sr	0.79780 <.0001	0.70225 0.0008	0.67266 0.0016	0.04753 0.8468	0.15961 0.5139	0.32940 0.1685	0.45781 0.0487	0.43015 0.0660	0.66439 0.0019	0.42165 0.0722
K K	0.38258 0.1060	0.46272 0.0461	0.43799 0.0607	-0.15647 0.5224	0.01129 0.9634	0.22874 0.3462	0.26699 0.2692	0.31163 0.1940	0.25500 0.2921	0.06166 0.8020
Na Na	0.07743 0.7527	0.32895 0.1691	0.34047 0.1538	-0.12824 0.6008	0.00833 0.9730	0.10032 0.6828	0.19035 0.4351	0.26563 0.2717	-0.07182 0.7701	-0.07587 0.7576
Mg Mg	0.68512 0.0012	0.46913 0.0427	0.61762 0.0048	0.04714 0.8480	0.08945 0.7157	0.27813 0.2489	0.13905 0.5702	0.23620 0.3303	0.52523 0.0209	0.18524 0.4477
V_51 V/51	0.55954 0.0127	0.58951 0.0079	0.63562 0.0034	0.34597 0.1468	0.21585 0.3748	0.23273 0.3376	0.12441 0.6118	0.33900 0.1557	0.37626 0.1123	0.33694 0.1584
Se_82 Se/82	0.54473 0.0159	0.13639 0.5777	0.61952 0.0047	0.86088 <.0001	0.68289 0.0013	0.61356 0.0052	0.40898 0.0821	0.50438 0.0277	0.51080 0.0254	0.46381 0.0455
Sb_121 Sb/121	0.32172 0.1792	0.09290 0.7052	0.68257 0.0013	0.45322 0.0513	0.74186 0.0003	0.59528 0.0072	0.68371 0.0012	0.82991 <.0001	0.33486 0.1611	0.47050 0.0421
Age_to_2007 Age to 2007	-0.28271 0.2409	0.05106 0.8356	0.20010 0.4114	-0.38836 0.1004	0.13751 0.5745	0.05656 0.8181	0.23644 0.3298	-0.06141 0.8028	-0.40209 0.0879	-0.50972 0.0258

Table 5.19b: Cont. Results of the Pearson Correlation Analyses for Government Hill Group (EFs of 17 elements, 19 samples).

Pearson Correlation Coefficients, N = 19 Prob >  r  under H0: Rho=0								
	Sr	K	Na	Mg	V_51	Se_82	Sb_121	Age_to_2007_
<b>Fe</b> Fe	0.79780 <.0001	0.38258 0.1060	0.07743 0.7527	0.68512 0.0012	0.55954 0.0127	0.54473 0.0159	0.32172 0.1792	-0.28271 0.2409
<b>Mn</b> Mn	0.70225 0.0008	0.46272 0.0461	0.32895 0.1691	0.46913 0.0427	0.58951 0.0079	0.13639 0.5777	0.09290 0.7052	0.05106 0.8356
<b>Ba</b> Ba	0.67266 0.0016	0.43799 0.0607	0.34047 0.1538	0.61762 0.0048	0.63562 0.0034	0.61952 0.0047	0.68257 0.0013	0.20010 0.4114
<b>Zn</b> Zn	0.04753 0.8468	-0.15647 0.5224	-0.12824 0.6008	0.04714 0.8480	0.34597 0.1468	0.86088 <.0001	0.45322 0.0513	-0.38836 0.1004
<b>Pb</b> Pb	0.15961 0.5139	0.01129 0.9634	0.00833 0.9730	0.08945 0.7157	0.21585 0.3748	0.68289 0.0013	0.74186 0.0003	0.13751 0.5745
<b>As</b> As	0.32940 0.1685	0.22874 0.3462	0.10032 0.6828	0.27813 0.2489	0.23273 0.3376	0.61356 0.0052	0.59528 0.0072	0.05656 0.8181
<b>Cd</b> Cd	0.45781 0.0487	0.26699 0.2692	0.19035 0.4351	0.13905 0.5702	0.12441 0.6118	0.40898 0.0821	0.68371 0.0012	0.23644 0.3298
<b>Cu</b> Cu	0.43015 0.0660	0.31163 0.1940	0.26563 0.2717	0.23620 0.3303	0.33900 0.1557	0.50438 0.0277	0.82991 <.0001	-0.06141 0.8028
<b>Al</b> Al	0.66439 0.0019	0.25500 0.2921	-0.07182 0.7701	0.52523 0.0209	0.37626 0.1123	0.51080 0.0254	0.33486 0.1611	-0.40209 0.0879
<b>Ti</b> Ti	0.42165 0.0722	0.06166 0.8020	-0.07587 0.7576	0.18524 0.4477	0.33694 0.1584	0.46381 0.0455	0.47050 0.0421	-0.50972 0.0258
<b>Sr</b> Sr	1.00000	0.36987 0.1191	0.17025 0.4859	0.68105 0.0013	0.57363 0.0102	0.37981 0.1087	0.27529 0.2540	0.03676 0.8812
<b>K</b> K	0.36987 0.1191	1.00000	0.82530 <.0001	0.49635 0.0307	0.16524 0.4990	0.05760 0.8148	0.06155 0.8023	0.13443 0.5832
<b>Na</b> Na	0.17025 0.4859	0.82530 <.0001	1.00000	0.19913 0.4138	0.09932 0.6858	0.02884 0.9067	0.10182 0.6783	0.08902 0.7170
<b>Mg</b> Mg	0.68105 0.0013	0.49635 0.0307	0.19913 0.4138	1.00000	0.65877 0.0022	0.34080 0.1533	0.03574 0.8845	0.15090 0.5375
<b>V_51</b> V/51	0.57363 0.0102	0.16524 0.4990	0.09932 0.6858	0.65877 0.0022	1.00000	0.67619 0.0015	0.30586 0.2028	0.10220 0.6772
<b>Se_82</b> Se/82	0.37981 0.1087	0.05760 0.8148	0.02884 0.9067	0.34080 0.1533	0.67619 0.0015	1.00000	0.67904 0.0014	-0.20196 0.4070
<b>Sb_121</b> Sb/121	0.27529 0.2540	0.06155 0.8023	0.10182 0.6783	0.03574 0.8845	0.30586 0.2028	0.67904 0.0014	1.00000	-0.04941 0.8408
<b>Age_to_2007_</b> Age to 2007	0.03676 0.8812	0.13443 0.5832	0.08902 0.7170	0.15090 0.5375	0.10220 0.6772	-0.20196 0.4070	-0.04941 0.8408	1.00000

In the Kern Place and Government Hill groups the correlated elements are different. Due to low EFs of these elements, their sources were not examined. Importantly, the highest correlations were observed among Pb, As, Cd, Cu, Sb and Se in all groups. For this group of elements the values for the correlation coefficients ranged from  $0.70 < r < 0.96$  at a 99 % confidence level which strongly suggests their common industrial source.

The results of the Correlation analysis are parallel to the MANCOVA results in terms of distinguishing the same group of elements, i.e. Pb, As, Cd, Cu, Sb and Se (and excluding Zn).

#### **5.3.4 Cluster analysis**

Using the EFs of 17 elements from a total of 51 samples, Cluster Analysis (described in subsection 4.6.3.4) was performed to examine how these elements potentially group together. Cluster analysis, based on the results of Pierson correlation analysis, organizes homogenous subgroups and constructs a “hierarchical tree” with the most closely related elements that are at the lower levels of the tree. In our case, they are Fe, Mn, Al, K, Sr, Mg, Na, Ba, V, Se, Ti and Pb with Cd.

Figure 5.19 (p. 114) shows three groups of closely related elements, e.g. three clusters. The first cluster comprises 11 related elements plus As, the second includes Pb, Cd, Cu, Sb and the third includes only Zn. Because Zn did not follow the general patterns of other heavy metals, it was separated into an individual cluster. However, if we consider only 2 clusters (with a cut-off between 0.1 and 0.3), Cluster 1 contains the same elements, but Zn can be added to Cluster 2:

Cluster 1: Fe, Mn, Al, K, Sr, Mg, Na, Ba, V, Se, Ti, As;

Cluster 2: Pb, Cd, Cu, Sb, Zn.

Cluster 1 unexpectedly contained As probably because of its greater similarity with the EFs of elements unified by Cluster 1 (much lower than the elemental EFs from Cluster 2) and not because of some underlying common process affecting the concentration of these elements in the samples analyzed. Result of Cluster Analyses express as a cluster History (basic for construction of Hierarchical tree) is presented in Table 5.20 below.

Table 5.20: Results of Cluster Analyses for elemental EFs (17 elements, 51 samples).

Cluster History						
NCL	Clusters Joined		FREQ	SPRSQ	RSQ	T i e
16	Al	K	2	0.0000	1.00	
15	Mn	CL16	3	0.0000	1.00	
14	Sr	Mg	2	0.0000	1.00	
13	Ba	V/51	2	0.0000	1.00	
12	CL15	CL14	5	0.0000	1.00	
11	CL13	Se/82	3	0.0000	1.00	
10	CL12	Na	6	0.0000	1.00	
9	CL11	Ti	4	0.0000	1.00	
8	CL10	CL9	10	0.0000	1.00	
7	Fe	CL8	11	0.0000	1.00	
6	Pb	Cd	2	0.0039	.996	
5	CL7	As	12	0.0052	.991	
4	CL6	Cu	3	0.0239	.967	
3	CL4	Sb/121	4	0.0724	.894	
2	Zn	CL3	5	0.3347	.560	
1	CL5	CL2	17	0.5597	.000	

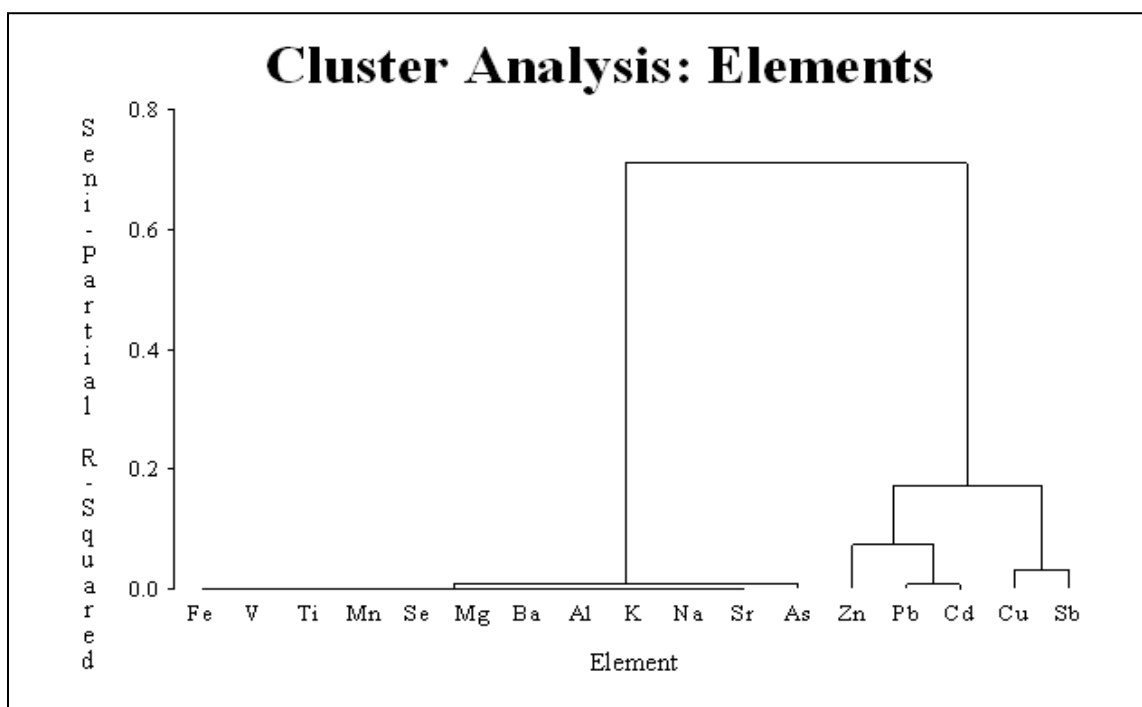


Figure 5.19: The Hierarchical Tree Obtained from the Cluster Analysis of 17 elemental EFs.

### 5.3.5 Principal Component Analysis

The Principal Component analyses applied to the same data matrix (see Methodology, subsection 4.6.3.5), revealed the four principal components or factors (factors 1-4) that explain 77% of the total variation in the data. The choice of 4 factors was based on the Scree Plot. An element is said to load on a given component if the factor loading is greater than or equal to 0.40 for that component. Factor loading  $> 0.71$  is considered excellent, and factor loading  $< 0.32$  is very poor (Grimm and Yarnold 2000 in Garcia et al. 2004).

In Table 5.21 (presented on page 116), we can observe that each of the four significant factors is associated with a specific subset of elements:

Factor 1 is associated with Pb, As, Cd, Cu, Se and Sb with loading 0.95, 0.93, 0.93 0.89, 0.85 and 0.92 respectively. This factor explained 31.4% of the data variance;

Factor 2 extracted Fe, Ba, Al, K, Mg and V with loading 0.40, 0.78, 0.85, 0.77, 0.73, and 0.90 respectively. It explained 22.6 % of the data variance;

Factor 3 was organized from Ti and Sr with loading 0.89 and 0.84 (Mn with load -54 can be interpreted as a contrast for this group). It explained 12.0% of the data variance;

Factor 4 was composed of Zn and Na with loading 0.86 and 0.89. It explained 11.0 % of the data variance.

Clearly, the first factor is the most important and furthermore it grouped all investigated heavy metals together (excluding Zn).

Table 5.21: Results of PCA analysis for elemental EFs (17 elements, 51 dust samples).

Rotated Factor Pattern							
		Factor1		Factor2		Factor3	Factor4
Fe	Fe	-6		40 *		-12	30
Mn	Mn	34		34		-54 *	-3
Ba	Ba	1		78 *		-23	-6
Zn	Zn	19		-9		1	86 *
Pb	Pb	95 *		-17		-5	-6
As	As	93 *		-16		-15	-8
Cd	Cd	93 *		-20		-16	-6
Cu	Cu	89 *		-21		-20	0
Al	Al	-24		85 *		20	-12
Ti	Ti	-17		30		89 *	-12
Sr	Sr	-12		-16		84 *	-2
K	K	-20		77 *		-7	17
Na	Na	-9		-1		-6	89 *
Mg	Mg	-22		73 *		-2	-11
V_51	V/51	-12		90 *		15	-8
Se_82	Se/82	85 *		4		-3	36
Sb_121	Sb/121	92 *		-18		-14	7
Printed values are multiplied by 100 and rounded to the nearest integer. Values greater than or equal 0.4 are flagged by an '*'.							

All statistical analyses revealed the same elemental set with small exceptions. This set includes Pb, As, Cd, Cu, Zn, Sb and Se. The MANCOVA analyses drop Zn and Se out from this set; Correlation analysis excludes Zn; Cluster Analysis Se and As; PCA again eliminates Zn. Taking into consideration the deficiency and errors of each statistical analysis, the outcome from the analytical analysis and the mode of dust particle transport and deposition in attics, one can conclude that all indicated heavy metals likely came from the same one source.

## **Chapter 6**

### **DISCUSSION**

In investigating sources of heavy metal pollution in the Paso del Norte region, the analytical examinations of sampled materials (attic dusts and soil) for their elemental content (Environmental Forensic Tracer technique) were provided first. Emissions from several local industrial sources potentially left traces in the surrounding environment according to their specific geochemical characteristics. Indeed, sampled media showed the presence of target heavy metals/metalloids such as Pb, Cd, Sb, As, Cu, Zn and Se.

The next step, EF calculation (Environmental Forensic Ratio Technique), was performed to distinguish the anthropogenic from the natural origin of the investigated elements (particularly of heavy metals) and to assess the relative residential exposure. Since the attic can be used as a surrogate for evaluation of human exposure to ambient air pollutants and because human health risk thresholds for harmful elemental concentrations in attic dust are not established, the EFs can substitute for these thresholds (even though they are presented in relative values) (Ilaqua 2002). Therefore, the focus was on the analyses of the elemental EFs. The obtained results are discussed next.

#### **6.1 Summary and Interpretation of Obtained Results. Elucidating Heavy Metal Sources**

The EF calculation revealed two sets of elements: slightly enriched and strongly enriched. The first set is comprised of the elements Fe, Mn, Ba, Al, Ti, Sr, K, Na, Mg, V and Se. Their relatively low enrichment values (less than 10) confirm that the presence of these elements in attic dust was due predominantly to crustal contributions. Although Fe is considered to be of

essential crustal origin (Lundren and Dean 1979; Ilaqua 2002, Korzhova 2011), its slightly higher enrichment (47) in the oldest dust samples (J V4+V5) from downtown Cd. Juarez may be explained by the emissions of Fe compounds from the local sources such as ferrous industries, transport activities, welding, heat and power engineering after 1946 (a time when dust started accumulating in the Victoria Theater location) (Korzhova 2011).

The second set includes Pb, Cd, As, Sb, Cu, and Zn. Anomalously high enrichments (reaching hundreds of units) of these trace elements compared to local soil indicate their mainly anthropogenic origin from several industrial sources, not only local, but distant as well. For instance, the presence of Pb compounds in local attic dusts can be explained by smelters and refinery emissions, gasoline derivatives (Harrison and Laxen 1981; Jaworski 1987 in Hutchinson and Meema, Whitson 2002; Korzhova 2011), and, in some cases, by lead-containing paint chips (Samuel and Bennett 1983). Before 1980, 80% of the homes built in the USA contained lead-based paints (ATSDR 1999 in Ilaqua 2002), and before 1940 some paints were 50 % leaded (Samuel and Bennett 1983). Compounds of Cd may be emitted to the air from smelting, electroplating, manufacturing plastics, metal alloy production, welding metals, battery production, photoelectric-cell production, paint (pigments) manufacturing, etc. (Samuel and Bennett 1983; Hutton M. 1987). Arsenic may be released to the atmosphere by burning coal (major sources are coal-fueled power plants), from copper, zinc and lead smelters, and as a result of cotton gins, cloth, glass, pesticides and fungicide productions (Samuel and Bennett 1983; Chilvers and Peterson 1987; Buat-Menard 1987). Copper compounds may result from nonferrous metal mining, nonferrous metal production, iron and steel production, industrial applications, coal combustion, oil and gasoline combustion, wood treatment, waste incineration, and phosphate fertilizer manufacturing (Ayres et al. 2002). Additionally, Cd, Cu, & Zn compounds

together are usually derived from car tire abrasion, lubricants, incineration emissions, ferrous and nonferrous metallurgy (Bradl 2005; Meza-Figueroa 2006) and Cd, As & Sb compounds may derive from heat and power engineering and smelting processes (Korzhova et al. 2011).

Statistical analyses applied to the calculated EF elemental data set, facilitated the interpretation of the analytical data and the differentiation among possible heavy metal sources. The summary statistics showed the highest mean enrichment values for Pb, Cd, As, Sb, Cu and Zn (the second set of elements). At the same time, these values were higher in the attic dusts from Kern Place in Westside El Paso, suggesting that the main source of the indicated heavy metals/metalloids was located nearer to the Kern Place location. Such a source could potentially be the ASARCO plant as it was the most powerful and largest source of heavy metals (and other harmful materials) on the west side of El Paso for more than 100 years and it was located closely upwind of the Kern Place neighborhood.

Testing this hypothesis, it was important to analyze not only spatial, but also temporal variability (Environmental Forensic Trend Technique) of the EFs of the investigated elements, especially heavy metals. Examining the elemental EF data from two group/locations of El Paso by the MANCOVA tests, it was found that the EFs of only Pb, Cd, As, Cu, Se and Al present in dust showed simultaneous dependence on both the dust sampling location and the age of sampled dusts. Moreover, this tendency occurred only for the Kern Place group/location. In this group, the EFs of Pb, Cd, As, Cu and Se gradually increased over time of dust accumulation, with their much higher values relative to those of the Government Hill group, which changed very little over time. Such a pattern can be explained by the fact that the prevailing wind direction for the last 80 years promoted the spreading of pollution from the ASARCO facility mostly towards the North and Northeast (Novlan et al. 1997), affecting both areas, but to different degrees. The

Government Hill area in the central part of El Paso is not only more distant (8.45 km) from ASARCO than Kern Place (2.5 km), but it also is located across the Franklin Mountains, which could create a topographic obstacle for aerosol dispersion from both sides.

As pertains to the elemental EF distribution over time, one can observe in the table of calculated EFs (Table C7, Appendix C) that the EF values of Pb, As, Cd, Cu and Sb are much higher in the dust from older attic surfaces than from newer surfaces (recent editions, scuttle covers, new ducts, vent pipes, etc.) across all sampled locations. This pattern indicates heavy metal deposition while the plant was still in full operation, but which started decreasing after the precautionary measures were implemented and continued after the gradual decommissioning of the smelters.

However, as revealed by ANCOVA (Age by Group Interaction) test, carried out for two time periods, a radical change in heavy metal EF distribution appeared after 1966 (when ASARCO constructed the new 252.4 m smokestack) only in the Kern Place group/location. That such a pattern occurs strongly supports the hypothesis that the heavy metal/metalloids found in attic dusts were derived mainly from the ASARCO stack emissions.

On the other hand, the steadily decreasing heavy metal emission from the ASARCO plant coincided with the gradual phase-out of Pb from leaded gasoline (since 1973 until the end of 1995 in USA, and officially not until 1998 in Mexico). The particularly high enrichment of Pb and Cd might additionally be attributed to their compounds' emissions from the nearby highways, roads, and railroads. However, transport emissions could only be an additional, but not a dominant source of heavy metals, given the distinctive spectrum of emitted chemicals and due to almost equal distance from the roads (and therefore influences) at both sampling locations.

In addition to ASARCO, alternate sources of Zn and Sb were found to exist due to the dissimilarity of their EF dispersal patterns as compared to other heavy metals, especially in the Government Hill group/location. The large variability of Zn EFs values reflected its several anthropogenic and natural sources that overlap and affect the statistical analyses. Zn is spread uniformly everywhere from numerous industrial sources, especially from ferrous and nonferrous metallurgies and transport. Furthermore, it exists in soil as an essential plant nutrient and is applied to crops and agricultural plants by fertilizers. Zn is also common in minerals of the Rio Grande Rift lithology. Additionally, as in this research some dusts were sampled from a galvanized box surface (sample K3 galv.), near this box (sample K3 wood) and from a tube surface (sample K5 side) and pipe (sample L2 attic pipe), these samples had an extremely high Zn content with EFs of 3632, 966, 1792 and 1712 respectively. The atypical for heavy metals Zn “behavior” found in this study was also noted in other local studies by Barnes (1993) and Garcia (2004).

In contrast to Zn, the EF distribution of Sb in dusts from the Government Hill group/location appears only slightly different compared to other heavy metal EF fluctuation from this location (Figure 5.11, p.97), but has an EF distribution pattern similar to other heavy metals from the Kern Place group/location. This can be explained by the influence of some additional sources of Sb, such as heat and power engineering from the central and eastside of El Paso and possibly also by Fort Bliss and the International Airport (Korzhova et al. 2011). Such a pattern may also be related to partially gaseous Sb emissions as well as to an analytical outcome from ICP-MS. Imposition of all these factors can confound the results of statistical analysis of Sb as well as Se (and may be As) since both were also emitted from the ASARCO stack in a mainly

gaseous rather than a particle phase (Bradl 2005; Huang 2008) and was analyzed by the same analytical technique.

Even though Se EFs fluctuations follow the pattern of heavy metals with high enrichments, its EFs were very low in all dust samples. However, as a by-product of copper smelter emission, Se should be highly enriched in the local environment. In fact, Barnes found high Se enrichment in soil compared to subsoil levels (Barnes 1993). In Garcia's research, however, Se was below detection limit (Garcia et al. 2004).

The EF distribution pattern of the crustal indicator Al (similar to that of the heavy metals Group by Age interaction) can be explained by the relatively recent appearance (in the last 30 years) of new sources of Al in the central part of El Paso and east side, not far from the Government Hill area. Because the Al did not show any enrichment, it must be derived from the aluminosilicate particles of soil components as a result of dust storms or similar dust emission and distribution events.

With respect to the EF distribution of the other elements (Fe, Ba, Mn, Ti, Sr, V, K, Na and Mg), that did not show an interaction effect (simultaneous influence of location and time on dust accumulation) in the ANCOVA test; they did, however, show group effect (location influence). Because all of these elements are found below an anthropogenic level of enrichment, the investigation of their sources is outside the scope of this investigation.

Correlation and then Cluster and PCA exploratory analysis confirmed that the set of anthropogenic elements, i.e. Pb, Cd, As, Sb and Cu in attic dusts mainly originated from ore smelting processes rather than from other industrial emission sources. It is well known that during the smelting processes each smelter emits specific concomitants, co- and by- products of smelting metals (Smith1987; Pacyna 1987; Ketterer 2006; Tye 2006). Primary lead smelters

typically emit As, Cd, Sb, Zn, Bi, In and Te main concomitants (Eckel 2000; Drexler 2005); primary copper smelters emit As, Cd, Sb, Se, Ag, Bi, In, Te, S, Re, Ge and Tl concomitants (Ayres et al. 2002) and zinc smelters release Pb, As, Cd, Sb, Cu, Mo, Ag and S concomitants (Ketterer et al. 2001; Gulson et al. 2004; Ketterer 2006; John et al. 2007).

For our understanding of the atmospheric transport and the dispersal of ASARCO stack emissions it was sufficient to analyze only the Pb, As, Cd, Sb, Cu and Zn distribution, the “basic” elements for all smelting processes. The strongest connectivity among them (with  $0.76 < r < 0.96$  and  $p < 0.0001$ ), revealed by the Correlation analyses, suggests a common smelting process source from primary lead, copper or zinc smelters, either individually or combined. Interestingly, the correlation coefficients between the EFs of Pb, As, Cd, Sb and Cu were higher (see Results, section 5.3.3) in dust sampled from Kern Place than from the Government Hill location. This fact again proves that their anthropogenic source was located closer to the Kern Place area and it was another strong argument that the main source of found heavy metals was the ASARCO plant. Zn, possibly for reasons previously mentioned, was not correlated to other heavy metals. Blanchard and Stronberg (1987 in Garcia et al. 2004) do not attribute Zn to the smelter elements.

The typical source of Pb (before abatement), Cd, Sb, Zn, and Cu together with Co, Cr, Ni, Ba and Mn was common house paint (Korzhova et al 2011). There is some probability that house paint fragments may have been suspended in the air and settled also into attics (Ilaqua 2002). Nevertheless, low enrichments of Ba and Mn and the absence of their correlation with heavy metals in this research exclude such a source as important.

For some highly correlated elements such as Ti and Sr ( $r = 0.725$ ,  $p < 0.0001$ ), some less correlated elements such as Zn, Se and Na ( $0.57 < r < 0.62$ ,  $p < 0.0001$ ) and Ba, V, K and Al ( $0.52$

$< r < 0.684$ ,  $p < 0.0001$ ), there is no evidence for common sources. Sr and Ti are found together in strontium titanate, and artificial soft optical material, but again they have very low enrichments. Both elements are found in the local calcareous soils, and their correlation is likely from a common crustal source. Other elements are essential plant nutrients (K) and crustal indicators (Ba, Al and V) and there is no similarity in valence, common anion salts, etc. Zn and Na also share very little in common. The sources of correlated elements other than heavy metals were not considered because of their low enrichment.

Even though the correlation among elements ideally reflects common sources of provenance, the absence of correlation (but not association) among them does not completely exclude their commonality (Reinmann et al. 2002). We should take into consideration the mode of dust particles transport and their deposition into the attics as well as chemical properties and behavior during analytical examination (Ilaqua 2002).

In some studies, correlation analysis was sufficient to determine the source of the pollutants, especially if these came from smelting and mining activities (Ketterer 2006). Taking into account the deficiency of each statistical analysis, in this research Cluster and PCA analyses were additionally used to confirm the assumption of one smelting source for the found heavy metals.

Cluster analysis, resulted in a different classification of data than did correlation analysis, organizing all investigated elements into three main groups-clusters. The first cluster comprised all elements (Fe, Mn, Al, K, Sr, Mg, Na, Ba, V, Ti, Se, As) with low enrichments that are unlikely to be from the same source. Metalloid As was unexpectedly added to this cluster because of its relatively low enrichments as compared to heavy metals. Since As does not show any correlations with V and Ti, its concomitants from coal and oil combustion sources, these

sources were not significant and may be only minor sources of the whole amount of emitted As. Geogenic trace elements from this cluster (in Garcia's research they were grouped into four clusters) may be attributed to natural-rock weathering and chemical processes in the soil (Garcia et al. 2004; Balabanova 2011). Zn, for the above mentioned reasons, augments the Cluster 2 by itself, but may be also added to Cluster 3 that unified all heavy metals (Pb, Cd, Cu and Sb) emitted from smelters.

The PCA, using an alternative to the cluster analysis method for elemental grouping, extracted four factors from the investigated elemental EF set, which underlay its four potential sources. Factor 1, the most important, included all heavy metals (Pb, As, Cd, Cu, Se and Sb) associated with ASARCO emissions. Although the results of PCA in this study does not completely coincide with the cluster analysis, the "basic" heavy metals, i.e. Pb, Cd, Cu and Sb, in both analyses were grouped together, signifying their common (smelting emission) source. Factor 2 unified (the same as Cluster analysis) mostly naturally occurring geogenic trace elements (i.e. Fe, Ba, Al, K, Mg and V). Their sources, as well as the sources of elements from Factor 3 and 4, or lack thereof, have already been discussed. When describing the sources, we have to remember that our data was judged by statistical reasoning and our statistical analyses were performed with a limited number of chemical elements.

In general, dust samples from the Government Hill and Juarez areas have higher concentrations of Fe, Al, Ba and Ti (which are crustal indicators) than do those from the Kern Place. Therefore, the dust samples from Government Hill and Juarez have a greater contribution from surface soil than from anthropogenic particulates (including sulfates and fly ash), while the Kern Place dust samples have a greater contribution from anthropogenic particulates.

As a whole, the overall degree of heavy metal pollution (Environmental Forensic Quantity technique), was substantially higher in the west side of El Paso and anthropogenic sources of several trace elements were much larger contributors to the environment than in the other part of the city. There is no opinion regarding heavy metal dispersal patterns and their industrial sources in Juarez due to the insufficient amount of dust samples.

Summarizing the results of the application of Trace, Trend, Ratio (and to a lesser degree Quantity) Forensic techniques and statistical analyses, one can conclude that the major source of heavy metals found in attic dusts was the ASARCO plant. This conclusion coincides with popular documentation such as witnesses' reports, magazine and newspaper articles (Bernstein 2005; Valdes 2005; Berlin Snell 2006; Kolenc 2006; Ramirez 2006; Meritz 2007; Gomez Licon 2008).

Taking into account the background levels observed in the figures of all heavy metal EFs distribution from both locations one may assume that their additional emissions derived from several minor sources, most likely transportation, fire places, combustion of different fuels or from emissions of other local industries, which will require further research for their differentiation.

Other Environmental Forensic methods that could be additionally applied to ascertain these results were not applicable in our case. Particle size (and its distribution) analysis, commonly used for dust source identification, was not performed due to the limited amount of investigated dust in each attic dust sample. Dust particle microscopic investigation was also not very suitable for the goals of this research, since the particles may be transformed during thermal processes and our target elements all derived from smelting processes. The isotope analysis, a very powerful tool in speciation studies, was not explored because of uncertainty about a large variety

of mines and thus variable isotopic composition of ores that ASARCO used for smelting for over a century. Only access to the ASARCO archives will help to obtain records about all ores used throughout the time of the facility's operation. Nevertheless, even with limited information about ores, Drexler and Ketterer carried out isotope analysis of local soil and, combining it with other methods, came to the same conclusion that the ASARCO emission was the dominant source of Pb in most sampled locations (Drexler 2003; Ketterer 2006).

## **6.2 Comparison of Obtained Results with Previous Local Findings**

### **6.2.1 Similar Finding in Previous Local Studies**

Results of previous investigations conducted in the PdN region during last 40 years correspond to the findings of this research with respect to:

#### **1. Relation to distance from ASARCO**

Concentrations of metals, associated with the smelting process were highest in the area around the ASARCO plant and decreased with distance from the plant. Previous researchers mainly used soil as a medium of investigation (Miller 1972 in Dulin 2005; Rosenblum et al. 1975; Landrigan et al. 1975; Schatzman 1977 in Landrigan 1981; Ordonez undated in Barnes 1993; Landrigan and Baker 1981; TCEQ 1989; Barnes 1993; NDame 1993; Devahalli 1994; Drexler 2003; Garcia et al. 2004; Pingitore et al. 2005; Dulin 2005; Ketterer 2006), with a few exceptions (Landrigan et al. 1975, Pingitore et al. 2005; Dulin 2005; Del Toro 2010).

#### **2. Relation to time**

Anthropogenic metal content (Pb, As, Cd, Cu and Zn) in different media decreased with time and in particular after the facility was decommissioned. Measures of seasonal and spatial

fluctuation of heavy metals obtained from filter archives starting in 1977 (and then in 1980, 1987, 1994 and 2001), documented changes in heavy metal content throughout this time period in the Paso del Norte air shed, indicating also that the air quality in the northeast was better than in the west side of El Paso (Pingitore et al. 2005). Generally, the clear trend toward better air quality in the regional air shed was not only attributed to the phase-out of leaded gasoline, but especially to the gradual cessation of heavy metal emissions from the ASARCO facility.

### 3. Interrelation of the elements

According to soil studies (Barnes 1993; Drexler 2003; Garcia et al. 2004; Ketterer 2006), the highest correlations were found among trace elements associated with smelting processes. At the same time, the highest correlation coefficients were observed among these elements found in soil samples taken in close proximity to the ASARCO plant. Interestingly, statistically significant inter-element correlations were found not only between As, Cd, Pb, Sb and Cu, but also Zn. This may reflect a specific soil property, which is different from dust. Correlation analysis revealed the same two groups, “anthropogenic” and “naturally present in local soil and sediments” from ten analyzed elements (As, Cd, Pb, Cu, Zn, Se, Ba, Ca, Cr and Ni) in the Barnes study. Even though Barnes’ research approaches were different, the anthropogenic As, Cd, Cu, Pb and Zn were attributed to the smelting process.

### 4. Ratios

Investigating levels of pollution in soil, some studies use comparison of elemental concentration in the surface soil samples to their concentration in subsurface soil samples. Previous local studies indicated that surface soil samples generally have a higher concentration

of heavy metals in areas affected by pollution from ASARCO than do subsurface samples. In contrast, there were no significant differences between concentrations of heavy metals in the surface and subsurface samples in distant locations from ASARCO (Dydek 1990 in Srinivas 1994; Barnes 1993; Ndam 1993; Devahalli 1994; Srinivas 1994). Another type of ratio approach, calculation of enrichment factors of local soils relative to the composition of the Earth's crust, was used by Garcia separately for fine and coarse soil particles. High enrichments were found for trace elements (including As, Cd, Cu, Pb, Sb and Zn) derived from smelting processes for both types of particles and were higher for these elements in fine fractions at the site near UTEP (Garcia et al. 2004).

### **6.2.2 Contradictory Conclusions in the Previous Investigations**

Inconsistent conclusions about sources of elevated heavy metal levels found in the regional environment occurred in some local studies as a consequence of examining media (soil, SHD) that have limitations in terms of recording past air pollution events. For instance, when soil was investigated during the time of ASARCO operations, it more accurately mirrored the plant's emissions (Landrigan 1975; Barnes 1993; Ndam 1993). Frequent high wind events, dust storms, and sparse vegetation were and are conducive to further soil dispersion, redistribution and redeposition, thus entangling pollution source identifications (particularly heavy metal source apportioning).

Several early local studies conducted in the 1970s not only recognized that a potential for high heavy metal concentration existed, but also that ASARCO was allegedly the source of the elevated Pb, As, and Cd found in air, dust and soil throughout the Paso del Norte Valley (Landrigan 1975; Barnes 1993; Dulin 2005; Shapleigh 2008). The best confirmation of this

conclusion was the fact that the BLL of children at that time was related to the distance from ASARCO (Landrigan et al. 1975; Rozenblum et al. 1973 in Barnes 1993; Shapleigh 2008).

Conversely, some studies pointed to five equally responsible sources of the elevated heavy metal levels: Smeltertown, highways, the Standard Oil and Texaco refineries, Fort Bliss, and the El Paso International Airport (Miller 1972 in Barnes 1993; Garcia et al. 2003). Additional major sources of Pb were discussed including lead paint in older houses, water sources, emissions from automobiles before Pb was removed from fuels, the former Phelps Dodge refinery, and other nearby mining and smelting operations even though the emissions of Pb, Zn, Cd, As and Cu from ASARCO were not comparable quantitatively to the emissions from these minor sources (Shapleigh 2008).

A good example of conflicting evidence is represented in “Assessment of Environmental Pb, found in soil and indoor dust in communities of the city of Sunland Park, New Mexico” (Dulin 2005). At the time of this assessment soil sampled in Sunland Park’s residential properties, public sites and industrial locations, showed Pb levels below the threshold (500mg/kg). Neither did any of the indoor dust samples show elevated levels above the threshold (40  $\mu\text{g}/100\text{cm}^2$ ). Nonetheless, high Pb concentrations in soils were detected at sampling sites on Mount Cristo Rey in which half of the samples had Pb levels above the threshold. One possible explanation is that heavy metals, released by ASARCO during its operation, were deposited in soil and dust in the Mount Cristo Rey area and were somehow preserved by this natural barrier. In contrast, Sunland Park City’s soils and dusts do not show elevated levels of Pb because ASARCO had been inactive for several years at the time of sampling and were more exposed to wind which would have spread the heavy metal deposits beyond the area (Dulin 2005).

Contradictions in data interpretation occurred also in risk assessment studies, particularly those based on soil investigation of parks and public areas of the region (USACE 2001). Soil from these areas may have been affected not only by heavy metal smelter stack emissions, but additionally by fertilizers that were produced by the El Paso-based fertilizer company Ioanet (now out of business). This company used slag from the Oglebay Norton slag-crushing company in west El Paso. In its turn, Oglebay Norton received slag from ASARCO's by-products of smelting processes (Shapleigh 2008). This practice was not unique in El Paso and such a slag (otherwise referred to as a biosolid) was widely used all over the country especially before the 1970s (Stauber and Rampton 1995; Wong 2005). In fact, the differences in concentrations of As and Pb found in backyards and front yards of some residential properties in El Paso before the Removal Project in 2004 may also be explained by the use of these fertilizers. For this and for other reasons (mentioned in Chapter 3, section 3.1.3.1), soil in residential risk assessment can only be used as an auxiliary medium. Nevertheless, soil investigation is imperative because soils highly contaminated by heavy metals may pose a threat to human health indirectly, even though the polluted areas are not frequented by the general public. In this case soil redispersion and redistribution may play a role in delivering heavy metal over long distances (Laidlaw and Filippelli 2008).

Another important question is whether ASARCO, being the dominant source of heavy metals in the regional air shed, was also the significant source of  $PM_x$  (Garcia et al. 2004). Clearly, during the plant's operation, emissions of  $PM_x$ , which carried heavy metals, were the inevitable outcome of smelting processes (Ayres et al. 2002).

Considering all of the above, it is necessary to underline, that the ASARCO plant during its operations was not only a significant but the predominant source of heavy metal emissions into

the Paso del Norte air shed, especially on the west side of the Franklin Mountains. The total amount of toxic chemicals contributed to the environment from the ASARCO stack and from its waste and slag is still unknown.

It also should be noted that the process of accumulation of toxic materials in the local environment occurred not only before any environmental controls of atmospheric emissions were implemented at ASARCO (Srinivas 1994). After their implementation the heavy metals were continuously emitted into air but in lower amounts and deposited at greater distances (Drexler 2003; Ketterer 2006; Dulin 2005). Consequently, for over a century ASARCO operations heavily degraded the environment and potentially affected human health even though it was not always documented.

## **6.3 Heavy Metal Emission Impacts on the Local Ecosystem and Community Health**

### **6.3.1 Environmental Damage**

The biogeochemistry of semi-arid and arid ecosystems shows distinctive parameters of elemental turnover and dynamics in natural fluxes compared to other ecosystems. The desert ecosystem is one of the most intensive in the cycling of different chemical species; complete renewal of all ecosystem biomass takes place over a very short period (Bashkin 2008). The turnover rate of different elements is not uniform. For instance, some elements such as Mg, V, Cr, turning over much slowly than other elements such as Zn, Cu, and Sr (Bashkin 2008).

The combined effect of local geochemical conditions and human activity can alter this tendency significantly. The ecosystem in the Paso del Norte region does not exist in its original form. The destruction of natural vegetation, its replacement with crops and pasturing, the

overgrazing for long term period subsequently led to desertification. Any additional burdens to the local ecosystem, such as constant heavy metal pollution, may cause irreversible consequences for its balance and function (Clark 2002).

The local soil already is damaged by erosion, salinization and urbanization. High heavy metal levels in soil change its biogeochemistry, profoundly influence soil chemical, physical and biological processes and their interactions. Pollution of soil by heavy metal compounds may transform soil texture, disturb balance of pH, inhibit microbial enzyme activity, and reduce the diversity of populations of soil flora and fauna that consequently affect soil fertility (Lepp 1992; Förstner 1995; Picardal and Cooper 2005; Huang 2008; Smolder et al 2009).

Metals generally concentrate in the soil surface horizons (Bohn et al. 2005). The arid climate and near neutral acidity (6-8.5 pHs) of the local soil is more conducive to very low metal mobility (Ross 1994; Hering 1995). The increasing burden of heavy metal compounds influence the availability of pollutants to plants (Treshow and Anderson 1989; Jjemba 2005; Pichtel 2005) and may contaminate surface and ground water (Forstner 1995) causing ecological damage (Jjemba 2005).

“Trace elements as pollutants in the biosphere, in a particular ecosystem, all have pointed out the triangular relationships between contents of inorganic pollutants in air, soil and plants” (Introduction in Kabata-Pendias 2001). Regional studies, conducted while ASARCO was in operation, demonstrated heavy metal accumulations in some desert plants and invertebrates (Mackay 1998, 1999). Furthermore, even after ASARCO had been inactive for several years, desert soil, seeds and ant populations of Chihuahuan Desert near El Paso continued to show signs of heavy metal bioaccumulation. Concentrations of Cd, Pb, As and Cu were high in all these media and declined in soil and seeds with their distance from ASARCO (Del Toro et al. 2010).

The investigations of distribution and bioaccumulation patterns of heavy metals in multiple desert trophic levels are not completed. It is important to continue to examine the impact of heavy metal pollution on the desert ecosystem in order to better understand its toxicity effect.

### **6.3.2 Community Health Threat**

Contaminants released from ASARCO damaged the environment and potentially affected the health of residents, not only in Smeltertown, but also in surrounding communities. Several factors assisted in aggravating the impact of air pollution: the local topography (ASARCO is surrounded by mountains); annual duration of temperature inversion which influences the dispersion of heavy metals in the atmosphere (Žibret 2008); arid climate; frequent dust storms; a long windy season with high and low wind events; absence of moist surfaces; and limited contact with leaves and plant stems that could trap dust particles (Grineski et al. 2011). Also, the wind, which generally comes from the Southwest, additionally may affect the air quality of the region (Baddock et al. 2011).

Fine size dust particles emitted by a smelter stack have the highest heavy metal concentrations and the highest mobility due to prevailing winds (Davis and Gulson 2005; Hogervost et al. 2007); clearly, heavy metals (in dust or  $PM_x$ ) were constantly present in outdoor and indoor environments and accumulated on different house surfaces. Since American residents usually spend an average 90% of their time in indoor environments (Chapter 3, subsection 3.1.3.3), the nature of contaminated air may have been detrimental to the health and well-being of building occupants. Indoor air quality was never tested during ASARCO operations in other than the Smeltertown areas, even though the American National Standards Institute had implemented a standard for acceptable indoor air quality.

Residents were potentially exposed to heavy metals present in air, indoor dusts as well as in outdoor dust and soil. Additionally, they may have been exposed to the harmful materials in attic dusts during house renovation or remodeling (active exposure) or due to defective construction of houses (passive exposure). In case of consumption of vegetables growing in garden soil contaminated by heavy metals it was another vehicle of exposure (Forstner 1995; Hogervost et al. 2007). The effects of all these factors of exposure should have been evaluated by community-based cumulative risk assessment (CBRA), yet it was not conducted.

The total exposure during ten decades that residents of the west side of the Franklin Mountains in El Paso and some parts of Cd. Juarez underwent has not been determined precisely but cannot be underestimated. Nor can it be for the students, professors and staff from the University of Texas in El Paso located close (2.2 km) to ASARCO. However, abnormally high Pb levels in the blood of children and adults tested in different locations of the PdN region during the time of ASARCO operations and the fact that the BLL was related to the distance from the smelter (Landrigan et al. 1975; Rozenblum et al. 1973 in Barnes 1993) was the most obvious evidence of residential acute exposure to heavy metals released from ASARCO. Furthermore, a positive correlation was found between BLL and Pb concentration in soil and dust (contaminated by ASARCO emissions) as well as the Pb levels in household dust (ATSDR 2004.). Extremely high heavy metal enrichments found in attic dusts in this study show additional evidence that in the past residents were exposed to harmful materials emitted from ASARCO.

Local border communities face multiple stressors (including poverty and poor nutrition). In this region, one of dustiest places in North America (Rivera Rivera et al. 2009), the most detrimental natural factor for residential health is elevated levels of  $PM_x$  which induce allergies,

respiratory and cardiovascular diseases, and may even result in premature death (Parks et al. 2003; Scalzo 2006; Grineski 2011). Furthermore, ozone, the second of the two most widespread air pollutants after  $PM_x$ , was found to be present in the regional airshed. Clearly, constant heavy metal anthropogenic  $PM_x$  emissions created additional health risks for an already vulnerable population.

According to a holistic approach “the best measure we have for designing our future is human health. It is here that we feel the greatest urgency to solve problems of environmental pollution and it is here that the consequences of our actions are most dramatically demonstrated” (Samuel and Bennett 1983, p. 93). In the past, decisions made regarding air pollution in El Paso most often favored economics than potential impacts on human health and the environment (Schatzman in Shapleigh 2008). Only in 2010 despite all arguments ASARCO smelter was decommissioned permanently; undoubtedly it was the only reasonable decision from all points of view.

The smelters decommissioning definitely assures cleaner air not only in the El Paso-Juarez twin cities but in the whole region as well and greatly reduces the future potential residential and environmental health threats. Moreover, it also proved to be economically beneficial for the community. No longer is it necessary to regularly screen the BLL of children, provide large remediation activity or place El Paso on the EPA’s National Priority List with its economic repercussions. Yet, there are other benefits which cannot be estimated such as the improvement of the health of each individual (in the given population of over of 2.2 million in the twin cities alone) and the sparing of pollution related expenditures. Now residents only have to decide how to deal with the “remains” of ASARCO and its heritage as waste, and how to use its property most effectively for public use (Valodya A. 2010; Aguilera 2011).

Ever since scientific assessments began to elucidate the evidence of heavy metal contamination, public opinion has increasingly confirmed ASARCO to be the main source of pollution in the region (Valdes 2005; Berlin Snell 2006; Kolenc 2006). Still, in order to make local community play a more active and effective role in protecting the environment, it is essential to inform and educate the public to a greater degree and provide them access to all timely released complete scientific data (results). Scientists themselves must be more responsive to the community and participate in the public arena (Oppenheimer 2011). The improvement of data and knowledge exchange between science and society would raise the environmental conscience and help in critical decision making by the community on complex environmental issues that should supersede the customary economic priorities (Buck1991; Fisher 2000).

The sustainable development of our future requires environmental management that would be supervised by competent experts who would use a holistic approach and pay more attention to environmental ethics and environmental justice, especially important in border regions (Barrow 1999; Ericson and King 1999; Fisher 2000). It is also vital to bring up a new generation that will build a healthier relationship between humans and the environment, who can responsibly understand local and global environmental issues, and who will advocate to solve these problems that seriously impact our planet.

One of the main criteria for a sustainable future in the US is to maintain healthy air quality across the country. Mining & smelting industries are among the major sources of heavy metals in the atmosphere, as in the Paso del Norte region. Considering their adverse effects on the local ecosystem, the environment and community health, there is a need for more effective regulations and stricter standards regarding heavy metal emissions as well as industrial waste disposal.

## CHAPTER 7

### SUMMARY and CONCLUSIONS

#### 7.1 Significant Outcomes

This research confirmed that the accumulation of heavy metals in the Paso del Norte region occurred as a result of air pollution events related to anthropogenic activities. The results of this research provide a strong argument that the ASARCO plant was the primary source that affected the atmospheric deposition of toxic metals in the region, particularly in the areas in close proximity to and downwind from the facility. Scientific evidence of ASARCO pollution was acquired via the application of Environmental Forensic methods to attic dust as a medium of investigation.

Attic dust has been recognized as less variable and more sensitive to anthropogenic impact than soil (Žibret 2008). For historical records of past air pollution in the Paso del Norte region, attic dust was found to be a suitable and may be the optimal medium for heavy metal source identification, considering local climate and other environmental conditions. The approaches utilized for an assessment of analytically processed attic dust elemental data such as calculation of the EFs of elements and their Correlation, Cluster, PCA and MANCOVA statistical analyses proved to be valuable tools for the purpose of this research.

The EFs calculation illustrated six strongly enriched heavy metals/metalloids  $Pb_m$  (263),  $As_m$  (81),  $Cd_m$  (333),  $Sb_m$  (644),  $Cu_m$  (475) and  $Zn_m$  (376) suggesting their anthropogenic origin. The elemental EF statistical analyses proved the hypothesis that ASARCO was the main source of these elements' presence in the local environment given the irrefutable evidence. The MANCOVA tests examining the spatial and temporal fluctuations of elemental EFs show that the EFs only of the heavy metals/metalloids were much higher in areas in close proximity to

ASARCO and furthermore that the EFs of these elements dropped significantly dating from post 1966 (after ASARCO built its new 252.4 m smokestack in an effort to reduce local pollution). Correlation analysis revealed very high correlations ( $r > 0.92$ ,  $p < 0.0001$ ) among the same heavy metals/metalloids being highest in samples originated from closest to ASARCO sampling locations. This result was confirmed by Cluster and PCA analyses by uniting them in one cluster and factor signifying their common ore smelting source.

The finding of this research that the ASARCO facility has been a major source of heavy metal pollution in some parts of the Paso del Norte region for decades suggests that ASARCO emissions may have disrupted the natural cycling of elements in the surrounding environment and possibly over a much greater distance. By- and co-products of Pb, Cu, and Zn smelting processes were constantly emitted into the air, deposited and accumulated in different media that potentially interfered with and affected the natural biochemical cycling of trace elements and sulfur as well as their interactions. The consequences of several cycles' perturbations and impact on local ecosystems need to be determined in future research.

It has been proven that ASARCO polluted several and different environmental compartments. Local studies found heavy metal accumulations in the soil at numerous urban areas of the region. Plants, seeds and ant population of the Chihuahua Desert also demonstrate an increase of heavy metal content related to the distance from the smelter plant (Del Toro et al. 2010).

For more than a century the harmful materials were dispersed by air and redispersed by dust at immense distances and impacted the environment and human health locally and possibly in distant communities and ecosystems. Since this region already experiences severe problems

with air pollution and elevated levels of  $PM_x$  any additional burden or stress is crucial with respect to the health risks of the residents and ecosystems.

Apparently, the decision to demolish the historical plant of ASARCO was the one and only right solution for the local sustainable development and to benefit the next generations in the El Paso del Norte region.

## **7.2 Suggestions for Future Work**

The Paso del Norte is a unique and promising region for the investigation of past air pollution events and their impact on the local ecosystems. As semi-arid and arid ecosystems occupy a significant part of the globe, it will be important to explore on a local scale several processes that occurred as a result of diverse ecosystem stressors, particularly smelter activities over the ten decades. Evaluation of trace metal concentrations in different media in this combined desert and urban ecosystem will help to calculate the total flux released into the environment and to reconstruct the air pollution history during the 20th century in the region.

In order to obtain the whole picture of air pollution and to understand the role of ASARCO, it is necessary to examine a broader spectrum of trace elements, especially co and byproducts of the smelting process in attic dusts from additional areas in the region, particularly from Juarez. At the same time, it will be valuable to examine the usage of attic dusts for the estimation of residential exposure. It will also be important to inspect the level of heavy metals in technogenic media such as smelter waste and the environmental response to contamination in natural media including urban and wild trees and lake sediments that may provide the temporal records of past pollution events. Some specific questions can be answered such as accumulation of trace metals

depending on plant species, which elements are the most extensively absorbed, general trends towards the selective uptake of trace elements and so on.

If the Asarco archive will be disclosed and if the information about ores supplies can be acquired, the heavy metal isotope analysis of different media may not only permit researchers to accomplish a fuller picture of ASARCO pollution in the region, but also to better understand the trace elements' sources and differentiate them in the local environment. Developing other innovative forensic techniques for tracking metal contamination passage through the environment and for identifying the source of the contamination will help to distinguish clearly between the relative impacts of distant sources compared to local sources.

Accumulation of information about trace elements' dispersion in different media and on different scales will clarify the mechanism that rules the transportation of contaminants and help to create a database for mapping and modeling local trace element cycles, including dust cycles. The local experiences may be useful for creating conceptual models for other, active smelting sources, with analogous meteorological and ecological conditions.

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## APPENDIX A

### Attic Sketches and Sampling Descriptions

I took 3 dust samples from the attic shown in figure A1, specifically from beams 1, 2 and 3 on July 10, 2007.

On July 16, 2007 I took another 5 dust samples:

The first sample was taken from approximately  $10 \times 10 \text{ cm}^2$  of the surface of an air conditioner tube instead of missing beam 4.

The second sample was taken from beam 4, which had fallen from its original place and actually located as shown in the figure.

The third sample was taken from a  $100 \times 2 \text{ cm}^2$  surface of beam 5.

The fourth sample was taken from a  $100 \times 2 \text{ cm}^2$  surface of beam 6.

The fifth sample was taken from a  $100 \times 2 \text{ cm}^2$  surface of beam 7.

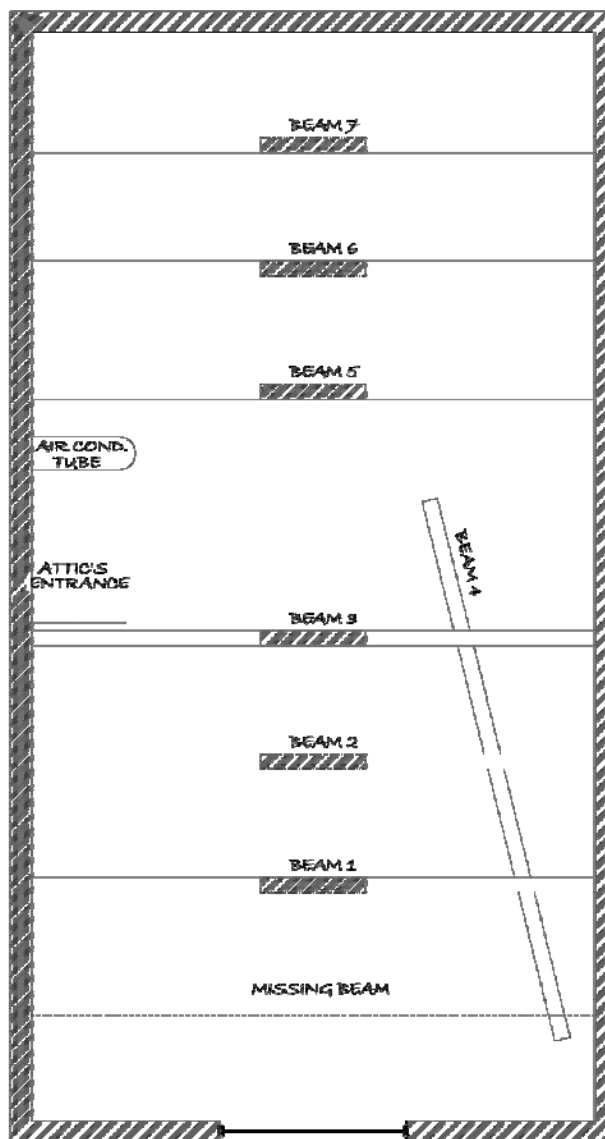


Figure A1: Sketch of Attic of House Kern- 5 (1930's).

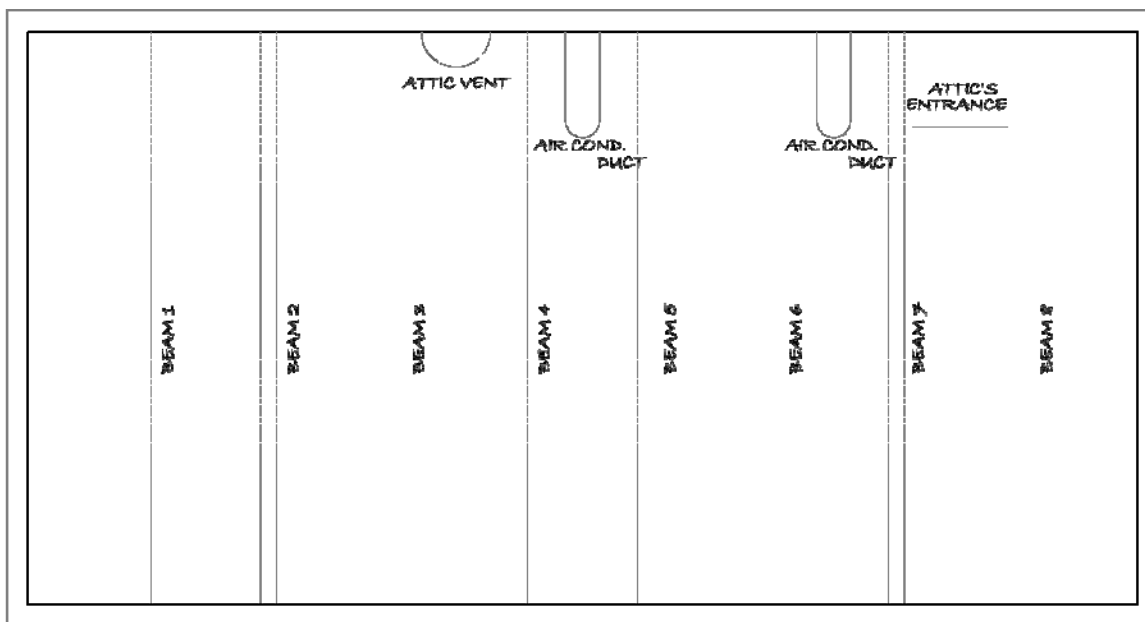


Figure A2: Sketch of an 'Old' Attic of House Kern- 6 (1939).

I took 11 dust samples on July 16 from an old attic (1939, Kern Place area):

The first sample from the right small beam on 0.5 m distance from the Western vents;

The second sample from the left side of beam 1;

The sample from the surface of beam 1 (appr. 240 cm, 1m distance from the W vents:

The fourth sample was taken from the complete surface of beam 2;

The fifth sample was taken from the complete surface of beam 3;

The sixth sample was taken from the complete surface of beam 4;

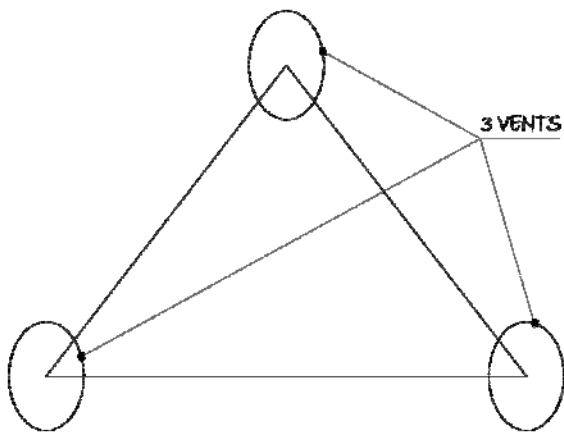
The seventh sample was taken from the complete surface of beam 5;

The eighth sample was taken from the complete surface of beam 6;

The ninth sample was taken from the complete surface of beam 7;

The tenth sample was taken from the complete surface of beam 8;

The eleventh sample was taken from the complete surface of the beam perpendicular to the other beams between two air conditioner ducts (not shown in picture).



Both attics, the “old” and the “new”, have one open vent (fan) on the roof, but the old attic has also three small vents on the east and west sides (of the attic).

Figure A3: section scheme of ‘new’ attic:  
house Kern – 6 (≈1950s-1960s).

On July 30 , 2007 I collected dusts from the floor beams (around the attic’s entrance) of a “new” attic (1950s –or 1970s) of the same house Kern K-6. From these dusts only 1 sample was composed.

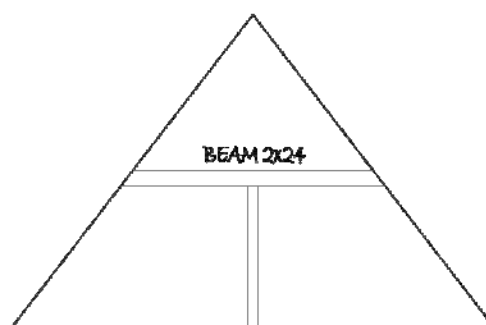


Figure A4: section scheme of ‘new’ attic: house Kern – 6 (≈1950s-1960s).

The attic of house K-7 (1916) has 4 vents (2 big and 2 small) in its western and eastern sides.

In 1997 the northern part of the attic was t remodeled.

I sampled only the southern part on July 31, 2007.

Six dust samples were taken:  
The first sample was taken from a section close to the west vent;

The second sample was taken from a section above east vent;

The third sample was taken from the beam between east and south vents;

The fourth was taken sample from the beam on the left side of east vent;

The fifth sample was taken from the surfaces of 3 electrical boxes (10 years old) in the middle of the attic; and

The sixth sample was taken from the surfaces of 2 round light boxes (approx. 3 years old).

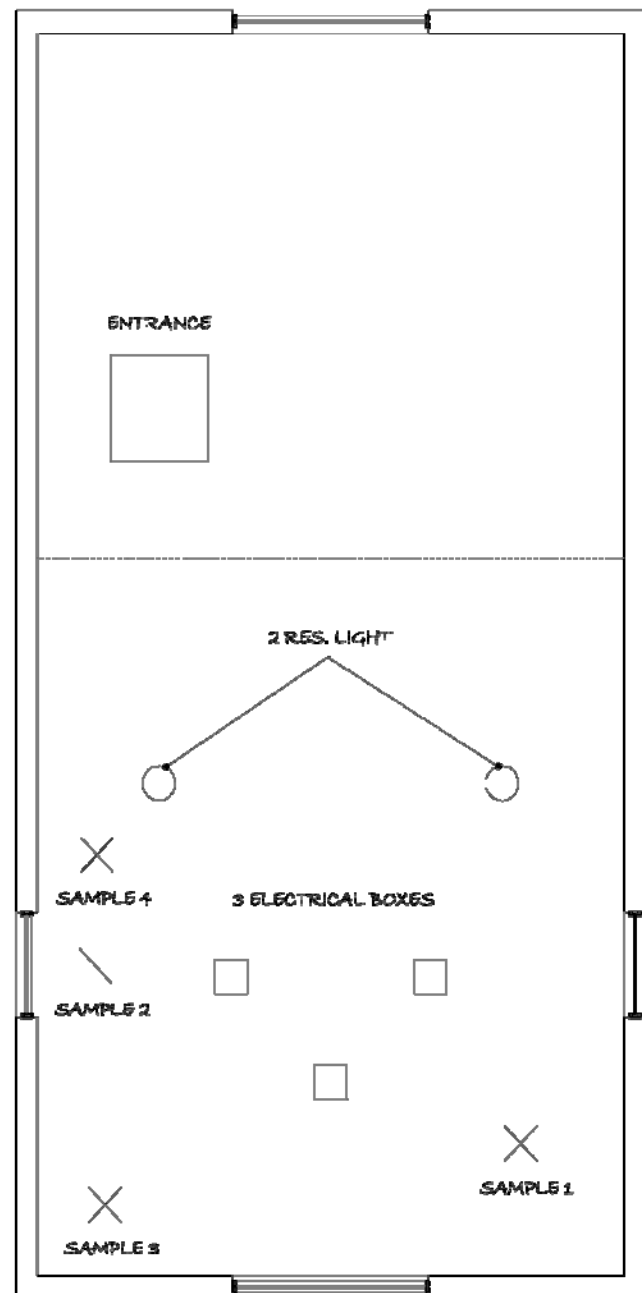


Figure A5: Sketch of attic: house Kern - 7 (1916).

The attic of house K-8 (1924, Kern Place area) has no fan, and air “naturally” enters the attic through the 2 wooden flats near the closed window.

I took six dust samples on July 30, 2007:

- Sample 1 from the big beam on the far left side of the attic;
- Sample 2 – from the same side of the attic but closer to the window;
- Sample 3 – from the beam very close to the left flat;
- Sample 4 – from the beam near right flat;
- Sample 5 – from the beam in the central part of the attic, very close to the window;
- Sample 6 – from the beam in the left corner of the attic.

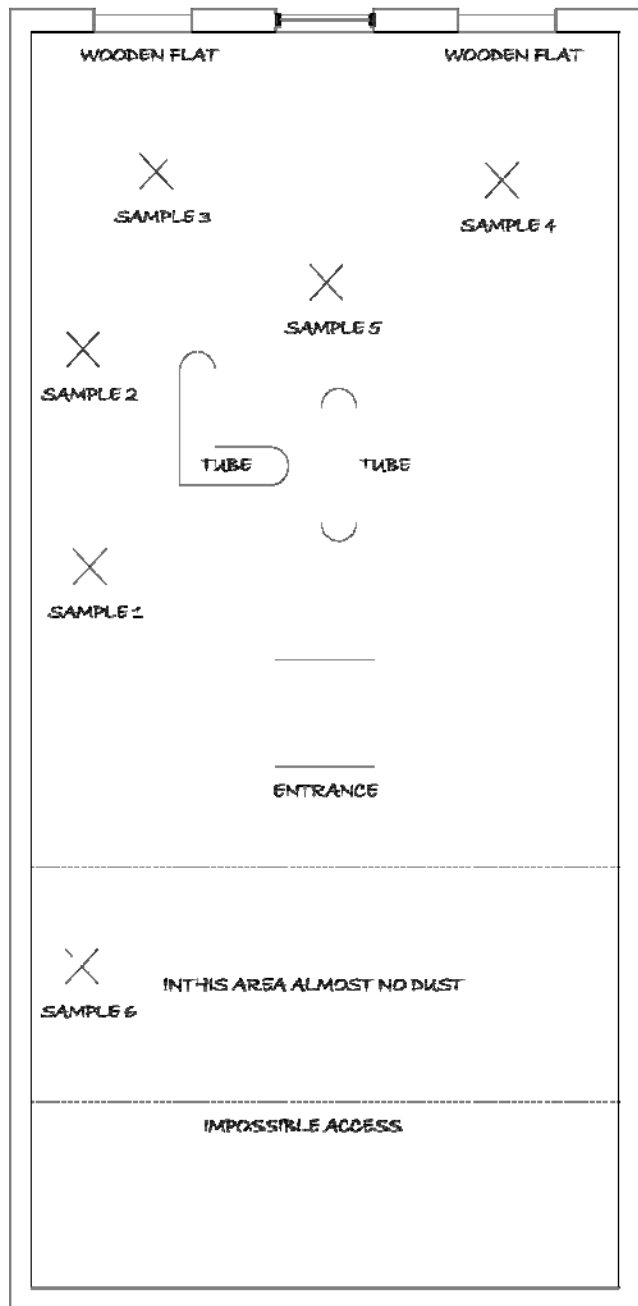


Figure A6: Sketch of attic: house Kern - 8 (1924).

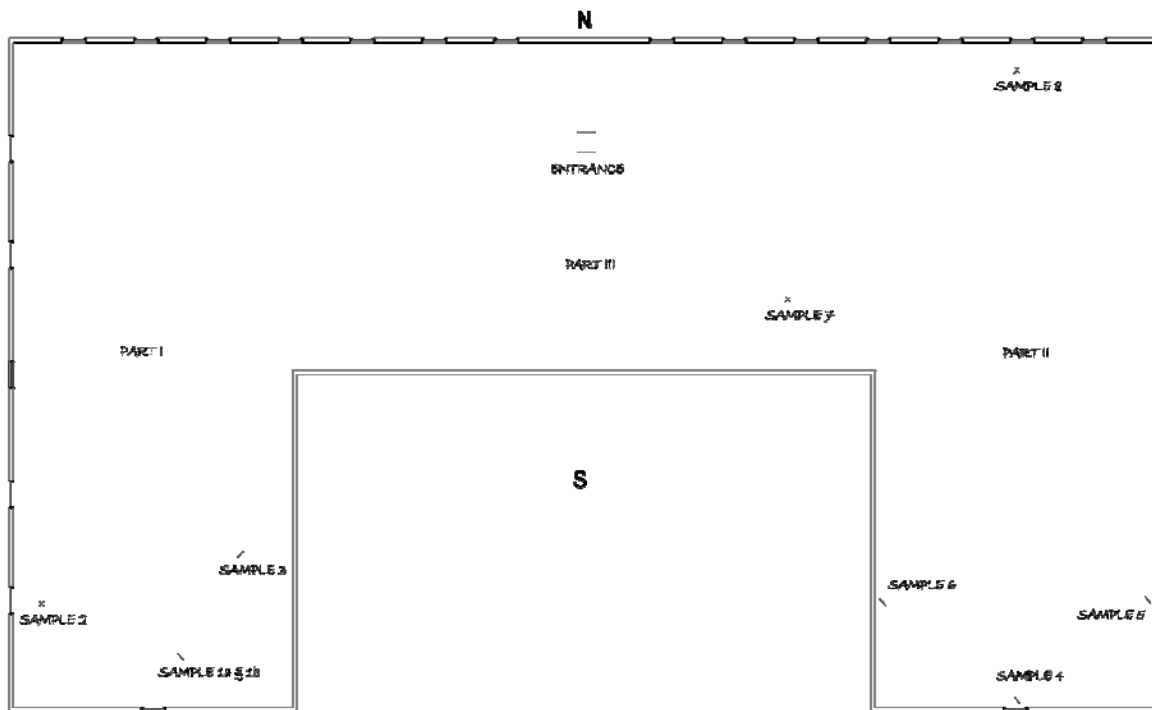


Figure A7: Sketch of the attic: building S (1927), Government Hill location.

The attic of this building was very big, but it was very difficult to find undisturbed areas. Because of the several open windows, protected only by flats, there was a lot of bird littering. The picture of a typical window from this attic is presented in Methodology (Figure 4.4).

On July 17, 2007 I took 3 dust samples (one was combined from samples a and b) from “part I” of the attic, 3 dust samples from “part II” and 2 dust samples from “part III”.

Part I. The first sample was combined from sample a, taken from the parallel blank board close to the window on the south side of the attic part I, and sample b, taken from the “inclined” board above the same window;

The second sample was taken above the first window on the southwest corner of the attic’s part I;

The third sample was collected from the section located on the opposite side to the sampling location of the second sample.

Part II. In this part of the attic the sampling procedure was repeated as above:

Sample 4 was taken from the “inclined” board above the window in the southern corner of part II;

Sample 5 was taken from the “inclined” board above the window in the south eastern corner of part II;

Sample 6 was taken from the beam across from the previous sampling area.

Part III.

Sample 7 was taken from the beam in the corner;

Sample 8 was taken from the board close to the window in the northeastern area of this Part.

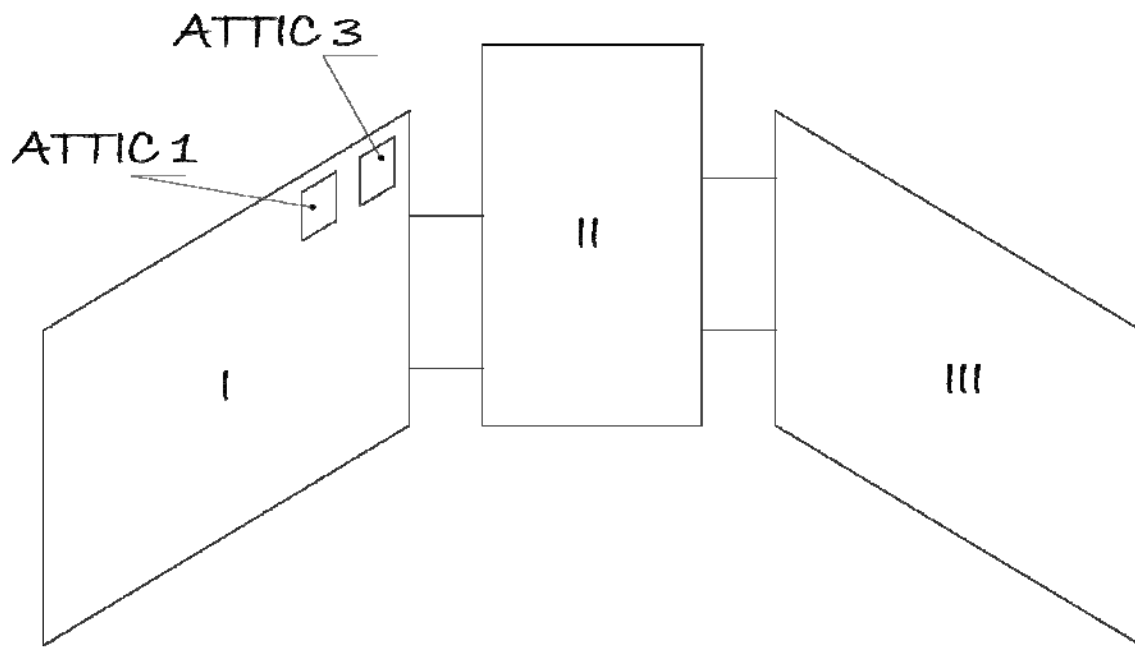


Figure A8: Sketch of building L (1927), Government Hill location.

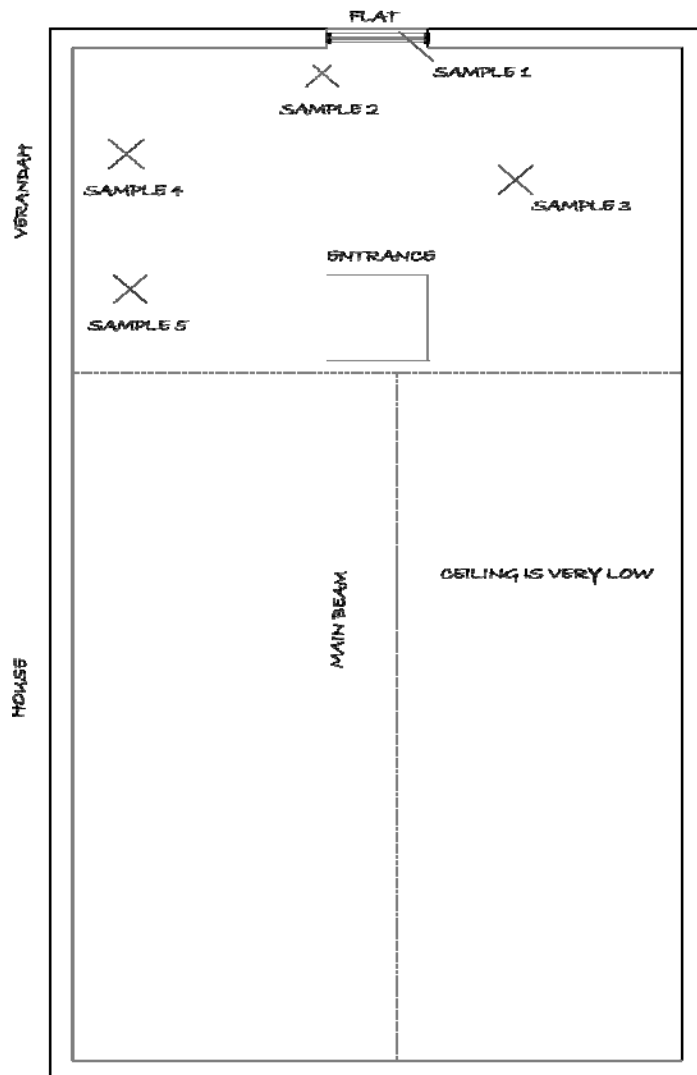
All attics from three parts of the building L were examined in order to sample an undisturbed dust. All of them have a similar structure. Some dust samples were already taken from the beams and floor of the attic 2 on July 2007. Additionally, I gathered 6 dust samples on August 2, 2007 from two neighboring relatively small attics 1 and 3 without windows. In these attics I sampled only surfaces from newer objects, which had been added year later : sheet metal pipe (1993), air conditioner tube (2000), door (1993), two plastic wardrobe liners (the late 1960s).

From attic 1 was taken 5 samples. The first sample was taken from liner 1; the second sample was taken from liner 2; the third sample was taken from the pipe's surface; the fourth sample was taken from the aluminium air conditioner tube, the fifth sample was taken from the wooden beam. Only one sample (sample 6) was taken from the Attic 3 from the door surface.

This attic consisted of two parts: 1. Above the house and 2. Above the “verandah”.

Air comes to the attic through the single flat.

I sampled only part above the verandah because the part above the house was not accessible and had a very little dust amount.



I collected 5 dust samples on  
September 1, 2007 :

The first sample – above the flat;

The second sample – below the flat;

The third sample – from the “basis”  
of the big beam;

The fourth sample – from the floor  
beam;

The fifth sample - from the beam  
located on the left side of the attic.

Figure A9: Sketch of attic : house S-1 (1918),  
Government Hill location.

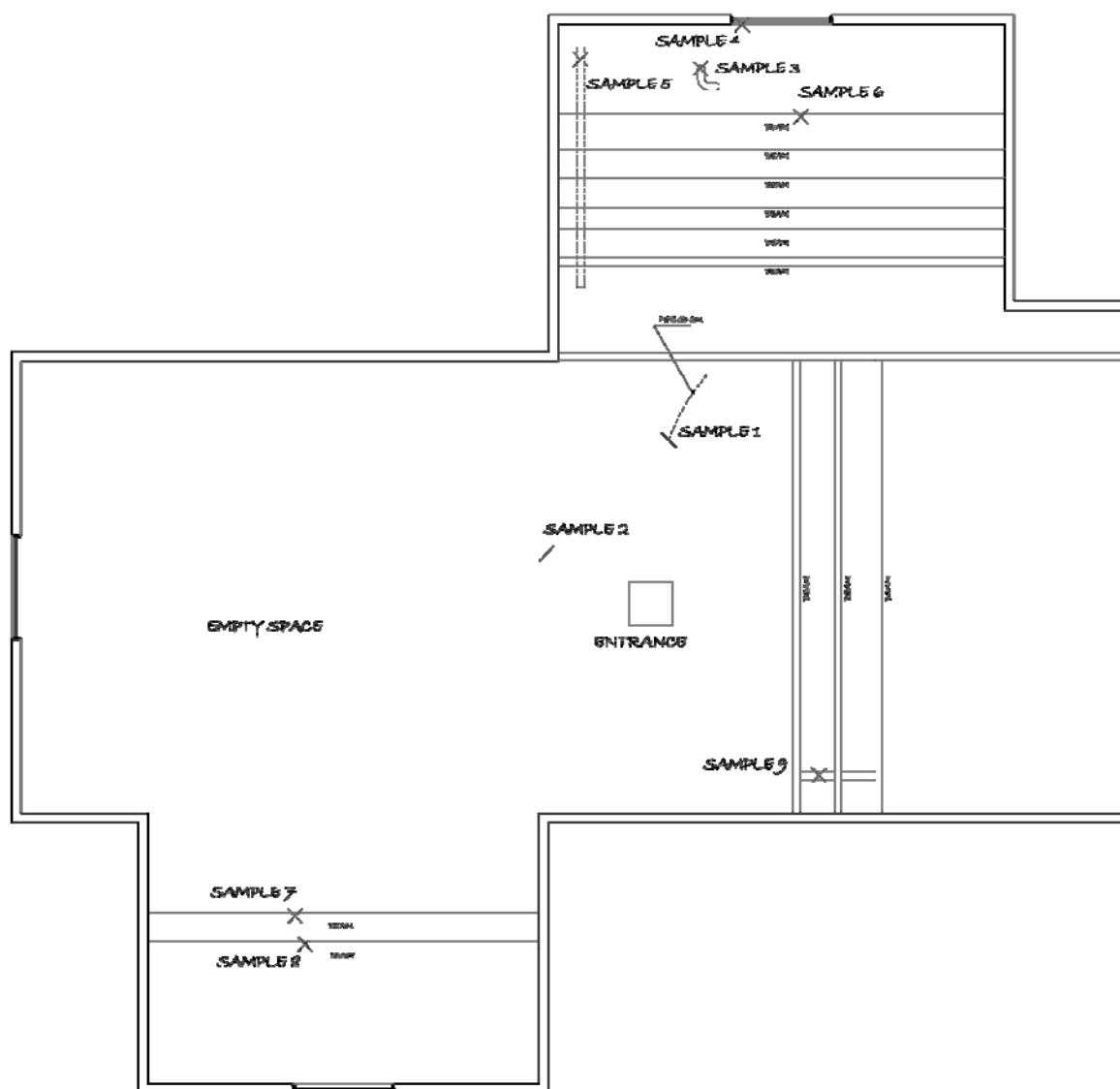


Figure A10: Sketch of attic, house MS-1 (1935), Government Hill location.

This attic has 4 flats (“windows”). The southern window was completely closed by mud. The window on the northern part of the attic was even without net and completely open. The biggest and less disturbed part of this attic was the northern.

I took 9 dust samples on September 11, 2007 (see Figure A10):

The first sample was taken near the entrance of the attic from a small round electrical box.

Because there was not enough dust, I also took dust from the 50 cm joined pipe surface;

The second sample was taken close to the first electrical box from the surface of the biggest electrical box;

The third dust sample was taken from near the northern window from the surface of a leaded brass tube;

The fourth sample was taken from the small board near the northern window;

The fifth sample was taken from the cross beam on the right side of northern window;

The sixth sample was taken from 'first beam in the central part of the attic;

The seventh sample was taken near the southern window from the entire surface of the beam (174x2 cm);

The eighth sample was taken at the same area from the next beam;

The ninth sample was taken near the eastern window from the surfaces of two cross beams due to a small amount of dust.

## **APPENDIX B**

### **Individual Sample Weights and Specification of Sample Combination**

In the Tables B 1a and B 1b, presented on the pages 13-14, the sample weights and combination sheet should be interpreted as follow:

Raw dust (col .1) is the dust was removed from the attic that often contained roofing materials, gravel, etc.;

Container (col.2) is the tare weight of the container that was under the nylon sieve;

Sieved + c (col.3) is the total weight of the sieved dust and container;

Sieved dust (col.4) is the net total weight of dust in the container.

In the Table B2 the weights are the actual sample weights that were extracted from preliminary combined 51 samples and sent to Texas Tech University GeoAnalytical Lab in Lubbock, TX for further analytical analyses.

Table B1a: Individual Dust Sample Weights.

Sample label	Raw dust (g)	container (g)	sieved + c (g)	sieved dust (g)
K1 a	5.3026	14.3838	15.1935	0.8097
K1 b	0.3384	14.6594	14.7808	0.1214
K1 c	5.1196	14.3985	14.9706	0.5721
K1 A (new)	7.0262	14.3823	14.5636	0.1813
K1 B (new)	0.4348	14.3655	14.4296	0.0641
K2 A	2.4813	14.6066	16.2338	1.6272
K2 B	0.2253	14.5350	14.7033	0.1683
K2 C	0.8077	14.4012	14.9542	0.5530
K2 D	11.3414	14.5404	14.8367	0.2963
K2 E	1.9365	14.6173	15.7599	1.1426
K2 F	0.5981	14.5955	15.0631	0.4676
K3 A	1.0612	14.3888	14.8414	0.4526
K3 B	0.5226	14.3753	14.5517	0.1764
K3 C	3.1935	14.6868	16.7606	2.0738
K3 D (10 yrs)	1.6565	14.4260	15.9300	1.5040
K4 AC Duct	1.0232	14.4213	14.8618	0.4405
K4 A (1986 pipe)	0.5556	14.4811	14.9489	0.4678
K4 B (back beam, far vent)	0.6580	14.3901	14.9421	0.5520
K4 (back beam)	0.4079	14.3684	14.6797	0.3113
K4 vent 1	5.3585	14.5260	18.1258	3.5998
K4 vent 2	5.2903	14.5282	18.2753	3.7471
K4 vent 3	5.2534	14.5733	19.2924	4.7191
K4 vent 4	1.0311	14.4142	15.3218	0.9076
K4 vent 5	2.3771	14.4111	16.0977	1.6866
K4 vent 6	1.4977	14.6225	15.7127	1.0902
K5 vent 1 (93 cm +122)	18.7339	14.4110	26.1492	11.7382
K5 vent 2	15.2414	14.4425	26.8786	12.4361
K5 vent 3	8.1278	14.4391	20.5107	6.0716
K5 vent 4 (tube, 10 cm)	0.2932	14.4938	14.7091	0.2153
K5 vent 4A (left)	0.0594	14.5320	14.8614	0.3294
K5 vent 5	1.2526	14.6156	15.5366	0.9210
K5 vent 6	2.9464	14.6096	15.1518	0.5422
K5 vent 7	3.0098	14.4240	15.3144	0.8904
K6 not R beam	0.2555	14.4412	14.5525	0.1113
K6 new attic (1950)	0.5445	14.6105	15.0139	0.4034
K6 M1	0.4479	14.3936	14.7803	0.3867
K6 M2 (123 cm)	0.2614	14.3831	14.5809	0.1978
K6 1(right)	0.3245	14.4440	14.6638	0.2198
K6 7 (between tubes)	0.0145	14.4322	14.4385	0.0063
K6 3 (Δ)	0.0907	14.4820	14.5390	0.0570
K6 4 (Δ) vent	0.0575	14.5890	14.6188	0.0298
K6 5 (Δ) gold	0.0423	14.3888	14.4070	0.0182
K6 6 (Δ) tube	0.0912	14.6162	14.6715	0.0553
K6 7 (Δ) vent	0.0316	14.6026	14.6250	0.0224
K6 8 (Δ)	0.0434	14.4793	14.5011	0.0218
K7 1	6.0032	14.4596	19.0398	4.5802
K7 west beam (1916)	3.7797	14.6022	17.8887	3.2865
K7 beam 2(se)	1.6086	14.3946	15.6380	1.2434
K7 3 east beam	4.1909	14.5616	18.1866	3.6250

Table B1 b: Individual Dust Sample Weights (Cont).

Sample label	Raw dust (g)	container (g)	sieved + c (g)	sieved dust (g)
k7 3 wool	0.2309	14.4758	14.6590	0.1832
K7 res. light 3yrs	0.1094	14.4602	14.5223	0.0621
K8 left corner	1.7789	14.3918	15.6164	1.2246
K8 center right window	10.8962	14.5771	24.5175	9.9404
K8 window 5	4.9420	14.5216	19.1614	4.6398
K8 center left window 2	9.9019	14.4172	23.2567	8.8395
K8 center left 2	2.7758	14.4740	17.0726	2.5986
K8 far left 1 (6)	2.2610	14.5458	16.5507	2.0049
L1 A (pipe)	2.0631	14.3954	16.1486	1.7532
L1 B (beam)	2.9606	14.4003	16.9078	2.5075
L1 C	2.6494	14.3936	16.6600	2.2664
L1 E (key top)	1.6913	14.3920	15.3152	0.9232
L1 E (kneeler)	4.3326	14.5487	18.2595	3.7108
L1 duct	4.4395	14.6869	18.4546	3.7677
L2 attic (cloth bag 1)	0.8318	14.4868	15.1800	0.6932
L2 attic (cloth bag 2)	1.2264	14.3946	15.3267	0.9321
L2 attic 2 (beam)	1.9079	14.4431	16.0318	1.5887
L2 attic 2 (pipe)	2.6581	14.4362	16.7187	2.2825
L2 attic 2 (air conditioner)	0.6632	14.4420	15.0251	0.5831
L3 attic door 1 (1993)	0.1512	14.5921	14.7030	0.1109
S1 window "1A"	0.7560	14.4964	15.1863	0.6899
S1 window 1A	1.1075	14.4417	15.4260	0.9843
S1 window 2A	0.7625	14.4934	15.1344	0.6410
S1 window 2-3	3.0872	14.4809	17.2064	2.7255
S2 window 1	3.6204	14.4682	17.7467	3.2785
S2 window 2	2.4000	14.4073	16.4505	2.0432
S2 3 (across window)	5.0281	14.5550	18.7567	4.2017
S3 (corner)	5.7130	14.4220	19.2403	4.8183
S3 (w.side)	2.0353	14.5169	16.3287	1.8118
J V1 (toilet)	1.0762	14.4749	15.3483	0.8734
J V2 (FE closet)	0.8750	14.5253	15.0112	0.4859
J V3 (soots)	4.3088	14.5221	18.5074	3.9853
J V4 (cupola @ front)	3.3354	14.4558	17.3444	2.8886
J V5 (electric box)	4.0158	14.4591	16.6075	2.1484
J V6 (glass bulb)	0.8396	14.6170	15.3690	0.7520
LH N1	0.4278	14.4431	14.7771	0.3340
LH N2	2.5764	14.6164	16.7610	2.1446
LH N3	0.6947	14.4518	15.0595	0.6077
LH N4 (floor beam)	0.2462	14.4592	14.6462	0.1870
LH N5 (beam left)	1.4285	14.5957	15.9189	1.3232
LS N1 (electric)	0.2374	14.5331	14.7265	0.1934
LS N2	1.5917	14.5476	15.7642	1.2166
LS N3 (yokha)	1.1803	14.5070	15.5022	0.9952
LS N4 (beam)	0.4399	14.4913	14.8614	0.3701
LS N5 (window)	2.3805	14.5848	16.5848	2.0000
LS N6 (window 1)	0.3510	14.3997	14.6833	0.2836
LS N7 (window 2)	1.0248	14.4053	15.3062	0.9009
LS N8 (window 2)	0.1911	14.4029	14.5443	0.1414
LS N9 (window 3)	0.0534	14.5862	14.6138	0.0276

Table B2: The actual sample weights of 51 combined samples and specification of sample combination.

Number	Sample	Weight	Consists of:
BS-1	K1 new	0.1218	K1a+K1b+K1c
BS-2	K1 old	0.2187	K1A(new)+K1B(new)
BS-3	K2 new roof	0.165	K2A+K2B
BS-4	K2 old attic	0.1571	K2C+K2D+K2E+K2F
BS-5	K3 wood	0.1702	K3A+K3B
BS-6	K3 galv	0.1048	K3C
BS-7	K3 scuttle	0.099	K3D (10yrs)
BS-8	K4 post 89	0.1218	K4 AC Duct+K4A (1986 pipe)
BS-9	K4 back beam	0.1265	K4B (back beam, far vent)+K4B (backbeam)
BS-10	K4 transect	0.1293	K4 vent 1 -- K4 vent 6
BS-11	K5 near vent	0.1413	K5 vent1+K5 vent2+K5 vent3
BS-12	K5 side	0.0907	K5 vent4 (tube,10sm)+K5 vent 4A (left)
BS-13	K5 far vent	0.1275	K5 vent 5+K5 vent6+K5 vent7
BS-14	K6 R beam	0.122	K6 not R beam + K61 (right)
BS-15	K6 new attic	0.1027	K6 new attic (1950)
BS-16	K6 M1&2	0.0841	K6M1+K6M2
BS-17	K6 4-8	0.0981	All other K6 (K6 7 + K6 3 - 8)
BS-18	K7 1	0.149	K7 1
BS-19	K7 west beam	0.1226	K7 west beam (1916)
BS-20	K7 Beam 2	0.1924	K7 beam 2 (se)
BS-21	K7 east beam	0.1047	K7 3 east beam
BS-22	K7 3 wool	0.1508	K7 3 wool
BS-23	K7 Res. Light	0.0366	K7 Res Light (3 yrs)
BS-24	K8 left corner	0.167	K8 left corner (1)
BS-25	K8 center right window	0.1206	K8 center right window (4)
BS-26	K8 windows & center left	0.1011	K8 window (5) + K8 center left window (3)
BS-27	K8 center left 2	0.1098	K8 center left (2)
BS-28	K8 far left 1	0.0988	K8 far left 1 (6)
BS-29	L1 a+b+c	0.1218	L1A (pipe)+L1B (beam)+L1C
BS-30	L1 E keytop	0.163	L1E (keytop)
BS-31	L1 E Kneeler	0.1661	L1E (kneeler)
BS-32	L2 attic bag	0.1178	L2 attic (cloth bag 1) + L2 attic (cloth bag 2)
BS-33	L2 Beam	0.1014	L2 attic 2 (beam)
BS-34	L2 attic pipe	0.1365	L2 Attic 2 (pipe)
BS-35	L2 attic airconditioner	0.1198	L2 attic 2 (air conditioner)
BS-36	L3 attic door	0.0997	L3 attic door (1993)
BS-37	S1 window	0.2369	window "1A" + window 1A+window 2A + S1 window 2-3
BS-38	S2 window	0.1686	S2 window 1 + S2 window 2 + S2 3 (across window)
BS-39	S3 corner & side	0.2744	S3 (corner) + S3 (w. side)
BS-40	J V1 + V2 closet and toilet	0.2125	J V1 (toilet seat) + J V2 (FE closet)
BS-41	J V3 soots	0.1127	J V3 (seats)
BS-42	J V4 + V5	0.1313	J V4 (cupola @ front) + J V5 (electric box)
BS-43	J V6 glass bulb	0.1092	J V6 glass light bulb
BS-44	LH N1	0.1037	LH N1
BS-45	LH N2	0.1193	LH N2
BS-46	LH N3	0.1048	LH N3
BS-47	LH beam N4+N5	0.1926	LH N4 (floor beam) + LH N5 (beam left)
BS-48	LH N1 + N2	0.1875	LS N1 (electric) + LS N2
BS-49	LS N3 + N4	0.1828	LS N3 (yokha) + LS N4 (beam)
BS-50	LS N5 +6 window	0.1043	LS N5 (window + LS N6 (window 1)
BS-51	LS N7-9 window	0.1551	LS N7 (window 2)+ LS N8 (window2)+ LS N9(window3)

## APPENDIX C

### Results of ICP-AES and ICP-MS Analyses and Table of Enrichment Factors

Table C1a: Check Standard Data for ICP- AES Analytical Runs.

Aqueous and <b>Acid</b> analytical runs for low concentrations													
<i>Check Standard</i>	<i>Fe ppm</i>	<i>Mn ppm</i>	<i>Ba ppm</i>	<i>Zn ppm</i>	<i>Pb ppm</i>	<i>As ppm</i>	<i>As ppm</i>	<i>Cd ppm</i>	<i>Cu ppm</i>	<i>Al ppm</i>	<i>Ti ppm</i>	<i>Se ppm</i>	<i>Sr ppm</i>
<i>Ck1 blank</i>	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.00
<i>Ck1 blank</i>	0.01	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00
<i>Ck1 blank</i>	0.02	0.00	0.00	0.00	0.02	0.05	0.02	0.01	0.00	0.00	0.01	0.02	0.01
<i>Ck1 blank</i>	0.02	0.00	0.00	0.00	0.00	0.05	0.01	0.00	0.00	0.00	0.01	0.01	0.00
<i>Ck1 blank</i>	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01
<i>Ck1 blank</i>	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.00	0.02	0.01
<i>Ck1 blank</i>	0.00	0.00	0.00	0.01	0.01	0.02	0.00	0.00	0.00	0.01	0.00	0.01	0.01
<i>Ck2 0.01 ppm</i>	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01
<i>Ck2 0.01 ppm</i>	0.02	0.01	0.02	0.02	0.02	0.05	0.03	0.02	0.01	0.01	0.02	0.03	0.02
<i>Ck2 0.01 ppm</i>	0.02	0.01	0.01	0.01	0.02	0.03	0.03	0.02	0.01	0.01	0.02	0.02	0.02
<i>Ck2 0.01 ppm</i>	0.03	0.01	0.01	0.01	0.03	0.06	0.02	0.02	0.01	0.03	0.02	0.03	0.02
<i>Ck2 0.01 ppm</i>	0.02	0.01	0.01	0.01	0.02	0.05	0.02	0.02	0.01	0.01	0.02	0.02	0.02
<i>Ck2 0.01 ppm</i>	0.01	0.01	0.01	0.02	0.02	0.02	0.01	0.02	0.01	0.02	0.01	0.02	0.02
<i>Ck2 0.01 ppm</i>	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.02	0.01	0.02	0.02
<i>Ck2 0.01 ppm</i>	0.02	0.01	0.01	0.02	0.02	0.02	0.01	0.02	0.01	0.01	0.01	0.03	0.02
<i>Ck2 0.01 ppm</i>	0.02	0.01	0.01	0.02	0.02	0.04	0.01	0.02	0.01	0.03	0.01	0.03	0.02
<i>Ck3 0.05 ppm</i>	0.05	0.05	0.05	0.06	0.06	0.05	0.05	0.06	0.05	0.06	0.05	0.05	0.05
<i>Ck3 0.05 ppm</i>	0.08	0.07	0.06	0.08	0.08	0.15	0.10	0.08	0.06	0.07	0.07	0.09	0.06
<i>Ck3 0.05 ppm</i>	0.06	0.06	0.06	0.07	0.07	0.12	0.06	0.07	0.06	0.05	0.06	0.07	0.06
<i>Ck3 0.05 ppm</i>	0.06	0.06	0.06	0.06	0.07	0.08	0.05	0.06	0.06	0.07	0.06	0.04	0.06
<i>Ck3 0.05 ppm</i>	0.07	0.06	0.06	0.07	0.07	0.10	0.07	0.07	0.06	0.06	0.07	0.09	0.06
<i>Ck3 0.05 ppm</i>	0.08	0.08	0.07	0.09	0.10	0.14	0.11	0.09	0.07	0.08	0.08	0.13	0.07
<i>Ck3 0.05 ppm</i>	0.07	0.07	0.06	0.07	0.08	0.12	0.08	0.08	0.06	0.08	0.07	0.07	0.06
<i>Ck3 0.05 ppm</i>	0.08	0.07	0.07	0.08	0.09	0.14	0.11	0.09	0.07	0.10	0.08	0.09	0.07
<i>Ck3 0.05 ppm</i>	0.07	0.07	0.06	0.07	0.07	0.13	0.08	0.07	0.06	0.05	0.07	0.09	0.06
<i>Ck3 0.05 ppm</i>	0.05	0.05	0.05	0.06	0.06	0.07	0.07	0.06	0.06	0.06	0.05	0.06	0.06
<i>Ck3 0.05 ppm</i>	0.10	0.06	0.06	0.12	0.08	0.07	0.08	0.06	0.06	0.08	0.06	0.09	0.06
<i>Ck3 0.05 ppm</i>	0.05	0.05	0.05	0.06	0.06	0.06	0.04	0.05	0.05	0.06	0.05	0.05	0.05
<i>Ck3 0.05 ppm</i>	0.05	0.05	0.05	0.06	0.05	0.05	0.03	0.05	0.05	0.04	0.05	0.05	0.05
<i>Ck3 0.05 ppm</i>	0.06	0.05	0.05	0.07	0.06	0.08	0.08	0.06	0.05	0.06	0.06	0.07	0.06
<i>Ck3 0.05 ppm</i>	0.08	0.06	0.06	0.08	0.06	0.07	0.09	0.07	0.06	0.06	0.06	0.09	0.06
<i>Ck3 0.05 ppm</i>	0.07	0.05	0.06	0.07	0.07	0.08	0.08	0.06	0.05	0.07	0.06	0.08	0.06
<i>Ck4 0.1 ppm</i>	0.12	0.12	0.11	0.10	0.12	0.10	0.10	0.10	0.11	0.13	0.12	0.11	0.11
<i>Ck4 0.1 ppm</i>	0.14	0.13	0.12	0.14	0.14	0.17	0.15	0.15	0.12	0.11	0.13	0.14	0.12
<i>Ck4 0.1 ppm</i>	0.14	0.14	0.13	0.15	0.15	0.21	0.18	0.16	0.13	0.12	0.14	0.14	0.13
<i>Ck4 0.1 ppm</i>	0.15	0.14	0.13	0.15	0.17	0.21	0.19	0.16	0.13	0.14	0.14	0.15	0.13
<i>Ck4 0.1 ppm</i>	0.14	0.14	0.13	0.15	0.15	0.21	0.18	0.15	0.13	0.12	0.14	0.17	0.13
<i>Ck4 0.1 ppm</i>	0.10	0.10	0.11	0.10	0.10	0.12	0.11	0.10	0.10	0.10	0.10	0.10	0.11
<i>Ck4 0.1 ppm</i>	0.11	0.10	0.10	0.12	0.11	0.11	0.12	0.11	0.10	0.12	0.10	0.11	0.10
<i>Ck4 0.1 ppm</i>	0.14	0.12	0.11	0.14	0.12	0.15	0.16	0.12	0.12	0.13	0.12	0.14	0.11
<i>Ck4 0.1 ppm</i>	0.13	0.12	0.12	0.13	0.12	0.13	0.16	0.12	0.12	0.13	0.12	0.15	0.11

*Note: the check standards for the acid digested samples are in red*

Table C1 b: Check Standard Data for ICP- AES Analytical Runs (Cont.).

Aqueous and Acid analytical runs for low concentrations													
Check Standard	Fe ppm	Mn ppm	Ba ppm	Zn ppm	Pb ppm	As ppm	As ppm	Cd ppm	Cu ppm	Al ppm	Ti ppm	Se ppm	Sr ppm
Cl5 0.5 ppm	0.52	0.51	0.51	0.55	0.53	0.54	0.56	0.54	0.51	0.49	0.50	0.53	0.50
Cl5 0.5 ppm	0.51	0.50	0.50	0.51	0.52	0.52	0.50	0.50	0.50	0.53	0.50	0.48	0.50
Cl5 0.5 ppm	0.68	0.67	0.60	0.69	0.73	0.74	0.74	0.75	0.59	0.59	0.63	0.69	0.59
Cl5 0.5 ppm	0.58	0.56	0.52	0.58	0.61	0.55	0.57	0.61	0.53	0.54	0.54	0.57	0.52
Cl5 0.5 ppm	0.61	0.61	0.56	0.62	0.63	0.64	0.64	0.66	0.55	0.56	0.58	0.61	0.55
Cl5 0.5 ppm	0.59	0.59	0.56	0.63	0.64	0.61	0.61	0.64	0.56	0.57	0.56	0.62	0.56
Cl5 0.5 ppm	0.65	0.64	0.59	0.68	0.70	0.73	0.75	0.72	0.58	0.59	0.62	0.69	0.59
Cl5 0.5 ppm	0.66	0.65	0.59	0.69	0.72	0.72	0.74	0.75	0.59	0.60	0.62	0.69	0.59
Cl5 0.5 ppm	0.67	0.66	0.60	0.69	0.72	0.77	0.79	0.75	0.60	0.62	0.63	0.72	0.60
Cl5 0.5 ppm	0.66	0.64	0.60	0.66	0.70	0.73	0.73	0.72	0.59	0.59	0.62	0.66	0.58
Cl5 0.5 ppm	0.66	0.65	0.59	0.67	0.70	0.74	0.77	0.73	0.59	0.59	0.62	0.69	0.60
Cl5 0.5 ppm	0.47	0.48	0.47	0.48	0.46	0.49	0.49	0.48	0.47	0.46	0.48	0.45	0.46
Cl5 0.5 ppm	0.65	0.52	0.51	0.65	0.53	0.54	0.53	0.51	0.51	0.56	0.50	0.50	0.48
Cl5 0.5 ppm	0.53	0.51	0.51	0.50	0.50	0.51	0.50	0.50	0.50	0.51	0.51	0.47	0.46
Cl5 0.5 ppm	0.48	0.47	0.47	0.48	0.46	0.47	0.48	0.46	0.45	0.44	0.46	0.45	0.44
Cl5 0.5 ppm	0.62	0.54	0.53	0.57	0.52	0.57	0.60	0.54	0.52	0.57	0.53	0.55	0.50
Cl5 0.5 ppm	0.59	0.53	0.51	0.52	0.51	0.56	0.56	0.52	0.51	0.53	0.52	0.51	0.49
Cl5 0.5 ppm	0.60	0.54	0.54	0.55	0.53	0.57	0.60	0.55	0.53	0.55	0.53	0.57	0.51
Cl6 2 ppm	1.96	1.96	1.94	2.02	1.96	2.00	2.01	2.03	1.95	1.92	1.95	2.05	1.95
Cl6 2 ppm	2.09	2.06	2.10	2.08	2.11	2.08	2.12	2.06	2.10	2.18	2.05	2.12	2.06
Cl6 2 ppm	2.63	2.60	2.33	2.62	2.76	2.77	2.76	2.89	2.28	2.37	2.46	2.82	2.38
Cl6 2 ppm	2.37	2.39	2.20	2.39	2.48	2.44	2.46	2.58	2.22	2.21	2.28	2.43	2.28
Cl6 2 ppm	2.46	2.41	2.25	2.57	2.60	2.56	2.54	2.69	2.27	2.34	2.33	2.65	2.34
Cl6 2 ppm	2.53	2.55	2.34	2.58	2.70	2.70	2.73	2.83	2.31	2.29	2.41	2.73	2.39
Cl6 2 ppm	2.62	2.57	2.34	2.66	2.82	2.74	2.73	2.93	2.29	2.33	2.44	2.71	2.37
Cl6 2 ppm	2.62	2.58	2.39	2.69	2.85	2.76	2.81	2.96	2.35	2.41	2.51	2.88	2.42
Cl6 2 ppm	2.65	2.58	2.41	2.65	2.80	2.71	2.71	2.90	2.31	2.42	2.47	2.76	2.41
Cl6 2 ppm	2.60	2.59	2.37	2.65	2.75	2.81	2.83	2.85	2.33	2.39	2.47	2.74	2.41
Cl6 2 ppm	2.16	2.12	2.08	2.12	2.08	2.08	2.06	2.06	2.06	2.01	2.06	2.07	2.07
Cl6 2 ppm	2.52	2.06	2.05	2.43	2.15	2.01	2.02	2.03	1.99	2.16	1.98	1.95	2.03
Cl6 2 ppm	2.18	2.12	2.06	2.08	2.06	2.07	2.08	2.11	2.00	2.07	2.08	2.09	2.03
Cl6 2 ppm	1.98	1.97	1.93	1.94	1.90	1.94	1.92	1.93	1.88	1.91	1.93	1.87	1.90
Cl6 2 ppm	2.35	2.11	2.07	2.18	2.07	2.10	2.14	2.09	2.00	2.18	2.07	2.10	2.05
Cl6 2 ppm	2.28	2.13	2.06	2.11	2.07	2.06	2.09	2.09	1.99	2.07	2.01	2.11	2.04
Cl6 2 ppm	2.32	2.18	2.16	2.13	2.15	2.14	2.19	2.14	2.11	2.20	2.11	2.18	2.10
Cl7 4 ppm	4.04	3.92	4.01	4.04	4.03	3.95	4.07	4.07	3.95	4.08	3.95	4.10	3.93
Cl7 4 ppm	3.85	3.79	3.90	4.03	3.92	4.02	4.02	4.12	3.78	3.78	3.90	4.08	3.91
Cl7 4 ppm	4.13	4.00	4.11	3.87	4.13	3.84	3.94	3.97	4.06	4.05	4.05	3.82	4.01
Cl7 4 ppm	4.69	4.46	4.37	4.72	4.86	4.68	4.77	5.01	4.31	4.42	4.39	4.78	4.27
Cl7 4 ppm	4.76	4.68	4.43	4.74	4.89	4.90	4.88	5.10	4.36	4.47	4.57	4.82	4.38
Cl7 4 ppm	4.99	5.03	4.65	5.06	5.30	5.27	5.20	5.58	4.53	4.48	4.82	5.10	4.53
Cl7 4 ppm	5.10	5.08	4.71	5.12	5.49	5.35	5.32	5.71	4.56	4.57	4.85	5.36	4.57
Cl7 4 ppm	5.12	5.13	4.73	5.15	5.38	5.39	5.35	5.64	4.60	4.63	4.84	5.22	4.60
Cl7 4 ppm	4.23	4.25	4.30	4.40	4.35	4.24	4.11	4.18	4.13	4.26	4.17	4.23	4.06
Cl7 4 ppm	4.71	4.20	4.16	4.42	4.45	4.10	4.17	4.16	4.12	4.46	4.13	4.28	4.10
Cl7 4 ppm	4.98	4.17	4.21	4.61	4.29	4.00	3.95	4.04	3.95	4.70	4.02	3.92	4.02
Cl7 4 ppm	4.68	4.25	4.30	4.30	4.38	4.03	4.05	4.19	4.07	4.42	4.10	4.20	4.04
Note: the check standards for the acid digested samples are in red													

Table C1c: Check Standard Data for ICP- AES Analytical Runs (Cont.).

Aqueous and Acid analytical runs for >4ppm concentrations											
Check Standard	Acid samples								Aqueous samples		
	Fe ppm	Zn ppm	Pb ppm	Cu ppm	Al ppm	K ppm	Na ppm	Mg ppm	K ppm	Na ppm	Mg ppm
Cl1 blank	0.00	0.16	0.01	0.01	0.11	0.13	0.07	0.00	0.21	0.17	0.00
Cl1 blank	0.07	0.18	0.06	0.07	0.18	0.16	0.12	0.00	0.22	0.17	0.00
Cl1 blank	0.01	0.15	0.01	0.03	0.12	0.11	0.09	0.00	0.26	0.19	0.00
Cl2 0.1 ppm	0.15	0.30	0.17	0.18	0.26	0.27	0.23	0.10	0.31	0.26	0.04
Cl2 0.1 ppm	0.05	0.18	0.06	0.08	0.16	0.20	0.15	0.00	0.32	0.26	0.05
Cl2 0.1 ppm	0.14	0.27	0.11	0.11	0.23	0.22	0.18	0.05	0.35	0.27	0.09
Cl2 0.1 ppm	0.16	0.28	0.16	0.18	0.26	0.26	0.24	0.09			
Cl3 1 ppm	1.35	1.34	1.38	1.32	1.37	1.18	1.28	1.27	1.05	1.05	0.97
Cl3 1 ppm	1.01	0.96	0.95	1.02	1.02	0.97	1.04	0.90	1.06	1.00	1.13
Cl3 1 ppm	0.95	0.93	0.89	0.97	1.00	0.94	1.00	0.87	1.03	0.98	0.99
Cl3 1 ppm	0.96	0.92	0.90	0.99	1.02	0.95	0.97	0.85	1.04	0.98	1.05
Cl3 1 ppm	1.11	1.08	0.99	1.05	1.11	1.02	1.10	0.98			
Cl3 1 ppm	1.11	1.01	0.99	1.05	1.14	1.04	1.06	0.95			
Cl3 1 ppm	1.14	1.16	1.11	1.18	1.23	1.09	1.22	1.05			
Cl4 5 ppm	5.06	4.81	5.02	5.23	5.16	4.91	5.21	5.00	4.75	4.53	5.03
Cl4 5 ppm	4.84	4.59	4.74	4.92	4.90	4.74	4.91	4.74	4.86	4.79	4.73
Cl4 5 ppm	4.72	4.32	4.56	4.94	4.83	4.72	5.00	4.56	4.54	4.31	5.53
Cl4 5 ppm	4.63	4.22	4.48	4.76	4.60	4.68	4.72	4.56	4.67	4.55	4.94
Cl4 5 ppm	4.96	4.57	4.65	4.97	5.01	4.64	4.75	4.72	4.58	4.45	5.02
Cl4 5 ppm	5.06	4.36	4.60	4.98	4.90	4.97	4.89	4.63	4.60	4.39	5.16
Cl4 5 ppm	5.32	5.08	5.22	5.67	5.64	5.32	5.54	5.26	4.51	4.40	5.10
Cl5 10 ppm	9.75	9.32	9.50	10.01	9.83	9.77	10.22	9.79	9.96	9.32	10.04
Cl5 10 ppm	9.41	8.72	8.96	9.64	9.46	9.87	9.60	9.20	9.08	8.82	10.93
Cl5 10 ppm	9.27	8.95	9.12	9.93	9.37	9.70	9.82	9.47	9.53	9.52	10.31
Cl5 10 ppm	9.44	8.92	9.04	10.02	9.53	9.77	9.96	9.29	9.32	9.27	10.24
Cl5 10 ppm	9.75	9.22	9.16	9.87	9.93	9.75	10.19	9.44			
Cl5 10 ppm	9.53	8.58	8.67	9.68	9.66	9.76	10.79	9.10			
Cl5 10 ppm	10.6	10.3	10.3	11.4	11.2	11.3	12.0	10.5			
Cl5 10 ppm	11.1	11.6	10.9	11.5	11.6	12.3	12.2	11.1			
Cl6 20 ppm	20.1	19.8	19.3	20.2	20.3	20.0	20.5	19.9	20.3	20.8	20.1
Cl6 20 ppm	19.5	18.8	19.1	20.1	19.8	21.3	21.3	19.6	20.8	21.6	19.4
Cl6 20 ppm	18.8	18.4	18.0	19.3	19.4	20.3	20.2	18.7	19.0	19.0	21.8
Cl6 20 ppm	19.1	18.6	18.2	19.6	19.7	20.1	20.5	19.1	20.1	21.0	20.1
Cl6 20 ppm	20.2	21.3	20.4	22.3	21.4	23.6	24.0	20.5	20.0	19.9	20.4
Cl6 20 ppm									19.6	19.7	20.5
Cl6 20 ppm									19.8	19.2	20.6
Cl7 50 ppm	53.1	52.2	51.4	53.7	54.9	51.1	50.3	53.7	52.8	52.3	52.4
Cl7 50 ppm	47.5	45.2	45.5	48.8	49.3	48.4	48.1	46.8	50.1	49.5	50.7
Cl7 50 ppm	50.4	49.0	49.6	54.9	56.6	57.0	55.2	51.6	49.7	46.6	51.7
Cl7 50 ppm	54.3	54.6	54.8	57.8	59.7	56.8	56.5	55.9			
Cl1 100ppm	110	91	110	118	126	102	95	117			
Note: the check standards for the acid digested samples are in red											

Table C2: ICP- AES Elemental Data for Aqueous Digestion of Dust Samples.

		Aqueous samples																			
sample name		Fe	Mn	Ba	Zn	Pb	As	As	Cd	Cu	Al	Ti	Se	Sr	K	Na	Mg	weight			
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	g		
	BS BLANK 1	0.00	0.00	0.00	0.05	0.01	0.02	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.26	2.41	0.00			
	BS BLANK 2	0.00	0.00	0.00	0.01	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.32	1.91	0.00				
	BS BLANK 3	0.00	0.00	0.00	0.01	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.31	1.33	0.01				
	BS BLANK 4	0.00	0.00	0.00	0.00	0.01	0.05	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.27	1.16	0.00				
	BS BLANK 5	0.00	0.00	0.00	0.01	0.01	0.05	0.02	0.00	0.00	0.00	0.01	0.00	0.01	0.31	1.87	0.03				
	BS BLANK 6	0.00	0.00	0.00	0.03	0.00	0.03	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.40	3.65	0.00				
K1 new	BS1	0.00	0.19	0.07	0.04	0.01	0.06	0.06	0.01	0.06	0.01	0.01	0.00	2.06	7.69	17.53	5.10	0.1218			
K1 old	BS2	0.01	0.21	0.08	0.02	0.01	0.24	0.22	0.01	0.05	0.02	0.01	0.00	2.69	15.07	25.51	12.22	0.2187			
K2 new roof	BS3	0.01	0.89	0.12	0.21	0.01	0.27	0.23	0.02	0.57	0.01	0.01	0.01	0.49	10.44	24.48	8.35	0.1650			
K2 old attic	BS4	0.01	0.51	0.09	0.06	0.02	0.25	0.22	0.01	0.28	0.02	0.01	0.01	0.53	15.64	44.83	10.14	0.1571			
K3 wood	BS5	0.01	0.75	0.09	7.40	0.02	0.10	0.02	0.03	0.26	0.01	0.01	0.01	0.39	13.63	74.70	11.11	0.1702			
K3 galv	BS6	0.00	0.03	0.03	6.20	0.01	0.02	0.00	0.02	0.03	0.00	0.01	0.01	0.34	9.09	80.21	6.35	0.1048			
K3 scuttle	BS7	0.01	0.35	0.09	0.07	0.01	0.13	0.05	0.00	0.12	0.00	0.01	0.02	0.40	7.11	15.23	4.83	0.0990			
K4 post 89	BS8	0.01	0.80	0.11	0.89	0.01	0.16	0.08	0.02	0.96	0.01	0.01	0.01	0.51	14.00	37.44	8.81	0.1218			
K4 back beam	BS9	0.01	0.79	0.10	0.88	0.04	0.51	0.50	0.07	0.75	0.00	0.01	0.07	0.43	14.59	22.73	12.40	0.1265			
K4 back beam	BS9	0.01	0.68	0.09	0.68	0.05	0.43	0.42	0.06	0.70	0.03	0.01	0.06	0.40				0.1265			
K4 transect	BS10	0.01	0.27	0.08	0.06	0.03	0.32	0.27	0.03	0.19	0.01	0.01	0.02	0.30	6.73	8.62	3.49	0.1293			
K5 near vent	BS11	0.01	0.93	0.13	0.34	0.05	0.51	0.51	0.10	0.49	0.01	0.01	0.06	0.68	8.50	13.54	8.42	0.1413			
K5 side	BS12	0.01	0.88	0.13	11.43	0.03	0.12	0.05	0.11	0.33	0.01	0.01	0.08	0.44	8.27	14.28	5.29	0.0907			
K5 far vent	BS13	0.01	0.42	0.11	0.20	0.03	0.63	0.62	0.02	0.13	0.00	0.01	0.02	0.38	20.12	28.01	14.74	0.1275			
K5 far vent	BS13	0.01	0.66	0.12	0.13	0.04	0.52	0.54	0.03	0.21	0.02	0.01	0.04	0.52				0.1275			
K6 R beam	BS14	0.00	0.09	0.04	0.04	0.02	0.22	0.21	0.01	0.04	0.00	0.01	0.01	0.13	2.22	5.01	2.44	0.1220			
K6 new attic	BS15	0.01	0.24	0.06	0.12	0.01	0.18	0.17	0.01	0.06	0.00	0.01	0.00	0.29	6.81	12.49	7.16	0.1027			
K6 M1&2	BS16	0.00	0.07	0.06	0.00	0.02	0.18	0.17	0.01	0.02	0.02	0.01	0.01	0.20	5.84	10.18	4.95	0.0841			
K6 4-8	BS17	0.00	0.20	0.06	0.25	0.02	0.17	0.15	0.01	0.06	0.01	0.01	0.01	0.21	7.93	12.21	8.19	0.0981			
K7 1	BS18	0.00	0.30	0.09	0.04	0.04	0.27	0.27	0.03	0.08	0.01	0.01	0.02	0.55	12.36	19.31	13.87	0.1490			
K7 west beam	BS19	0.01	0.65	0.11	0.32	0.06	0.38	0.36	0.12	0.37	0.02	0.01	0.07	0.51	12.19	23.46	12.03	0.1226			
K7 Beam 2	BS20	0.00	1.00	0.15	0.14	0.03	0.45	0.46	0.08	0.46	0.02	0.01	0.09	0.84	17.28	25.28	18.80	0.1924			
K7 east beam	BS21	0.01	0.33	0.11	0.02	0.03	0.34	0.35	0.02	0.05	0.02	0.01	0.04	0.53	8.15	11.39	8.98	0.1047			
K7 3 wool	BS22	0.00	0.82	0.11	0.66	0.02	0.10	0.07	0.01	0.15	0.02	0.01	0.00	0.42	8.72	19.41	8.00	0.1508			
K7 Res. Light	BS23	0.00	0.04	0.05	0.02	0.01	0.04	0.04	0.00	0.01	0.02	0.01	0.00	0.18	2.93	8.43	2.01	0.0366			
K8 left corner	BS24	0.00	0.66	0.12	0.44	0.05	0.43	0.43	0.08	0.39	0.01	0.01	0.05	0.47	14.53	21.54	15.73	0.1670			
K8 center right window	BS25	0.00	0.14	0.08	0.02	0.02	0.27	0.24	0.02	0.03	0.00	0.01	0.03	0.44	8.22	13.89	9.22	0.1206			
K8 windows & center left	BS26	0.00	0.09	0.06	0.02	0.04	0.23	0.20	0.02	0.02	0.00	0.01	0.01	0.27	6.23	12.28	7.04	0.1011			
K8 center left 2	BS27	0.00	0.14	0.08	0.05	0.06	0.34	0.31	0.02	0.06	0.00	0.01	0.03	0.32	9.08	16.14	7.34	0.1098			
K8 far left 1	BS28	0.00	0.14	0.07	0.06	0.08	0.27	0.25	0.02	0.07	0.00	0.01	0.04	0.24	7.59	14.06	5.84	0.0988			
L1 a+b+c	BS29	0.00	0.46	0.14	0.28	0.03	0.29	0.27	0.01	0.28	0.00	0.01	0.00	0.47	12.07	25.80	8.88	0.1218			
L1 E keytop	BS30	0.01	1.22	0.19	0.24	0.01	0.12	0.09	0.01	0.25	0.01	0.01	0.00	0.67	13.09	22.67	9.06	0.1630			
L1 E Kneeler	BS31	0.00	0.83	0.15	0.07	0.02	0.12	0.07	0.00	0.13	0.00	0.01	0.00	0.60	9.66	18.18	6.55	0.1661			
L2 attic bag	BS32	0.00	0.06	0.08	0.01	0.01	0.07	0.02	0.00	0.01	0.01	0.01	0.00	0.37	5.64	13.40	3.77	0.1178			
L2 Beam	BS33	0.00	0.19	0.08	0.10	0.03	0.21	0.22	0.00	0.03	0.01	0.01	0.00	0.36	8.91	16.90	7.47	0.1014			
L2 attic pipe	BS34	0.00	0.07	0.16	1.07	0.02	0.12	0.07	0.01	0.02	0.00	0.01	0.01	0.28	4.88	11.57	4.16	0.1365			
L2 attic airconditioner	BS35	0.00	0.04	0.07	0.02	0.01	0.08	0.03	0.00	0.02	0.01	0.01	0.00	0.35	7.17	15.61	4.55	0.1198			
L3 attic door	BS36	0.00	0.16	0.07	0.05	0.01	0.07	0.02	0.00	0.14	0.01	0.01	0.00	0.29	8.45	18.00	5.62	0.0997			
S1 window	BS37	0.01	1.12	0.14	0.13	0.01	0.38	0.40	0.02	0.65	0.02	0.01	0.00	0.49	38.92	45.63	20.49	0.2369			
S2 window	BS38	0.00	0.38	0.15	0.01	0.01	0.37	0.37	0.01	0.07	0.01	0.01	0.00	0.52	13.42	19.54	10.36	0.1686			
S3 corner & side	BS39	0.01	0.98	0.08	0.02	0.02	0.30	0.29	0.00	0.59	0.01	0.01	0.00	0.54	51.21	47.14	23.03	0.2744			
J V1 + V2 closet and toilet	BS40	0.01	1.52	0.16	4.21	0.01	0.23	0.21	0.02	0.47	0.00	0.01	0.00	0.90	49.12	55.29	16.92	0.2125			
J V3 soots	BS41	0.00	0.36	0.13	0.13	0.01	0.30	0.30	0.01	0.09	0.01	0.01	0.02	0.58	13.28	17.51	5.36	0.1127			
J V4 + V5	BS42	0.03	0.63	0.10	1.02	0.01	0.09	0.03	0.05	0.89	0.01	0.01	0.00	0.50	28.72	54.82	9.77	0.1313			
J V6 glass bulb	BS43	0.00	0.15	0.10	0.03	0.01	0.07	0.02	0.00	0.03	0.01	0.01	0.00	0.42	7.57	19.23	4.49	0.1092			
LH N1	BS44	0.00	0.16	0.12	0.03	0.01	0.20	0.17	0.00	0.04	0.01	0.01	0.00	0.36	9.74	9.16	5.83	0.1037			
LH N2	BS45	0.00	0.05	0.08	0.00	0.01	0.08	0.01	0.00	0.00	0.01	0.01	0.00	0.24	4.72	7.40	4.65	0.1193			
LH N3	BS46	0.01	0.33	0.16	0.04	0.01	0.11	0.06	0.01	0.04	0.03	0.01	0.00	0.61	6.09	10.84	6.48	0.1048			
LH beam N4+N5	BS47	0.00	0.43	0.16	0.05	0.01	0.12	0.10	0.00	0.06	0.02	0.01	0.00	0.57	9.42	14.48	11.93	0.1926			
LH N1 + N2	BS48	0.01	1.52	0.17	3.02	0.01	0.16	0.15	0.02	0.31	0.00	0.01	0.00	0.68	15.46	29.69	12.08	0.1875			
LS N3 + N4	BS49	0.00	0.53	0.12	0.22	0.01	0.23	0.20	0.01	0.10	0.00	0.01	0.01	0.53	7.98	15.16	8.45	0.1828			
LS N5 +6 window	BS50	0.00	0.09	0.11	0.01	0.01	0.16	0.13	0.00	0.01	0.00	0.01	0.01	0.43	5.67	8.11	4.12	0.1043			
LS N7-9 window	BS51	0.00	0.38	0.11	0.02	0.00	0.20	0.17	0.00	0.10	0.00	0.01	0.00	0.53	7.62	14.09	6.09	0.1551			
NOTE: most of the aqueous analysis are below detection																					

Table C3: ICP- AES Elemental Data for Acid Digestion of Dust Samples.

Acid samples																	
sample name	Fe	Mn	Ba	Zn	Pb	As	As	Cd	Cu	Al	Ti	Se	Sr	K	Na	Mg	weight
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	g
BS BLANK 1	0.06	0.03	0.01	0.16	0.00	0.03	0.01	0.01	0.00	0.29	0.01	0.02	0.03	0.19	0.89	0.03	
BS BLANK 2	0.01	0.02	0.01	0.12	0.00	0.03	0.02	0.01	0.00	0.21	0.01	0.03	0.02	0.16	0.65	0.03	
BS BLANK 3	0.00	0.00	0.00	0.11	0.00	0.01	0.01	0.00	0.00	0.09	0.00	0.02	0.01	0.12	0.12	0.00	
BS BLANK 4	0.91	0.00	0.00	1.00	0.03	0.02	0.00	0.00	0.01	0.84	0.00	0.01	0.01	0.23	0.18	0.46	
BS BLANK 5	0.97	0.01	0.01	0.17	0.00	0.01	0.00	0.00	0.01	0.59	0.01	0.00	0.01	0.20	0.15	0.41	
BS BLANK 6	0.93	0.02	0.01	0.24	0.01	0.01	0.00	0.00	0.01	0.83	0.01	0.01	0.02	0.28	0.19	0.50	
K1 new	BS1	18.88	0.57	0.57	4.25	2.64	0.25	0.14	0.08	1.07	20.92	1.45	0.00	3.79	4.98	15.59	0.1218
K1 old	BS2	45.11	1.13	0.33	5.85	5.39	0.75	0.51	0.15	1.73	40.63	2.88	0.00	6.04	10.78	12.84	0.2187
K2 new roof	BS3	80.70	2.07	1.04	9.44	5.01	0.76	0.42	0.17	8.54	30.38	0.45	0.00	0.71	9.02	2.24	0.1650
K2 old attic	BS4	69.49	2.45	1.14	10.89	6.29	1.21	0.87	0.25	7.63	35.41	0.56	0.00	0.97	9.23	2.59	0.1571
K3 wood	BS5	86.35	1.66	1.23	56.52	8.28	1.16	0.72	0.21	7.74	29.66	0.43	0.00	0.75	8.81	2.39	0.1702
K3 galv	BS6	88.99	1.22	0.47	141.30	5.04	0.71	0.37	0.15	3.73	12.29	0.22	0.00	0.23	3.37	1.02	0.1048
K3 scuttle	BS7	24.77	1.20	0.58	6.74	1.44	0.22	0.07	0.08	2.45	15.13	0.26	0.00	0.43	4.22	0.90	0.0990
K4 post 89	BS8	35.70	1.10	0.97	11.74	3.66	0.54	0.32	0.14	4.50	19.96	0.31	0.00	0.49	5.48	1.56	0.1218
K4 back beam	BS9	40.80	1.43	1.32	10.06	11.92	1.93	1.81	0.49	6.08	24.22	0.43	0.00	0.59	6.70	1.26	0.1265
K4 transect	BS10	43.23	1.16	0.92	6.59	12.10	1.09	0.86	0.22	7.81	19.93	0.30	0.00	0.45	6.14	1.51	0.1293
K5 near vent	BS11	43.55	1.47	0.81	8.41	14.85	1.75	1.52	0.36	11.92	21.26	0.32	0.00	0.47	6.29	1.23	0.1413
K5 side	BS12	33.40	1.37	0.74	62.94	7.84	1.88	1.51	0.24	6.26	17.10	0.33	0.01	0.38	4.69	2.51	0.0907
K5 far vent	BS13	33.98	2.05	1.30	7.88	11.44	2.81	2.55	0.50	6.21	24.94	0.40	0.00	0.61	7.89	3.94	0.1275
K6 R beam	BS14	26.00	1.01	0.43	7.39	5.76	0.69	0.55	0.20	4.83	15.91	0.24	0.00	0.30	3.76	4.59	0.1220
K6 new attic	BS15	19.94	1.06	0.57	4.31	3.65	0.60	0.48	0.15	2.89	14.91	0.27	0.00	0.42	3.79	0.87	0.1027
K6 M1&2	BS16	26.83	1.26	0.55	3.89	5.48	0.63	0.44	0.19	4.51	14.06	0.32	0.00	0.37	3.90	1.18	0.1837
K6 4-8	BS17	23.70	0.91	0.62	5.89	3.96	0.59	0.43	0.18	2.59	15.93	0.38	0.00	0.42	4.03	1.13	0.0981
K7 1	BS18	32.82	1.69	0.99	5.64	10.32	1.99	1.77	0.36	6.34	27.09	0.43	0.00	0.63	8.93	1.54	0.1490
K7 west beam	BS19	49.82	1.99	1.07	12.11	23.39	4.10	3.81	0.73	13.99	30.24	0.47	0.00	0.59	8.31	1.56	0.1226
K7 Beam 2	BS20	72.35	2.87	1.88	11.99	17.26	3.75	3.42	0.60	9.39	52.88	0.78	0.00	0.97	16.74	2.71	0.1924
K7 east beam	BS21	22.62	1.13	0.69	3.46	6.32	1.09	0.97	0.20	4.38	18.51	0.28	0.00	0.35	5.48	1.27	0.1047
K7 3 wool	BS22	43.95	2.32	1.36	13.22	2.79	0.41	0.14	0.10	2.43	34.43	0.49	0.00	0.91	10.07	1.89	0.1508
K7 Res. Light	BS23	9.36	0.66	0.28	2.71	0.71	0.11	0.04	0.03	0.65	6.78	0.18	0.01	0.15	1.63	0.38	0.0366
K8 left corner	BS24	47.59	1.78	1.22	10.09	17.44	3.72	3.47	0.68	10.21	39.94	0.66	0.00	0.80	13.08	2.21	0.1670
K8 center right window	BS25	32.39	1.57	0.65	7.16	16.44	1.86	1.65	0.49	10.32	27.12	0.42	0.00	0.48	7.79	2.60	0.1206
K8 windows & center left	BS26	23.23	1.17	0.54	4.88	11.03	1.45	1.29	0.40	6.84	18.86	0.36	0.00	0.38	5.52	1.13	0.1011
K8 center left 2	BS27	29.33	1.60	0.62	6.81	16.68	2.30	2.13	0.55	10.01	18.78	0.31	0.00	0.46	6.04	1.18	0.1098
K8 far left 1	BS28	58.17	1.34	0.79	6.25	14.77	1.50	1.21	0.40	9.88	43.07	0.79	0.00	0.44	11.77	2.00	0.0988
L1 a+b+c	BS29	64.84	1.17	1.46	5.08	5.18	0.55	0.20	0.10	2.56	57.16	0.77	0.00	0.69	13.70	1.78	0.1218
L1 E keytop	BS30	94.63	1.70	1.19	3.61	1.44	0.16	0.00	0.03	1.68	84.44	1.16	0.00	0.71	19.70	2.26	0.1630
L1 E Kneeler	BS31	107.60	2.17	1.22	3.14	1.21	0.17	0.00	0.03	1.61	95.19	1.24	0.00	0.76	21.73	2.59	0.1661
L2 attic bag	BS32	56.44	1.28	0.88	3.92	1.09	0.14	0.00	0.09	1.31	50.94	0.75	0.00	0.56	11.79	1.52	0.1178
L2 Beam	BS33	52.77	1.25	0.98	5.23	3.26	0.45	0.13	0.09	1.69	50.11	0.76	0.00	0.55	11.78	2.15	0.1014
L2 attic pipe	BS34	78.05	1.27	1.32	90.69	6.21	0.77	0.34	0.09	2.57	72.29	0.93	0.00	0.56	14.46	1.79	0.1365
L2 attic airconditioner	BS35	57.01	1.40	1.01	6.98	1.39	0.13	0.00	0.03	1.33	50.80	0.65	0.00	0.63	11.81	1.78	0.1198
L3 attic door	BS36	47.51	1.12	0.78	4.64	1.34	0.12	0.00	0.02	3.01	42.27	0.63	0.00	0.49	10.02	1.22	0.0997
S1 window	BS37	108.40	2.35	1.74	3.26	4.68	0.48	0.00	0.12	3.59	97.60	1.03	0.00	1.14	27.94	2.86	0.2369
S2 window	BS38	83.40	1.98	1.44	2.87	4.42	0.61	0.11	0.13	2.88	77.49	0.81	0.00	0.81	19.39	2.27	0.1686
S3 corner & side	BS39	113.20	2.32	1.75	3.25	2.98	0.27	0.00	0.07	2.45	100.20	1.02	0.00	1.21	28.63	3.14	0.2744
J V1 + V2 closet and toilet	BS40	102.80	2.70	3.30	30.20	6.05	0.76	0.17	0.15	2.66	73.39	0.87	0.00	2.16	22.64	3.73	0.2125
J V3 soots	BS41	45.61	1.49	1.31	4.46	3.07	0.38	0.12	0.10	1.49	34.10	0.54	0.00	0.83	9.94	2.45	0.1127
J V4 + V5	BS42	557.30	1.57	1.46	7.15	5.32	0.66	0.00	0.21	5.64	46.48	0.49	0.00	0.89	8.93	1.59	0.1313
J V6 glass bulb	BS43	56.00	1.45	1.54	2.43	0.90	0.14	0.00	0.04	2.27	34.03	0.60	0.00	0.97	9.22	1.66	0.1092
LH N1	BS44	56.62	1.38	1.47	2.62	2.62	0.40	0.05	0.04	2.39	40.60	0.56	0.00	0.57	10.92	1.17	0.1037
LH N2	BS45	33.77	0.94	0.64	1.40	0.80	0.10	0.00	0.02	0.67	24.54	0.38	0.00	0.31	7.06	0.84	0.1193
LH N3	BS46	54.43	1.43	0.91	2.57	1.16	0.15	0.00	0.04	1.35	44.54	0.60	0.00	0.48	10.51	1.30	0.1048
LH beam N4+N5	BS47	70.42	1.56	1.56	2.87	2.66	0.32	0.00	0.05	1.58	61.36	0.63	0.00	0.75	17.47	1.80	0.1926
LH N1 + N2	BS48	153.30	3.25	2.27	26.04	3.70	0.63	0.00	0.11	4.30	123.00	1.19	0.00	1.43	30.01	6.12	0.1875
LS N3 + N4	BS49	92.49	1.89	1.87	6.01	5.07	0.61	0.06	0.09	2.74	81.06	1.16	0.00	0.85	20.47	2.60	0.1828
LS N5 +6 window	BS50	44.85	1.17	0.87	2.39	1.88	0.22	0.00	0.04	1.09	36.09	0.57	0.00	0.40	9.38	1.13	0.1043
LS N7-9 window	BS51	77.61	2.05	1.36	3.54	2.22	0.31	0.00	0.06	2.18	62.85	0.96	0.00	0.79	16.49	2.22	0.1551
AQBS12		0.26			15.18	0.01				0.79	0.34				13.09	68.41	10.70
AQBS5		0.04			10.32	0.04				0.42	0.17				7.98	14.68	4.69
AQBS6		0.12			13.72	0.00				0.08	0.20				8.33	72.72	6.18

=data outside calibration

=date outside calibration but 100ppm standard within 10%

Table C4a: ICP- AES Elemental and Check Standard Data for Acid Digestion of Buried Soil Samples.

Data and		Al		Ti		V		K		Na		Mg		P		Sr	
Chk	Stand		fact		fact		fact		fact		fact		fact		fact		fact
Ck7 20 ppm	102	20.00	20.330	1.02	20.190	1.01	20.140	1.01	20.040	1.00	19.730	0.99	20.150	1.01	20.440	1.02	13.640
Ck6 10 ppm	104	10.00	10.090	1.01	9.985	1.00	10.120	1.01	10.120	1.01	10.260	1.03	10.250	1.03	10.040	1.00	10.100
Ck5 5 ppm	105	5.00	5.377	1.08	5.008	1.00	5.118	1.02	5.128	1.03	5.375	1.08	5.288	1.06	5.239	1.05	5.123
Ck4 1 ppm	106	1.00	1.109	1.11	1.050	1.05	1.059	1.06	0.985	0.98	1.034	1.03	1.097	1.10	1.077	1.08	0.924
Ck3 0.5ppm	108	0.50	0.505	1.01	0.497	0.99	0.509	1.02	0.508	1.02	0.498	1.00	0.490	0.98	0.514	1.03	0.472
Ck2 0.1ppm	109	0.10	0.077	0.77	0.090	0.90	0.082	0.82	0.115	1.15	0.118	1.18	0.076	0.76	0.094	0.94	0.141
Ck1 blank	110	0.00	-0.041	0.01	-0.014		-0.020		0.012		0.010		-0.059		-0.024		0.064
BLK 1	112		0.250		-0.014		-0.030		0.342		3.482		0.062		0.022		0.067
BS-ELP-1	113		56.450		0.760		0.257		24.990		8.381		51.420		9.995		1.779
BS-ELP-2	114		39.210		0.619		0.114		14.250		8.099		29.910		5.813		1.049
BS-ELP-3	116		29.310		1.020		0.093		8.954		7.899		19.120		4.988		0.768
BS-ELP-4	117		41.810		0.977		0.139		14.250		9.077		30.190		5.515		0.823
Ck6 10 ppm	118	10.00	10.100	1.01	9.898	0.99	10.010	1.00	10.220	1.02	10.070	1.01	10.100	1.01	9.984	1.00	10.190
Ck4 1 ppm	120	1.00	1.100	1.10	1.019	1.02	1.037	1.04	1.002	1.00	1.011	1.01	1.065	1.07	1.104	1.10	0.898
Ck2 0.1ppm	121	0.10	0.098	0.98	0.094	0.94	0.085	0.85	0.121	1.21	0.121	1.21	0.087	0.87	0.115	1.15	0.148
BS-ELP-5	122		61.080		0.467		0.136		34.120		28.740		110.800		12.840		6.843
BS-ELP-6	124		55.920		1.187		0.250		18.510		18.270		58.890		20.250		1.925
BLK 2	125		0.475		-0.012		-0.033		0.278		2.586		0.280		0.060		0.075
Ck7 20 ppm	126	20.00	20.220	1.01	20.130	1.01	20.370	1.02	20.340	1.02	19.650	0.98	20.320	1.02	19.430	0.97	13.600
Ck5 5 ppm	128	5.00	5.178	1.04	4.934	0.99	5.066	1.01	5.103	1.02	5.369	1.07	5.102	1.02	5.201	1.04	5.127
Ck3 0.5ppm	129	0.50	0.529	1.06	0.531	1.06	0.526	1.05	0.493	0.99	0.530	1.06	0.520	1.04	0.553	1.11	0.492
BS-ELP-7	130		61.890		0.811		0.599		32.180		28.520		100.500		17.050		3.457
BS-ELP-8	132		49.320		0.604		0.228		23.030		27.850		126.200		13.000		5.923
Ck6 10 ppm	133	10.00	10.010	1.00	9.576	0.96	9.994	1.00	10.050	1.01	10.300	1.03	9.663	0.97	9.909	0.99	9.835
Ck4 1 ppm	134	1.00	1.124	1.12	1.003	1.00	1.031	1.03	0.966	0.97	1.074	1.07	1.133	1.13	1.058	1.06	0.889
Ck2 0.1ppm	136	0.10	0.118	1.18	0.096	0.96	0.081	0.81	0.119	1.19	0.128	1.28	0.103	1.03	0.131	1.31	0.147
BS-ELP-9	137		59.600		0.608		0.558		32.350		27.470		209.700		15.610		5.992
BS-ELP-10	139		60.000		0.880		0.340		32.720		27.370		262.300		17.230		7.609
BS-ELP-11	140		51.510		0.788		0.384		27.180		-255.200		255.800		20.670		10.120
BS-ELP-12	141		54.300		0.967		0.372		33.990		13.640		587.900		8.114		5.832
BLK 3	143		0.916		-0.011		-0.031		0.824		3.996		1.816		0.062		0.093
Ck6 10 ppm	144	10.00	10.330	1.03	9.657	0.97	9.951	1.00	10.490	1.05	10.060	1.01	10.390	1.04	10.270	1.03	10.080
Ck4 1 ppm	145	1.00	1.073	1.07	1.007	1.01	1.018	1.02	0.999	1.00	1.026	1.03	1.161	1.16	1.035	1.04	0.907
Ck2 0.1ppm	147	0.10	0.118	1.18	0.096	0.96	0.088	0.88	0.111	1.11	0.128	1.28	0.144	1.44	0.093	0.93	0.149
Ck1 blank	148	0.00	-0.019	0.01	-0.012		-0.022		0.009		0.018		-0.025		-0.007		0.066
Ck7 20 ppm	149	20.00	0.069		0.099		0.014		-0.007		0.035		0.073		20.550	1.03	0.160
Ck5 5 ppm	151	5.00	5.189	1.04	4.994	1.00	5.029	1.01	4.841	0.97	4.858	0.97	4.838	0.97	5.081	1.02	5.016
Ck3 0.5ppm	152	0.50	0.512	1.02	0.497	0.99	0.498	1.00	0.488	0.98	0.504	1.01	0.483	0.97	0.505	1.01	0.475

NOTES:

1) value of check standards in ppm

2) check standard which was greater than 10% different from true value

3) check standard ran out of solution so these values are incorrect

4) data higher than the highest calibration standard

Table C4b: ICP- AES Elemental and Check Standard Data for Acid Digestion  
of Buried Soil Samples (Cont.).

Data and Chk Stand			Fe	fact	Mn	fact	Ba	fact	Zn	fact	Pb	fact	As	fact	Cd	fact	Cu	fact
Ck7 20 ppm	102	20.00	20.310	1.02	20.310	1.02	20.030	1.00	20.180	1.01	20.430	1.02	20.280	1.01	20.610	1.03	20.420	1.02
Ck6 10 ppm	104	10.00	10.080	1.01	10.010	1.00	10.100	1.01	10.180	1.02	10.100	1.01	10.010	1.00	10.120	1.01	10.260	1.03
Ck5 5 ppm	105	5.00	5.135	1.03	5.152	1.03	5.033	1.01	5.313	1.06	5.193	1.04	5.184	1.04	5.162	1.03	5.161	1.03
Ck4 1 ppm	106	1.00	1.095	1.10	1.096	1.10	1.037	1.04	1.143	1.14	1.113	1.11	1.119	1.12	1.160	1.16	1.091	1.09
Ck3 0.5ppm	108	0.50	0.506	1.01	0.507	1.01	0.499	1.00	0.532	1.06	0.517	1.03	0.533	1.07	0.529	1.06	0.515	1.03
Ck2 0.1ppm	109	0.10	0.081	0.81	0.076	0.76	0.082	0.82	0.086	0.86	0.089	0.89	0.072	0.72	0.095	0.95	0.070	0.70
Ck1 blank	110	0.00	-0.030	0.00	-0.030	0.00	-0.023	0.00	-0.028	0.00	-0.028	0.00	-0.018	0.03	-0.015	0.00	-0.037	0.00
BLK 1	112		0.080		-0.030		-0.017		0.348		-0.005		-0.035	0.026	-0.017		-0.027	
BS-ELP-1	113		79.880		3.820		2.567		1.006		0.287		0.131	0.058	-0.013		0.129	
BS-ELP-2	114		47.240		2.244		2.156		0.589		0.131		0.030	0.021	-0.016		0.034	
BS-ELP-3	116		48.830		1.159		0.600		0.612		0.080		0.004	0.009	-0.017		0.021	
BS-ELP-4	117		58.440		1.949		0.517		0.645		0.140		0.035	0.046	-0.015		0.050	
Ck6 10 ppm	118	10.00	10.110	1.01	9.969	1.00	10.050	1.01	10.120	1.01	10.000	1.00	9.919	0.99	10.190	1.02	10.290	1.03
Ck4 1 ppm	120	1.00	1.105	1.11	1.041	1.04	1.041	1.04	1.106	1.11	1.076	1.08	1.083	1.08	1.093	1.09	1.070	1.07
Ck2 0.1ppm	121	0.10	0.103	1.03	0.083	0.83	0.090	0.90	0.092	0.92	0.088	0.88	0.101	1.01	0.103	1.03	0.076	0.76
BS-ELP-5	122		65.460		7.856		1.615		0.719		0.369		0.211	0.039	-0.006		0.144	
BS-ELP-6	124		99.710		1.745		0.740		0.827		0.323		0.163	0.053	-0.010		0.081	
BLK 2	125		0.372		-0.022		-0.016		0.341		-0.017		-0.035	0.015	-0.020		-0.031	
Ck7 20 ppm	126	20.00	20.390	1.02	19.790	0.99	19.910	1.00	20.110	1.01	20.310	1.02	19.640	0.98	20.280	1.01	20.430	1.02
Ck5 5 ppm	128	5.00	5.083	1.02	5.068	1.01	5.059	1.01	5.193	1.04	5.116	1.02	5.128	1.03	5.267	1.05	5.159	1.03
Ck3 0.5ppm	129	0.50	0.547	1.09	0.526	1.05	0.527	1.05	0.567	1.13	0.554	1.11	0.514	1.03	0.570	1.14	0.530	1.06
BS-ELP-7	130		87.220		2.167		0.440		0.998		0.455		0.189	0.048	0.003		0.177	
BS-ELP-8	132		53.600		5.519		1.162		0.644		0.249		0.126	0.050	-0.011		0.019	
Ck6 10 ppm	133	10.00	9.745	0.97	9.597	0.96	9.778	0.98	9.923	0.99	9.854	0.99	9.831	0.98	10.130	1.01	9.965	1.00
Ck4 1 ppm	134	1.00	1.113	1.11	1.037	1.04	1.031	1.03	1.082	1.08	1.061	1.06	1.051	1.05	1.081	1.08	1.056	1.06
Ck2 0.1ppm	136	0.10	0.103	1.03	0.084	0.84	0.086	0.86	0.089	0.89	0.095	0.95	0.064	0.64	0.106	1.06	0.078	0.78
BS-ELP-9	137		82.270		6.475		1.124		0.923		0.276		0.138	0.081	-0.005		0.076	
BS-ELP-10	139		94.700		9.311		2.840		0.897		0.369		0.183	0.039	-0.009		0.117	
BS-ELP-11	140		94.390		10.050		5.869		0.963		0.431		0.212	0.020	-0.004		0.210	
BS-ELP-12	141		95.300		7.208		3.813		0.880		0.530		0.279	0.022	-0.009		0.154	
BLK 3	143		0.605		0.003		0.002		0.386		-0.019		-0.052	0.049	-0.018		-0.020	
Ck6 10 ppm	144	10.00	9.826	0.98	9.703	0.97	10.050	1.01	10.370	1.04	9.957	1.00	9.957	1.00	10.080	1.01	10.120	1.01
Ck4 1 ppm	145	1.00	1.083	1.08	1.022	1.02	1.036	1.04	1.075	1.08	1.046	1.05	1.064	1.06	1.059	1.06	1.032	1.03
Ck2 0.1ppm	147	0.10	0.112	1.12	0.084	0.84	0.091	0.91	0.096	0.96	0.096	0.96	0.088	0.88	0.104	1.04	0.078	0.78
Ck1 blank	148	0.00	-0.018	0.00	-0.026	0.00	-0.020	0.00	-0.025	0.00	-0.027	0.00	-0.054	0.03	-0.012	0.00	-0.036	0.00
Ck7 20 ppm	149	20.00	0.702		5.389		0.106		20.310	1.02	20.340	1.02	20.550	1.03	20.560	1.03	0.075	
Ck5 5 ppm	151	5.00	5.009	1.00	4.993	1.00	4.961	0.99	5.211	1.04	5.041	1.01	5.241	1.05	5.161	1.03	5.085	1.02
Ck3 0.5ppm	152	0.50	0.502	1.00	0.499	1.00	0.512	1.02	0.528	1.06	0.523	1.05	0.478	0.96	0.546	1.09	0.501	1.00

**NOTES:**

1) value of check standards in ppm

2) check standard which was greater than 10% different from true value

3) check standard ran out of solution so these values are incorrect

4) data higher than the highest calibration standard

Table C5: Summarized Acid Digestion of Buried Soil Samples Data of  
ICP- AES Elemental Analyses

sample	order	Fe	Mn	Ba	Zn	Pb	As	Cd	Cu	Al	Ti	V	K	Na	Mg	P	Sr
BLK 1	112	0.08	-0.03	-0.02	0.35	-0.01	-0.03	-0.02	-0.03	0.25	-0.01	-0.03	0.34	3.48	0.06	0.02	0.07
BS-ELP-1	113	101	3.82	2.57	1.01	0.29	0.13	-0.01	0.13	83.7	0.76	0.26	26.7	8.38	57.2	10.0	1.78
BS-ELP-2	114	56.7	2.24	2.16	0.59	0.13	0.03	-0.02	0.03	48.2	0.62	0.11	14.3	8.10	33.9	5.81	1.05
BS-ELP-3	116	57.3	1.16	0.60	0.61	0.08	0.00	-0.02	0.02	33.0	1.02	0.09	8.95	7.90	21.2	4.99	0.77
BS-ELP-4	117	71.0	1.95	0.52	0.65	0.14	0.04	-0.02	0.05	52.4	0.98	0.14	14.3	9.08	33.2	5.52	0.82
BS-ELP-5	122	88.5	7.86	1.62	0.72	0.37	0.21	-0.01	0.14	142	0.47	0.14	58.5	44.5	132	12.8	6.84
BS-ELP-6	124	129	1.75	0.74	0.83	0.32	0.16	-0.01	0.08	91.1	1.19	0.25	18.5	18.3	68.4	20.3	1.93
BLK 2	125	0.37	-0.02	-0.02	0.34	-0.02	-0.03	-0.02	-0.03	0.47	-0.01	-0.03	0.28	2.59	0.28	0.06	0.07
BS-ELP-7	130	119	2.17	0.44	1.00	0.46	0.19	0.00	0.18	133	0.81	0.60	51.5	51.3	115	17.1	3.46
BS-ELP-8	132	69.9	5.52	1.16	0.64	0.25	0.13	-0.01	0.02	70.0	0.60	0.23	23.0	55.5	167	13.0	5.92
BS-ELP-9	137	114	6.48	1.12	0.92	0.28	0.14	0.00	0.08	152	0.61	0.56	77.6	55.0	245	15.6	5.99
BS-ELP-10	139	146	9.31	2.84	0.90	0.37	0.18	-0.01	0.12	160	0.88	0.34	77.1	58.1	312	17.2	7.61
BS-ELP-11	140	151	10.1	5.87	0.96	0.43	0.21	0.00	0.21	183	0.79	0.38	95.3	224	319	20.7	10.1
BS-ELP-12	141	157	7.21	3.81	0.88	0.53	0.28	-0.01	0.15	174	0.97	0.37	66.1	13.6	734	8.11	5.83
BLK 3	143	0.60	0.00	0.00	0.39	-0.02	-0.05	-0.02	-0.02	0.92	-0.01	-0.03	0.82	4.00	1.82	0.06	0.09

**NOTE:**

1) this set of data includes values that were less than the highest calibration standard and from the dilution run

2) all values are in ppm

3) samples are in the order run for the first analytical run

4) values from the dilution run

5) BLK - method blanks

Table C6 a: Results of Acid Digestion Dust and Soil Samples by ICP- MS Elemental Analyses (3 elements) and Check Standard Data.

Element	V / 51	Se / 82	Sb / 121	Standard value (ppb)	
Sample Name					
BLANK.D	0.0	0.0	0.0	0.0	calibration standards
0_32.D	0.3	0.3	0.3	0.3	
1_6.D	1.6	1.5	1.4	1.6	
8.D	8.0	7.6	7.6	8.0	
40.D	39.2	39.2	38.8	40.0	
200A.D	200.2	200.2	200.3	200.0	
8A.D	8.4	8.1	8.1	8.0	check standards
1_6A.D	1.6	1.6	1.5	1.6	
0A.D	0.0	0.0	0.0	0.0	
200A.D	200.2	200.2	200.3	200.0	
RINSE2A.D	0.0	0.0	0.0	rinse water	
ACIDBS1.D	106.0	6.4	17.0		
ACIDBS2.D	152.0	12.0	26.1		
ACIDBS3.D	119.0	9.1	62.0		
ACIDBS4.D	145.4	8.9	70.1		
ACIDBS1R.D	115.1	7.4	17.3		
ACIDBS2R.D	164.4	14.9	24.7		
ACIDBS5.D	134.2	15.8	67.3		
ACIDBLK1.D	48.4	0.6	0.5		
ACIDBS6.D	85.7	20.1	48.7		
ACIDBS7.D	87.1	7.3	20.7		
ACIDBS8.D	103.6	10.1	59.7		
40B.D	40.0	41.4	40.1	40.0	
8B.D	8.8	8.0	8.2	8.0	
1_6B.D	1.9	1.6	1.5	1.6	
0B.D	0.2	0.0	0.0	0.0	
ACIDBS9.D	120.4	13.6	96.5		
ACIDBS10.D	110.1	11.9	71.0		
ACIDBS11.D	108.4	15.8	85.6		
ACIDBS12.D	114.8	16.4	146.3		
ACIDBS13.D	127.6	14.6	91.5		
ACIDBS14.D	87.5	8.2	47.2		
ACIDBS15.D	90.4	8.6	35.9		
ACIDBLK2.D	53.4	0.6	0.3		
ACIDBS16.D	95.6	8.3	52.6		
ACIDBS17.D	94.3	8.6	41.0		
ACIDBS18.D	126.2	12.9	76.6		
40C.D	42.9	34.8	42.3	40.0	
8C.D	9.4	6.9	8.3	8.0	
1_6C.D	2.0	1.4	1.6	1.6	
0_32C.D	0.7	0.3	0.4	0.3	
0C.D	0.2	0.0	0.0	0.0	

Table C6 b: ICP- MS Elemental Analyses and Check Standard Data for Acid Digestion Dust and Soil Samples (Cont.).

Element	V / 51	Se / 82	Sb / 121	Standard value (ppb)
<i>Sample Name</i>				
ACIDBS19.D	128.3	19.8	149.4	
ACIDBS20.D	181.2	15.5	112.9	
ACIDBS21.D	96.4	9.7	52.5	
ACIBS19R.D	132.4	18.1	143.9	
ACIDBS22.D	147.5	11.7	40.4	
ACIDBS23.D	76.8	3.0	11.9	
ACIDBS24.D	156.3	16.0	112.7	
ACIDBS25.D	132.1	13.2	80.3	
ACIDBLK3.D	64.2	0.4	0.3	
ACIDBS26.D	117.5	10.5	80.5	
ACIDBS27.D	135.6	13.6	113.3	
40D.D	45.2	30.2	43.5	40.0
8D.D	9.9	6.4	8.8	8.0
1_6D.D	2.1	1.2	1.6	1.6
0D.D	0.3	0.0	0.0	0.0
ACIDBS28.D	153.0	15.0	112.5	
ACIDBS29.D	143.9	7.1	30.3	
ACIDBS30.D	190.0	8.2	17.0	
ACIDBS31.D	211.5	8.0	16.2	
ACIDBS32.D	154.4	6.1	22.7	
ACIDBS33.D	160.5	6.6	25.3	
ACIDBS34.D	214.6	16.5	38.9	
ACIDBS35.D	159.5	5.9	12.1	
ACIDBLK4.D	66.7	0.3	0.2	
ACIDBS36.D	147.5	5.9	27.4	
200E.D	230.7	151.6	226.1	200.0
40E.D	49.9	33.9	49.0	40.0
8E.D	9.2	5.9	8.4	8.0
1_6E.D	2.1	1.2	1.6	1.6
0E.D	0.3	0.0	0.0	0.0
ACIDBS37.D	230.2	10.5	34.2	
ACIDBS38.D	200.4	8.4	29.2	
ACIDBS39.D	238.4	10.4	19.7	
ACIDBS40.D	251.7	15.7	86.8	
ACIDBS41.D	152.7	7.4	29.6	
ACIDBS42.D	164.9	7.7	36.9	
ACIDBS43.D	179.2	8.4	19.8	
ACIDBS44.D	169.0	7.8	27.6	
ACIDBS45.D	143.1	4.5	8.2	
ACIDBLK5.D	79.6	0.4	0.2	
ACIDBS46.D	152.4	5.4	13.9	

Table C6 c: ICP- MS Elemental and Check Standard Data for Acid Digestion of Dust Samples and Soil Samples (Cont.).

Element	V / 51	Se / 82	Sb / 121	Standard value (ppb)
<i>Sample Name</i>				
40F.D	40.9	30.0	42.4	40.0
8F.D	8.4	5.8	8.5	8.0
1_6F.D	1.9	1.2	1.6	1.6
0_32F.D	0.6	0.2	0.3	0.3
0F.D	0.2	0.0	0.0	0.0
ACIDBS47.D	198.6	8.5	22.0	
ACIDBS48.D	275.4	14.9	31.7	
ACIDBS49.D	218.5	11.0	30.9	
ACIDBS50.D	156.4	5.5	12.0	
ACIDBS51.D	186.2	8.5	20.1	
ACIDBLK6.D	79.7	0.4	0.2	
ELPBLK1.D	210.1	1.3	1.2	
BSELP1.D	382.5	12.4	2.4	
BSELP2.D	276.4	9.2	2.0	
BSELP3.D	262.3	7.0	2.0	
ELPBLK2.D	217.2	1.4	1.2	
200G.D	189.9	145.9	211.0	200.0
40G.D	38.7	29.1	40.5	40.0
8G.D	7.8	5.9	7.6	8.0
1_6G.D	2.0	1.2	1.6	1.6
0G.D	0.3	0.0	0.0	0.0
BSELP4.D	285.2	6.9	2.3	
BSELP5.D	258.8	30.4	1.5	
BSELP6.D	350.3	12.1	2.3	
BSELP7.D	534.0	15.2	2.4	
BSELP8.D	228.8	46.9	1.5	
BSELP9.D	430.1	22.3	1.5	
BSELP10.D	331.7	30.2	3.4	
BSELP11.D	357.8	47.5	2.3	
BSELP12.D	649.1	94.5	3.8	
ELPBLK3.D	414.2	3.4	1.2	
BLANKR.D	1.4	0.1	0.0	0.0
0_32R.D	1.1	0.4	0.3	0.3
1_6R.D	1.8	1.3	1.4	1.6
8R.D	7.6	6.6	7.8	8.0
40R.D	36.8	32.3	40.5	40.0
200R.D	185.3	162.9	209.5	200.0
1000.D	893.5	803.6	1004.8	1000.0

**Note: standards less than or greater than 10% from true values highlighted in red**

Description	id	Decades	*Age	Fe	Mn	Ba	Zn	Pb	As	Cd	Cu	Al	Ti	Sr	K	Na	Mg	V	Se	Sb
K1 new	K1	1960-70	50	1.64	1.33	2.87	84.33	79.24	13.31	67.45	84.70	1.73	16.36	12.20	2.54	4.29	0.99	3.96	2.59	157.65
K1 old	K2	1920-30	85	2.24	1.32	1.02	65.64	90.01	27.13	92.08	74.50	1.90	18.07	10.16	2.95	4.14	1.26	4.33	2.85	135.56
K2 new roof	K3	1970-80	32	5.33	3.88	3.82	146.19	111.03	37.81	139.95	504.30	1.87	3.72	1.83	2.92	3.71	1.52	3.72	2.83	429.68
K2 old attic	K4	1940-50	68	4.81	4.07	4.30	175.02	146.56	56.83	211.10	460.69	2.30	4.92	2.41	3.95	7.22	1.76	5.61	2.89	509.83
K3 wood	K5	1920-30	82	5.53	3.05	4.24	966.48	177.99	44.98	183.01	429.55	1.77	3.49	1.66	3.28	11.06	1.66	4.51	4.89	447.83
K3 galv	K6	1920-30	82	7.16	2.57	2.57	3632.41	175.59	41.20	197.79	327.98	1.16	2.83	1.32	2.90	18.95	1.26	2.64	10.16	525.19
K3 scullie	K7	1990-2000	10	2.69	3.38	3.70	169.43	52.90	19.01	82.86	237.27	1.53	3.53	2.07	2.78	3.50	1.37	2.93	3.70	234.68
K4 post 89	K8	1980-90	17	3.17	3.37	4.85	261.51	109.80	33.82	168.50	409.14	1.65	3.46	2.06	3.96	7.57	1.34	3.75	4.25	554.60
K4 back beam	K9	1940-50	61	3.49	3.79	6.14	213.02	345.19	119.36	565.22	493.07	1.94	4.63	2.01	4.18	4.30	1.73	4.96	5.66	864.39
K4 transect	K10	1940-50	61	3.62	3.08	4.29	139.44	342.98	72.43	278.71	588.46	1.56	3.14	1.64	1.11	-0.18	1.22	3.97	4.91	621.42
K5 near vent	K11	1930-40	72	3.34	2.69	3.45	149.31	384.46	91.47	346.77	784.63	1.52	3.07	1.40	2.36	1.44	1.28	3.44	6.14	679.73
K5 side	K12	1930-40	72	3.98	4.67	4.96	1792.19	316.47	137.04	430.94	662.28	1.89	5.01	2.23	2.73	2.65	1.67	6.05	10.04	1811.44
K5 far vent	K13	1930-40	72	2.88	5.57	6.39	478.77	328.80	144.46	659.04	478.23	1.98	4.31	2.41	3.77	4.11	1.57	5.21	6.39	805.10
K6 R beam	K14	1930-40	68	2.29	2.48	2.39	154.10	172.83	64.38	224.97	370.49	1.31	2.69	1.34	4.69	6.01	1.78	2.21	3.70	428.65
K6 new attic	K15	1950-60	50	2.08	3.35	3.55	103.20	130.43	60.02	208.68	272.17	1.45	3.52	2.01	0.83	-0.27	0.90	2.82	4.67	387.11
K6 M1&2	K16	1930-40	68	3.43	3.37	3.76	110.81	238.23	56.03	296.13	492.44	1.67	5.22	1.34	1.52	0.87	1.39	3.96	5.59	687.35
K6 4-8	K17	1930-40	68	2.59	2.48	3.75	150.06	147.18	45.91	243.46	246.03	1.63	5.26	1.77	2.60	2.76	1.63	3.17	5.03	458.68
K7 1	K18	1910-20	91	2.38	2.62	4.00	92.33	253.66	94.74	315.06	390.89	1.85	3.94	1.61	3.16	2.64	1.38	4.07	5.19	565.35
K7 west beam	K19	1910-20	91	4.41	3.94	5.10	255.25	697.64	219.83	782.19	1048.70	2.51	5.20	1.73	3.66	2.86	1.75	5.11	9.95	1343.09
K7 Beam 2	K20	1910-20	91	4.09	3.66	5.68	157.55	328.50	132.62	423.91	450.94	2.81	5.51	2.19	4.24	3.23	1.89	5.87	5.01	646.10
K7 east beam	K21	1910-20	91	2.32	3.45	4.05	84.49	222.22	82.77	369.41	409.15	1.78	3.57	1.86	3.75	4.62	1.65	3.01	5.68	545.95
K7 3 wool	K22	1990-2000	10	3.16	4.45	5.36	223.25	67.84	29.96	133.42	168.81	2.33	4.44	2.62	3.91	3.30	1.92	5.20	4.93	288.28
K7 Res. Light	K23	2000-10	3	2.66	4.52	4.69	170.25	70.85	34.92	124.03	166.07	1.78	6.46	2.21	2.90	2.28	1.50	3.39	4.61	345.42
K8 left corner	K24	1920-30	83	3.09	3.47	4.37	162.64	381.77	142.98	521.83	568.00	2.44	5.40	1.89	3.38	3.18	1.21	5.11	6.31	722.55
K8 center right window	K25	1920-30	83	2.90	3.05	3.72	147.34	498.58	98.32	522.73	783.61	2.29	4.73	2.19	3.43	3.48	1.40	5.22	7.25	712.37
K8 windows & center left	K26	1920-30	83	2.47	3.34	3.32	123.80	399.47	104.85	555.00	639.72	1.88	4.86	1.61	3.51	3.14	1.46	4.80	7.00	843.79
K8 center left 2	K27	1920-30	83	2.88	3.37	3.45	153.46	555.47	143.72	664.12	835.37	1.72	3.80	1.93	3.02	2.67	1.49	5.83	8.55	1084.30
K8 far left 1	K28	1920-30	83	6.40	3.12	4.66	152.72	547.32	107.19	529.87	916.60	4.45	10.89	1.75	4.47	2.97	1.89	8.09	10.54	1196.50
L1 a+b+c	G1	1920-30	83	5.79	2.34	6.97	102.18	156.92	45.35	130.13	196.53	4.81	8.64	2.14	4.85	3.53	2.16	5.88	3.94	259.59
L1 E Keytop	G2	1980-90	20	6.33	2.54	4.37	53.46	35.08	20.70	48.06	100.55	5.32	9.70	1.70	4.92	3.36	2.10	6.96	3.40	107.31
L1 E Kneeeler	G3	1990-2000	15	7.07	3.63	4.65	49.69	27.22	18.68	35.70	110.03	5.89	10.18	2.12	5.75	5.25	2.40	7.91	3.22	99.85
L2 attic bag	G4	1960-70	40	5.39	3.94	4.68	83.11	33.55	9.72	101.44	115.35	4.42	8.68	2.21	4.50	3.44	1.98	6.79	3.38	196.91
L2 Beam	G5	1920-30	83	5.65	3.73	5.76	126.54	117.28	29.86	114.29	159.69	5.05	10.23	2.26	4.34	2.90	1.90	8.43	4.24	255.13
L2 attic pipe	G6	1990-2000	14	6.23	2.11	5.69	1712.57	166.14	36.62	81.27	172.74	5.43	9.34	1.80	3.81	2.70	2.13	9.71	8.20	290.33
L2 attic airconditioner	G7	2000-10	7	5.17	2.92	5.06	146.25	42.76	17.27	27.30	104.63	4.34	7.37	2.20	4.62	3.99	2.24	6.96	3.19	101.17
L3 attic door	G8	1990-2000	14	5.17	2.53	4.93	132.62	49.03	10.22	30.03	277.41	4.33	8.65	1.72	3.36	1.98	1.79	7.18	3.74	276.96
S1 window	G9	1920-30	80	4.99	2.21	4.35	32.29	72.07	14.43	61.20	139.89	4.23	5.97	1.94	4.43	3.12	2.11	6.11	2.91	146.79
S2 window	G10	1920-30	80	5.39	2.88	5.06	40.21	95.83	24.46	95.16	168.74	4.72	6.58	1.92	4.97	4.32	2.21	7.20	3.28	177.58
J1 V1 + V2 closet and toilet	J1	1980-90	18	5.28	3.23	8.99	363.87	104.03	34.76	94.37	118.06	3.54	5.62	3.35	4.66	3.02	1.44	8.08	5.06	429.04
J V3 seats	J2	1980-90	20	4.39	3.62	6.53	95.57	99.50	26.72	110.41	139.98	3.08	6.46	2.34	6.92	4.61	1.44	7.39	4.39	276.75
J V4 + V5	J3	1940-50	47	46.47	4.12	6.49	185.95	148.10	37.08	217.60	412.76	3.62	5.11	2.38	7.53	6.55	1.16	7.42	4.01	296.44
J V6 glass bulb	J4	1990-2000	12	5.57	3.54	8.32	52.85	30.05	22.18	46.82	196.79	3.17	7.46	3.53	5.03	3.76	1.25	10.45	5.30	192.34
LH N1	G12	1910-20	88	5.93	3.89	8.18	77.41	92.27	25.62	90.89	258.27	4.00	7.40	2.31	8.13	10.33	2.56	10.34	5.20	282.60
LH N2	G13	1910-20	88	3.06	1.99	3.43	24.10	24.38	6.31	16.74	53.69	2.08	4.38	1.58	3.15	4.43	1.81	6.85	2.57	71.97
LH N3	G14	1910-20	88	5.64	3.25	5.38	56.36	40.28	18.05	39.30	120.72	4.34	7.73	1.99	4.82	1.96	2.71	9.23	3.57	142.35
LH beam N4+N5	G15	1910-20	88	3.98	1.83	4.78	34.24	50.60	12.16	29.27	75.00	3.26	4.47	1.47	3.22	1.32	2.03	7.47	3.16	124.46
LS N1 + N2	G16	1930-40	72	8.93	4.44	7.46	355.59	72.12	25.26	61.69	139.48	4.55	8.74	3.40	5.45	2.89	3.09	12.01	5.81	186.64
LS N3 +N4	G17	1930-40	72	5.52	2.72	6.05	81.25	101.32	23.57	81.95	139.48	4.55	8.69	1.91	4.02	1.94	2.55	9.22	4.37	186.81
LS N5 +6 window	G18	1930-40	72	4.66	4.17	5.04	93.07	65.60	16.56	51.85	110.52	3.53	7.50	1.86	4.29	3.91	2.22	9.95	3.68	126.71
LS N7-9 window	G19	1930-40	72	5.45	3.48	5.16	56.78	52.15	18.83	47.68	133.10	4.15	8.49	2.00	3.74	2.11	1.87	8.83	3.91	145.37

\*Note: Dust age up to 2007

Table C7: Enrichment Factors

## APPENDIX D

### Results of MANCOVA Tests

Table D1: Results of test “Age by Group Interaction” for the  $\ln EF_{Fe}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	2.81552409	0.93850803	9.95	<.0001
Error	41	3.86846437	0.09435279		
Corrected Total	44	6.68398846			

R-Square	Coeff Var	Root MSE	logFe Mean
0.421234	21.92703	0.307169	1.400869

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	1.05133593	1.05133593	11.14	0.0018
Age_to_2007_	1	0.00255809	0.00255809	0.03	0.8700
Age_to_2007_*Group	1	0.14917566	0.14917566	1.58	<b>0.2157 ns</b>

ns = no significant interaction so can use Age as covariate

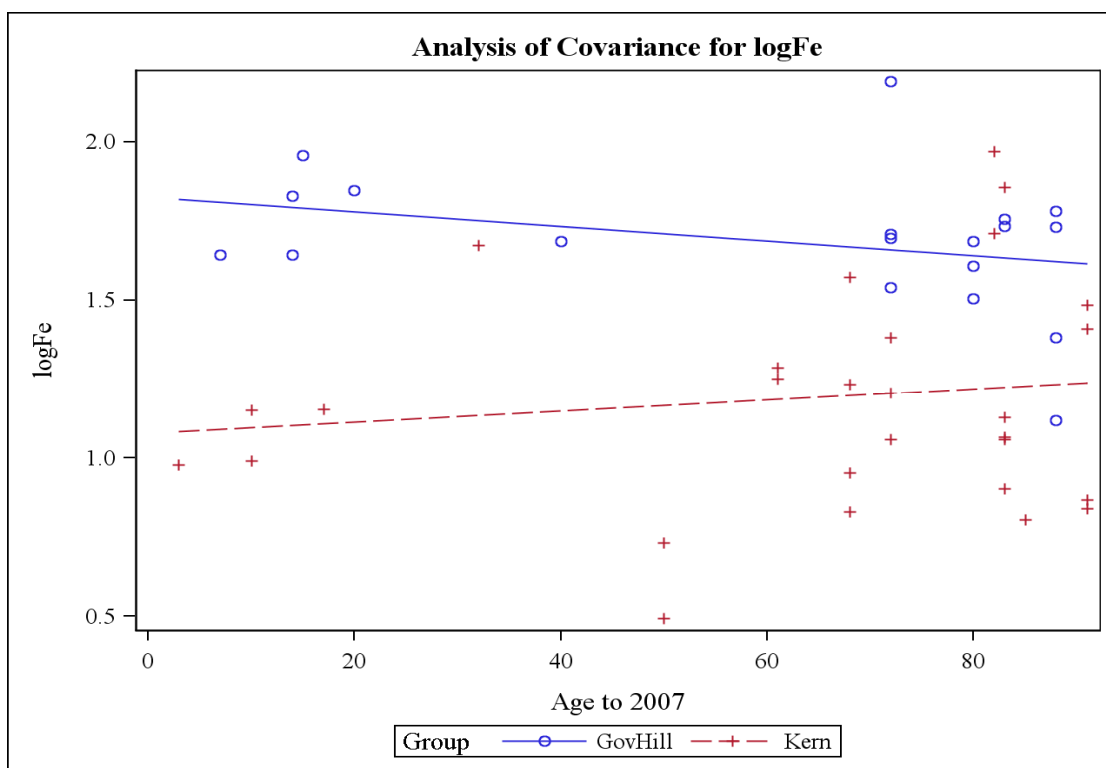


Figure D1: The  $\ln EF_{Fe}$  distribution with age of dust in 2 groups (locations of El Paso). The regression lines are fitted according to “Age by Group Interaction” test.

Table D2: Results of “Age effect” and “Group effect” tests for the  $\ln EF_{Fe}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	2.89675914	1.44837957	15.04	<.0001
Error	44	4.23609330	0.09627485		
Corrected Total	46	7.13285244			

R-Square	Coeff Var	Root MSE	logFe Mean
0.406115	22.41602	0.310282	1.384197

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	2.88476199	2.88476199	29.96	<.0001 *
Age_to_2007_	1	0.00002019	0.00002019	0.00	0.9885

\* = significant Group effect at the 0.05 alpha level

Group	logFe LSMEAN	H0:LSMean1=LSMean2 Pr >  t
GovHill	1.68562577	<.0001
Kern	1.17965576	

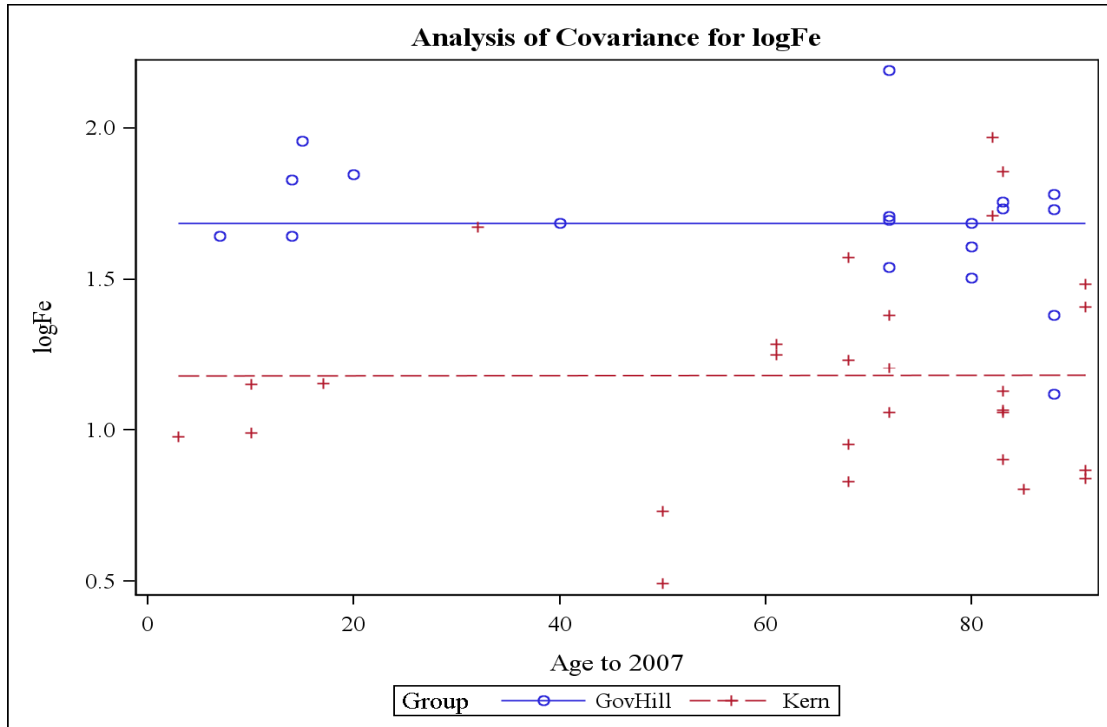


Figure D2: The  $\ln EF_{Fe}$  distribution with dust age in 2 groups (locations of El Paso). The fitted parallel lines illustrate “Group effect”.

Table D3: Results of test “Age by Group Interaction” for the  $EF_{Mn}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	2.62041657	0.87347219	1.13	0.3501
Error	41	31.82984650	0.77633772		
Corrected Total	44	34.45026306			

R-Square	Coeff Var	Root MSE	Mn Mean
0.076064	27.44851	0.881100	3.210011

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	1.77437256	1.77437256	2.29	0.1383
Age_to_2007_	1	0.49703871	0.49703871	0.64	0.4282
Age_to_2007_*Group	1	0.90646839	0.90646839	1.17	<b>0.2862 ns</b>

**ns = no significant interaction so can use Age as covariate**

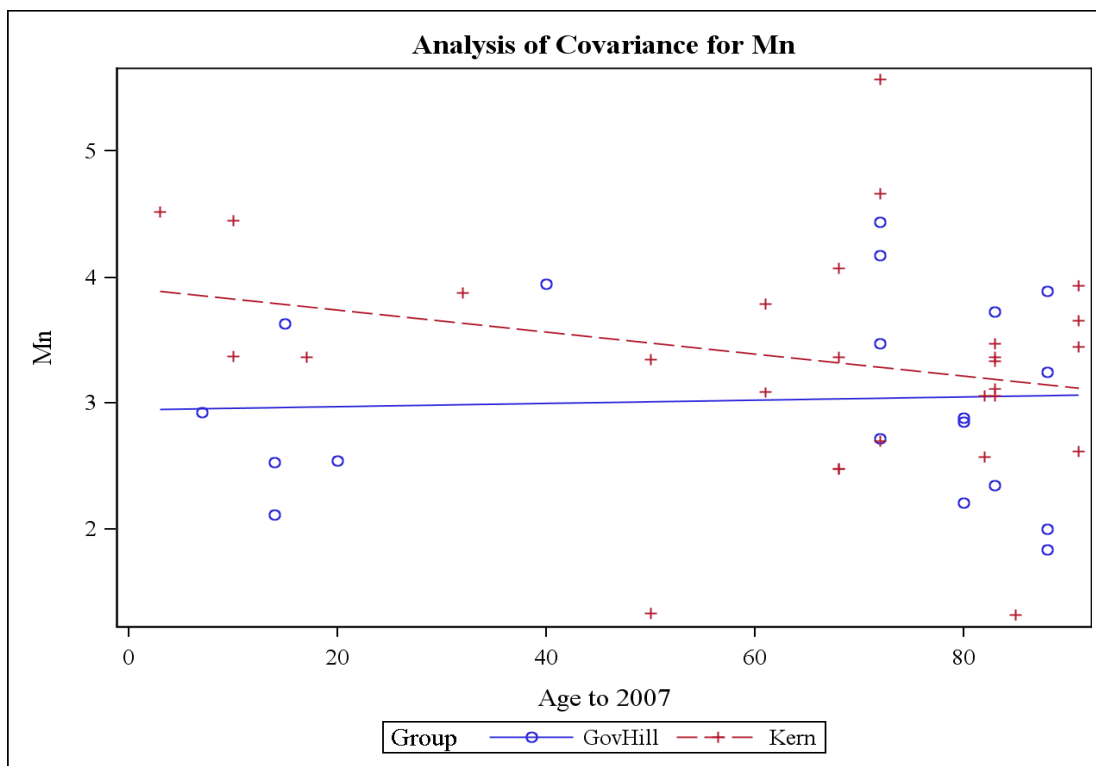


Figure D3: The  $EF_{Mn}$  distribution with age of dust in 2 groups (locations of El Paso). The regression lines are fitted according to “Age by Group Interaction” test.

Table D4: Results of “Age effect” and “Group effect” tests for the  $EF_{Mn}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	1.67317665	0.83658833	1.12	0.3348
Error	44	32.81281564	0.74574581		
Corrected Total	46	34.48599229			

R-Square	Coeff Var	Root MSE	Mn Mean
0.048518	26.89928	0.863566	3.210368

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	1.21159159	1.21159159	1.62	<b>0.2091 ns</b>
Age_to_2007_	1	0.56491987	0.56491987	0.76	0.3888

**ns = no significant Group effect**

Group	Mn LSMEAN	H0:LSMean1=LSMean2 Pr >  t
GovHill	3.01502000	0.2091
Kern	3.34292490	

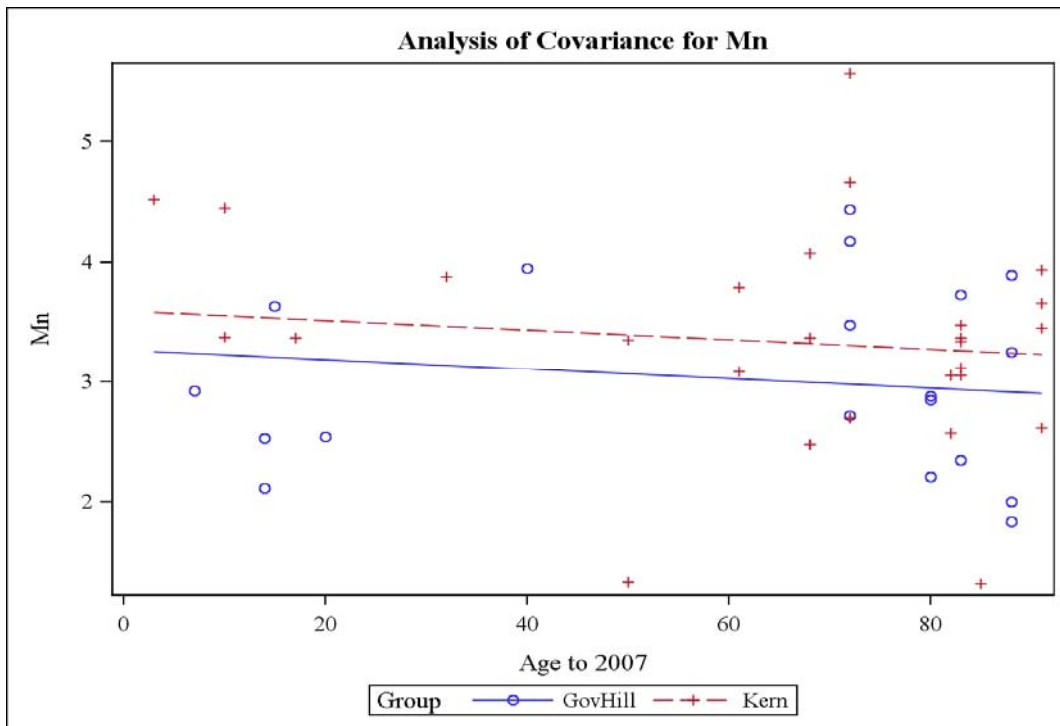


Figure D4: The  $EF_{Mn}$  distribution with dust age in 2 groups (locations of El Paso). The fitted parallel lines illustrate “Group effect”.

Table D5: Results of “Age by Group Interaction” test for the  $EF_{As}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	63679.2819	21226.4273	19.30	<.0001
Error	41	45088.9385	1099.7302		
Corrected Total	44	108768.2204			

R-Square	Coeff Var	Root MSE	As Mean
0.585459	59.37422	33.16218	55.85282

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	143.03587	143.03587	0.13	0.7202
Age_to_2007_	1	10964.75932	10964.75932	9.97	0.0030
Age_to_2007_*Group	1	10279.68287	10279.68287	9.35	<b>0.0039 *</b>

**\* = significant interaction so cannot use Age as covariate**

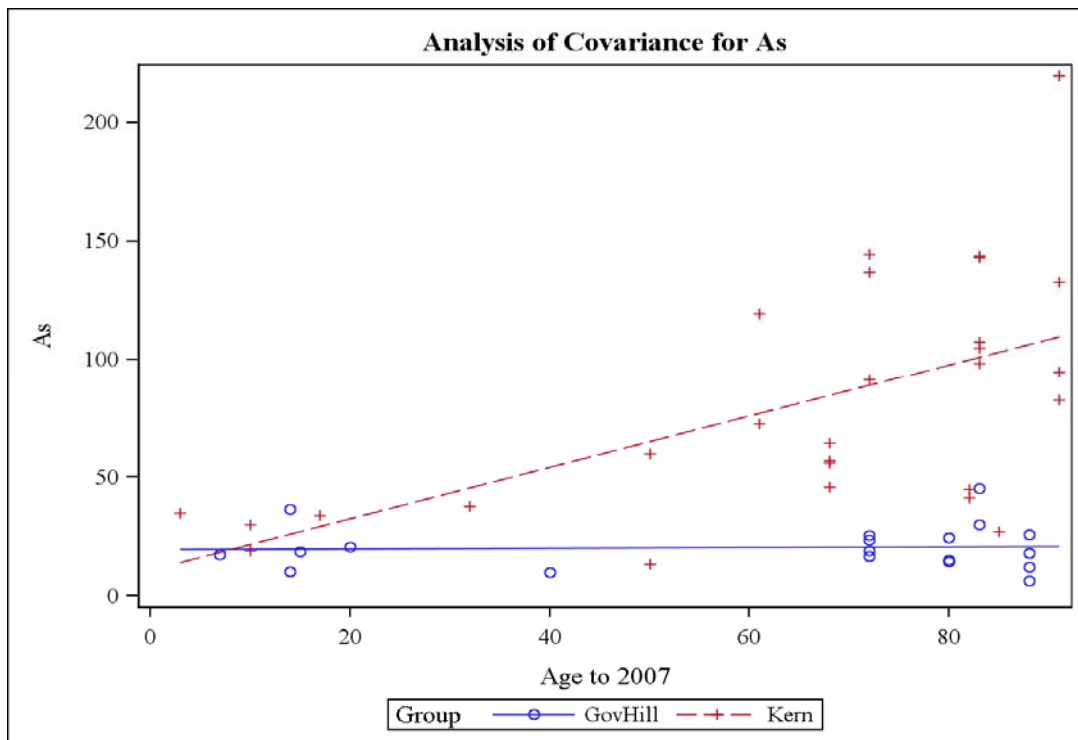


Figure D5: The  $EF_{As}$  distribution with age of dust in 2 groups (locations of El Paso). The regression lines are fitted according to “Age by Group Interaction” test.

Table D6: Results of the ANOVA test “Group effect” for the EF<sub>As</sub>.

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	40955.5922	40955.5922	27.06	<.0001
Error	45	68095.7228	1513.2383		
Corrected Total	46	109051.3151			

R-Square	Coeff Var	Root MSE	As Mean
0.375563	69.10191	38.90036	56.29420

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	40955.59222	40955.59222	27.06	<.0001 *

**\* = significant Group effect at the 0.05 alpha level**

Means with the same letter are not significantly different.			
t Grouping	Mean	N	Group
A	80.61	28	Kern
B	20.46	19	GovHill

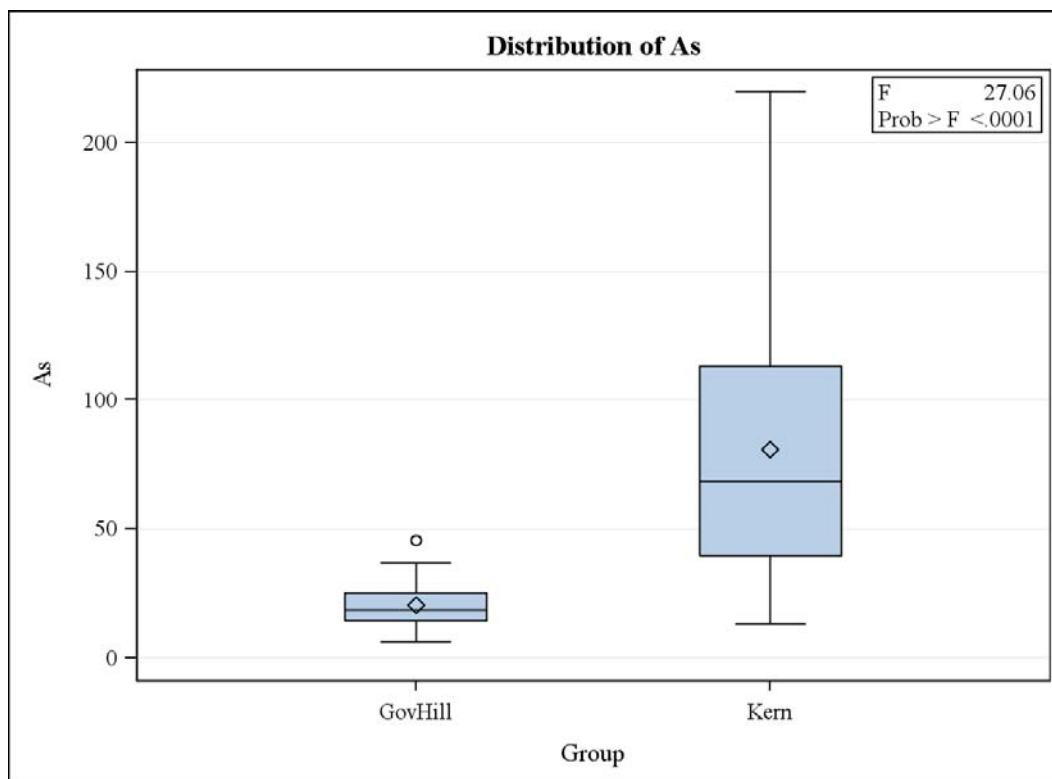


Figure D6: Box plots of EF<sub>As</sub> distribution in 2 groups (locations of El Paso).

Table D7: Results of “Age by Group Interaction” test for the EF<sub>Cu</sub>.

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	15.30006110	5.10002037	17.43	<.0001
Error	41	11.99771267	0.29262714		
Corrected Total	44	27.29777377			

R-Square	Coeff Var	Root MSE	logCu Mean
0.560488	9.775250	0.540950	5.533876

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	0.21913572	0.21913572	0.75	0.3919
Age_to_2007_	1	0.81229109	0.81229109	2.78	0.1033
Age_to_2007_*Group	1	1.20818485	1.20818485	4.13	<b>0.0487 *</b>

**\* = significant interaction so cannot use Age as covariate**

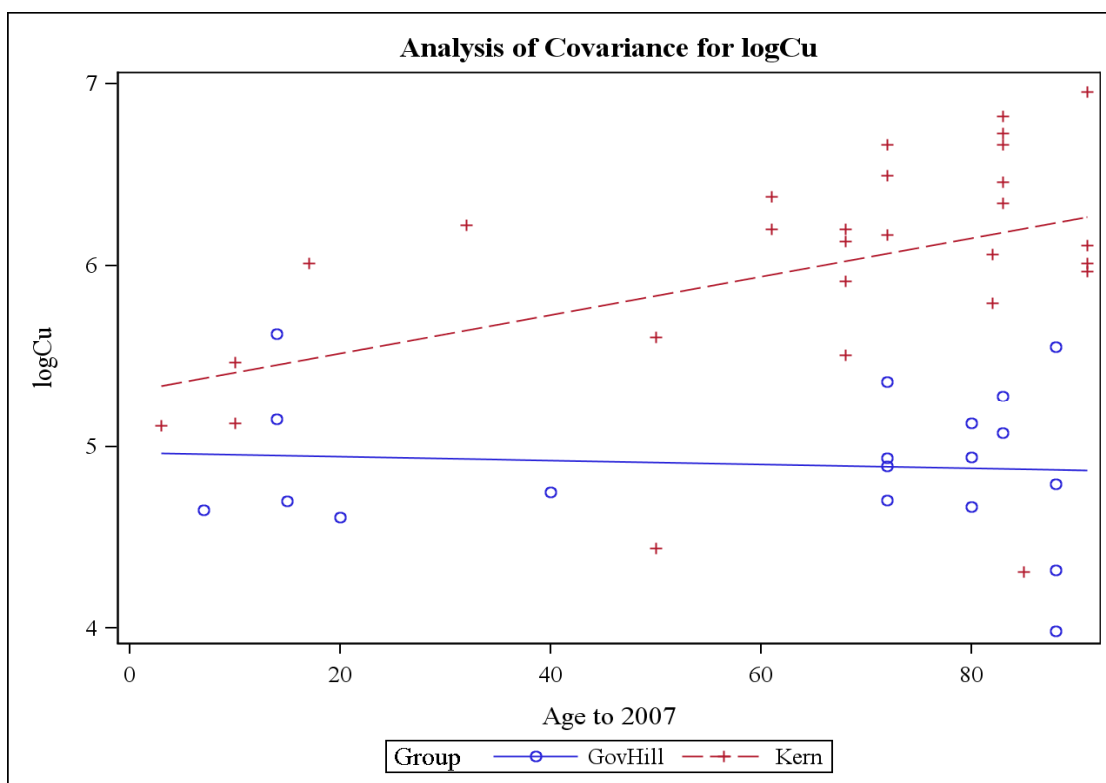


Figure D7: The EF<sub>Pb</sub> distribution with age of dust in 2 groups (locations of El Paso). The regression lines are fitted according to “Age by Group Interaction” test.

Table D8: Results of the ANOVA test “Group effect” for the  $\ln EF_{Cu}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	13.56560684	13.56560684	42.30	<.0001
Error	45	14.43128772	0.32069528		
Corrected Total	46	27.99689455			

R-Square	Coeff Var	Root MSE	logCu Mean
0.484540	10.19741	0.566300	5.553369

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	13.56560684	13.56560684	42.30	<.0001 *

\* = significant Group effect at the 0.05 alpha level

Means with the same letter are not significantly different.			
t Grouping	Mean	N	Group
A	5.9959	28	Kern
B	4.9012	19	GovHill

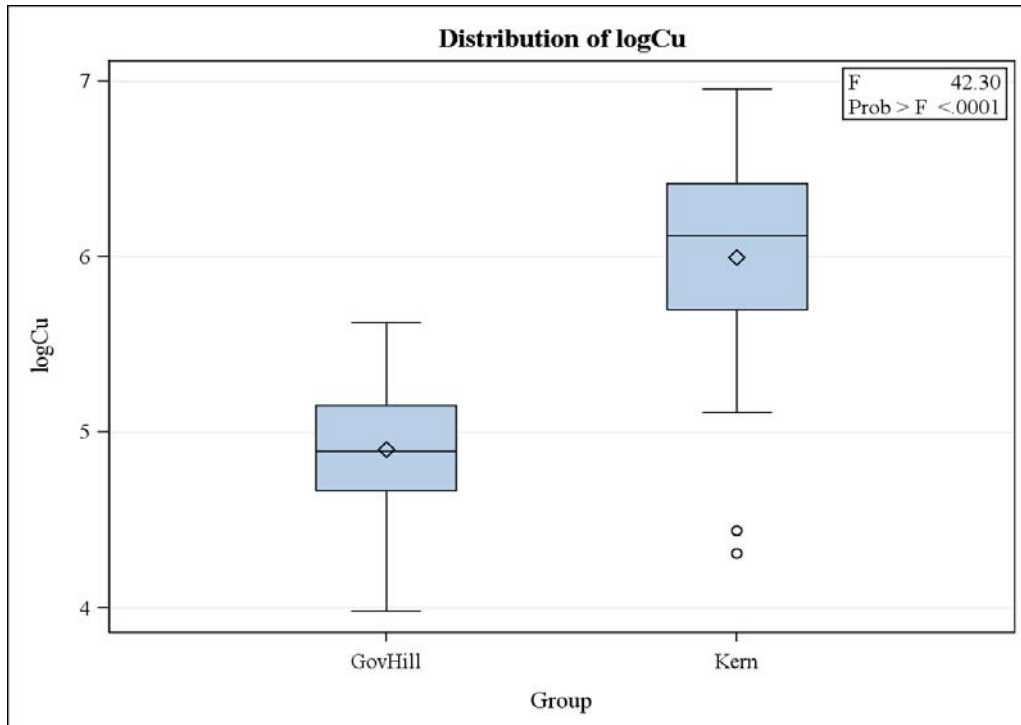


Figure D8: Box plots of  $\ln EF_{Cu}$  distribution in 2 groups (locations of El Paso).

Table D9: Results of “Age by Group Interaction” test for the  $\ln EF_{Ti}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	2.38303404	0.79434468	5.15	0.0041
Error	41	6.32777267	0.15433592		
Corrected Total	44	8.71080671			

R-Square	Coeff Var	Root MSE	logTi Mean
0.273572	22.16841	0.392856	1.772144

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	1.08764542	1.08764542	7.05	0.0113
Age_to_2007_	1	0.08479484	0.08479484	0.55	0.4628
Age_to_2007_*Group	1	0.25358051	0.25358051	1.64	<b>0.2071 ns</b>

**ns = no significant interaction so can use Age as covariate**

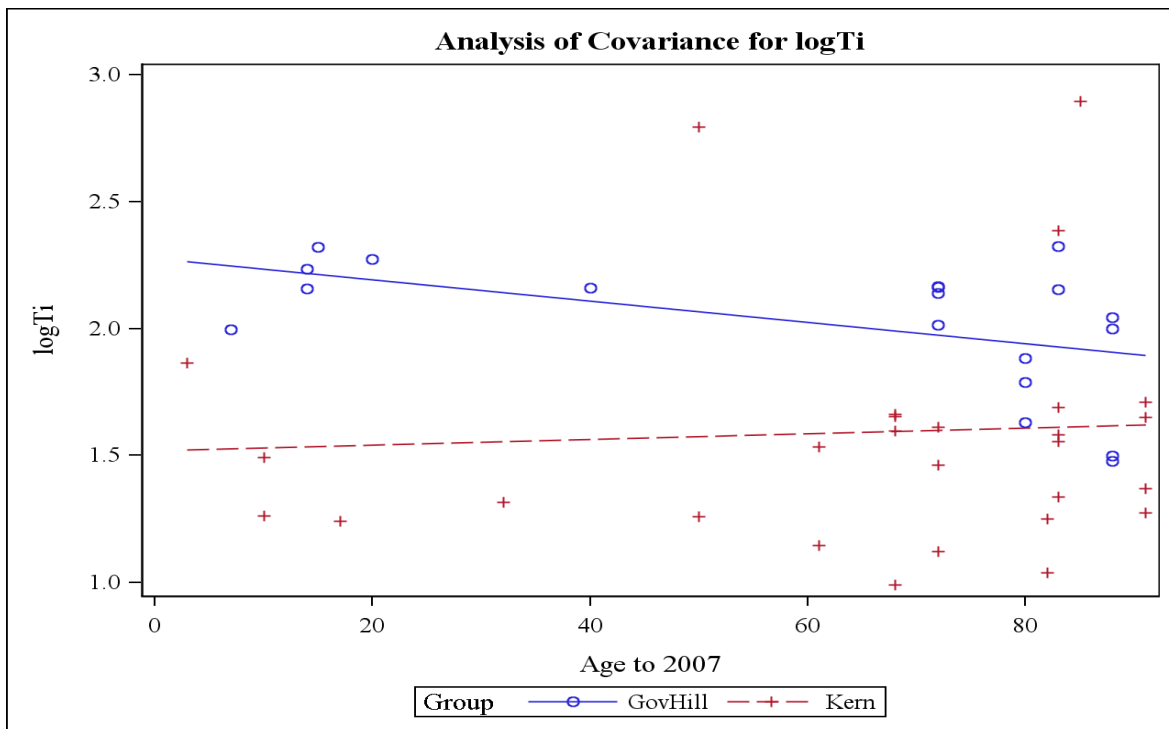


Figure D9: The  $EF_{pb}$  distribution with age of dust in 2 groups (locations of El Paso). The regression lines are fitted according to “Age by Group Interaction” test.

Table D10: Results of “Age effect” and “Group effect” tests for the  $\ln EF_{Ti}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	2.45602356	1.22801178	7.85	0.0012
Error	44	6.88293535	0.15643035		
Corrected Total	46	9.33895891			

R-Square	Coeff Var	Root MSE	logTi Mean
0.262987	22.62791	0.395513	1.747898

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	2.34551136	2.34551136	14.99	<b>0.0004 *</b>
Age_to_2007_	1	0.05248305	0.05248305	0.34	0.5654

**\* = significant Group effect at the 0.05 alpha level**

Group	logTi LSMEAN	H0:LSMean1=LSMean2 Pr >  t
GovHill	2.01969726	0.0004
Kern	1.56346231	

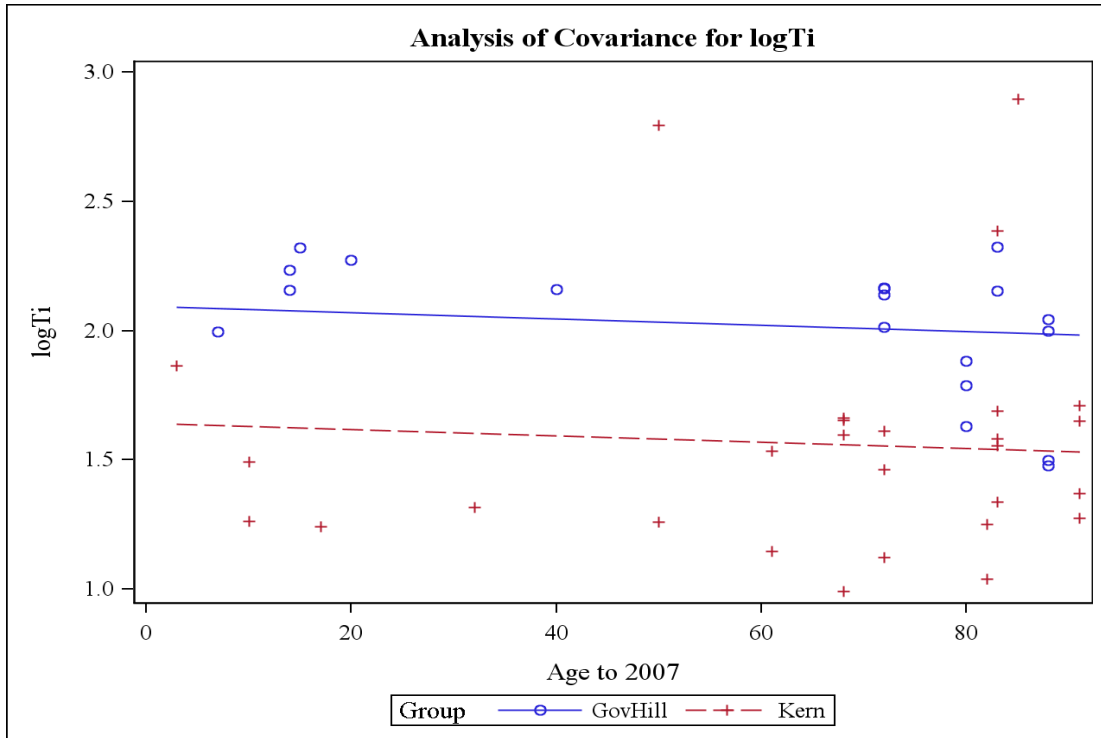


Figure D10: The  $\ln EF_{Ti}$  distribution with dust age in 2 groups (locations of El Paso). The fitted parallel lines illustrate “Group effect”.

Table D11: Results of “Age by Group Interaction” test for the  $\ln EF_{Sr}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	0.17217248	0.05739083	0.32	0.8095
Error	41	7.30921984	0.17827365		
Corrected Total	44	7.48139232			

R-Square	Coeff Var	Root MSE	logSr Mean
0.023013	58.24436	0.422225	0.724919

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	0.10420044	0.10420044	0.58	0.4489
Age_to_2007_	1	0.04601190	0.04601190	0.26	0.6142
Age_to_2007_*Group	1	0.05179323	0.05179323	0.29	<b>0.5928 ns</b>

**ns = no significant interaction so can use Age as covariate**

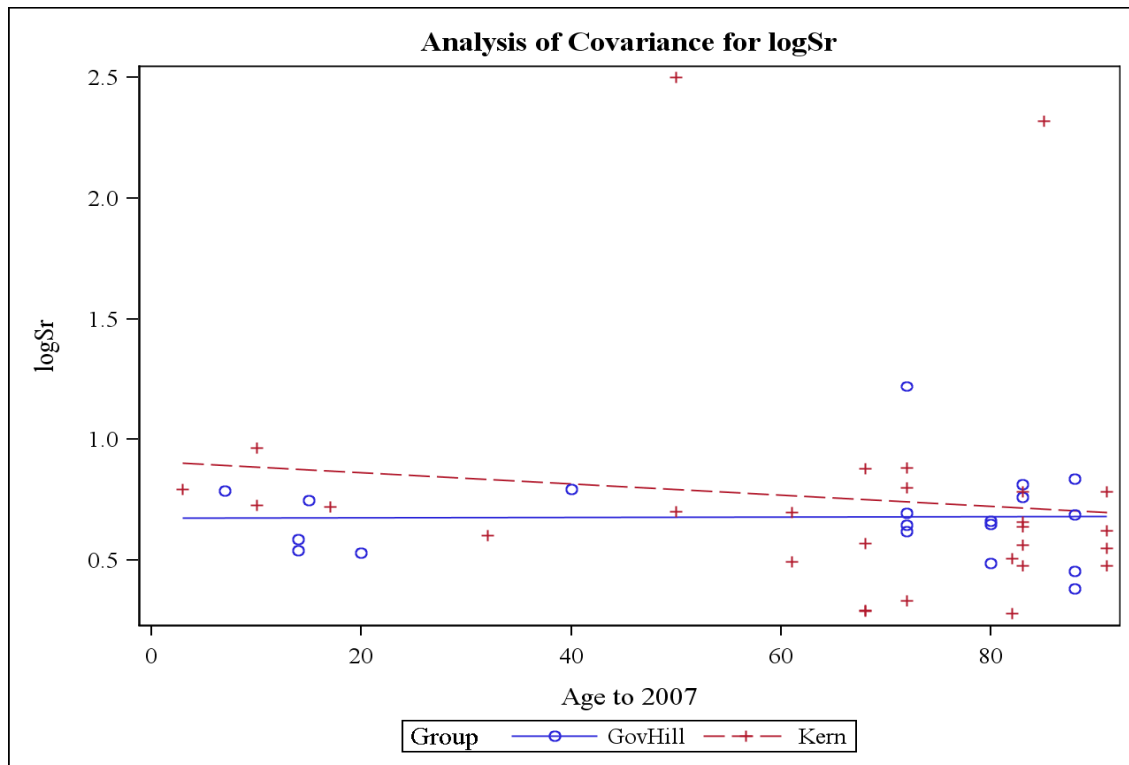


Figure D11: The  $\ln EF_{Sr}$  distribution with age of dust in 2 groups (locations of El Paso). The regression lines are fitted according to “Age by Group Interaction” test.

Table D12: Results of “Age effect” and “Group effect” tests for the  $\ln EF_{Sr}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	0.09880220	0.04940110	0.29	0.7480
Error	44	7.43543628	0.16898719		
Corrected Total	46	7.53423848			

R-Square	Coeff Var	Root MSE	logSr Mean
0.013114	57.13660	0.411081	0.719470

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	0.05823581	0.05823581	0.34	<b>0.5602 ns</b>
Age_to_2007_	1	0.04714309	0.04714309	0.28	0.6000

**ns = no significant Group effect at the 0.05 alpha level**

Group	logSr LSMEAN	H0:LSMean1=LSMean2 Pr >  t
GovHill	0.67664192	0.5602
Kern	0.74853132	

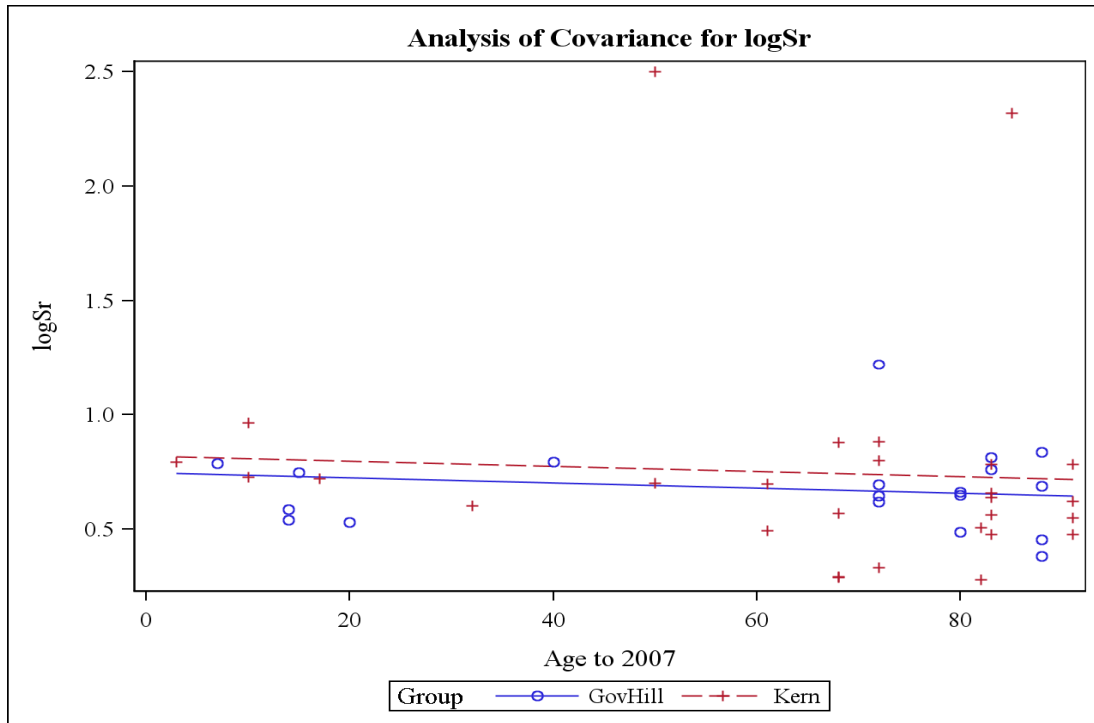


Figure D12: The  $\ln EF_{Sr}$  distribution with dust age in 2 groups (locations of El Paso). The fitted parallel lines illustrate non significant “Group effect”.

Table D13: Results of “Age by Group Interaction” test for the  $EF_K$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	21.03358150	7.01119383	7.28	0.0005
Error	41	39.47623029	0.96283489		
Corrected Total	44	60.50981179			

R-Square	Coeff Var	Root MSE	K Mean
0.347606	25.12610	0.981242	3.905268

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	2.75759729	2.75759729	2.86	0.0982
Age_to_2007_	1	0.57629725	0.57629725	0.60	0.4436
Age_to_2007_*Group	1	0.06449478	0.06449478	0.07	<b>0.7971 ns</b>

**ns = no significant interaction so can use Age as covariate**

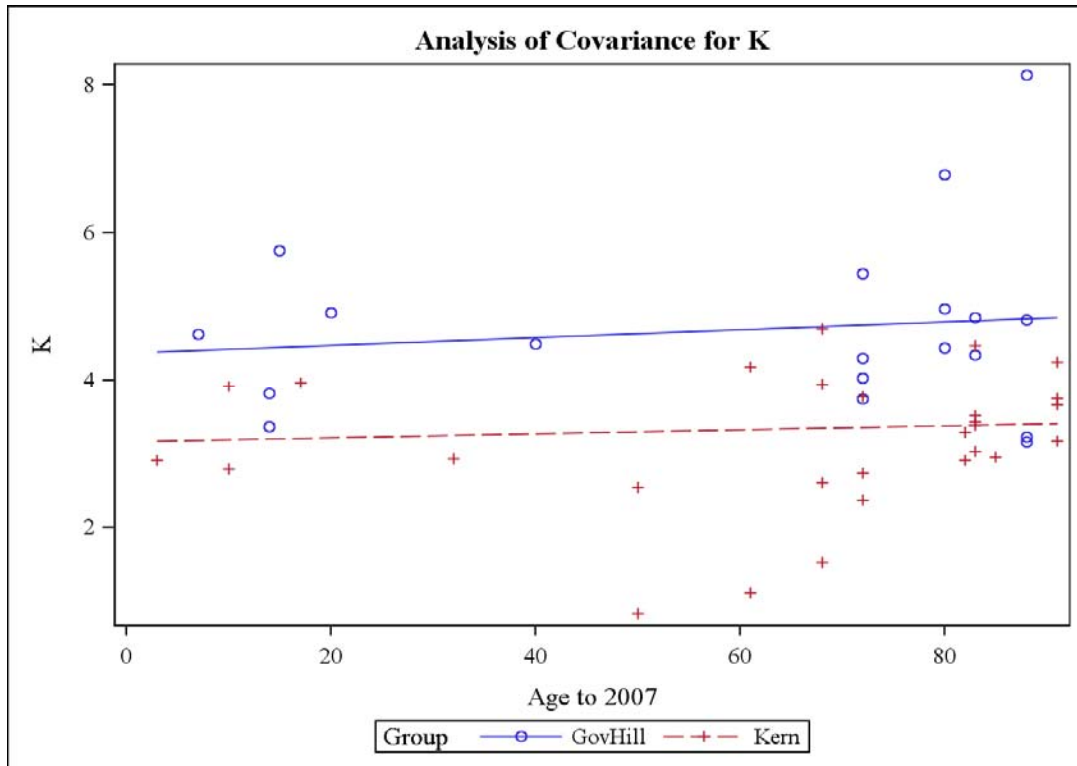


Figure D13: The  $EF_K$  distribution with age of dust in 2 groups (locations of El Paso). The regression lines are fitted according to “Age by Group Interaction” test.

Table D14: Results of “Age effect” and “Group effect” tests for  $EF_K$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	27.53246902	13.76623451	12.23	<.0001
Error	44	49.53187541	1.12572444		
Corrected Total	46	77.06434444			

R-Square	Coeff Var	Root MSE	K Mean
0.357266	28.06662	1.061002	3.780297

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	27.13433027	27.13433027	24.10	<.0001 *
Age_to_2007_	1	0.95749881	0.95749881	0.85	0.3614

\* = significant Group effect at the 0.05 alpha level

Group	K LSMEAN	H0:LSMean1=LSMean2 Pr >  t
GovHill	4.70476026	<.0001
Kern	3.15298317	

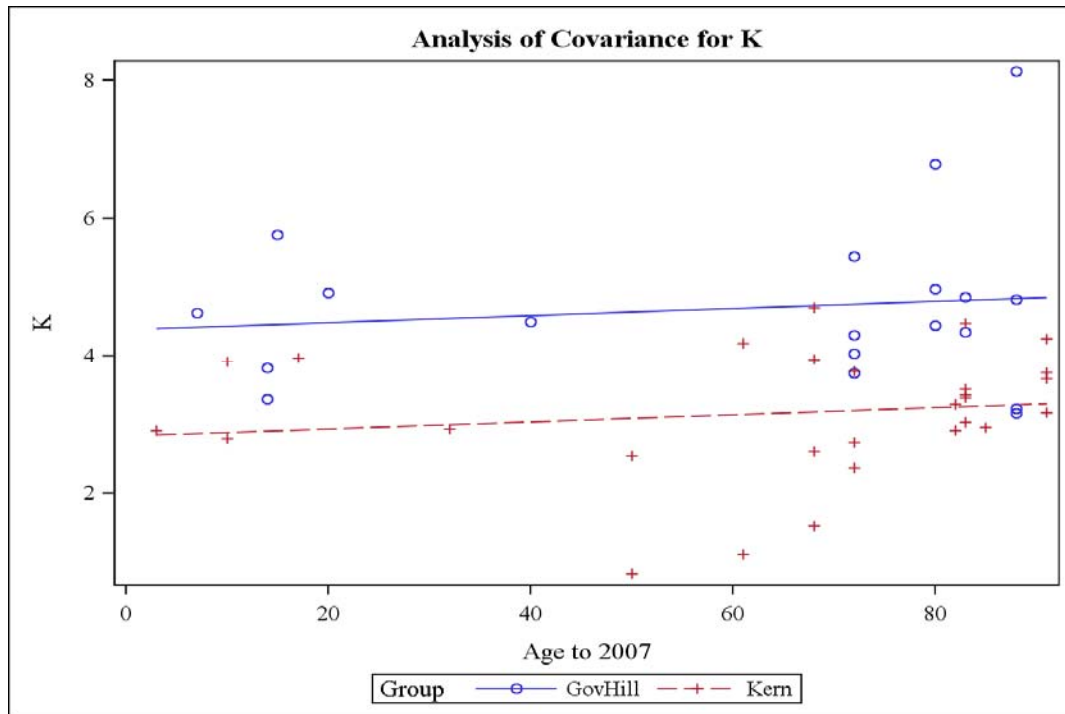


Figure D14: The  $EF_K$  distribution with dust age in 2 groups (locations of El Paso). The fitted parallel lines illustrate Group effect.

Table D15: Results of “Age by Group Interaction” test for the  $\ln EF_{Na}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	0.27284801	0.09094934	0.29	0.8326
Error	41	12.87056009	0.31391610		
Corrected Total	44	13.14340811			

R-Square	Coeff Var	Root MSE	logNa Mean
0.020759	44.57229	0.560282	1.257019

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	0.01420855	0.01420855	0.05	0.8326
Age_to_2007_	1	0.00487042	0.00487042	0.02	0.9015
Age_to_2007_*Group	1	0.00939800	0.00939800	0.03	<b>0.8635 ns</b>

**ns = no significant interaction so can use Age as covariate**

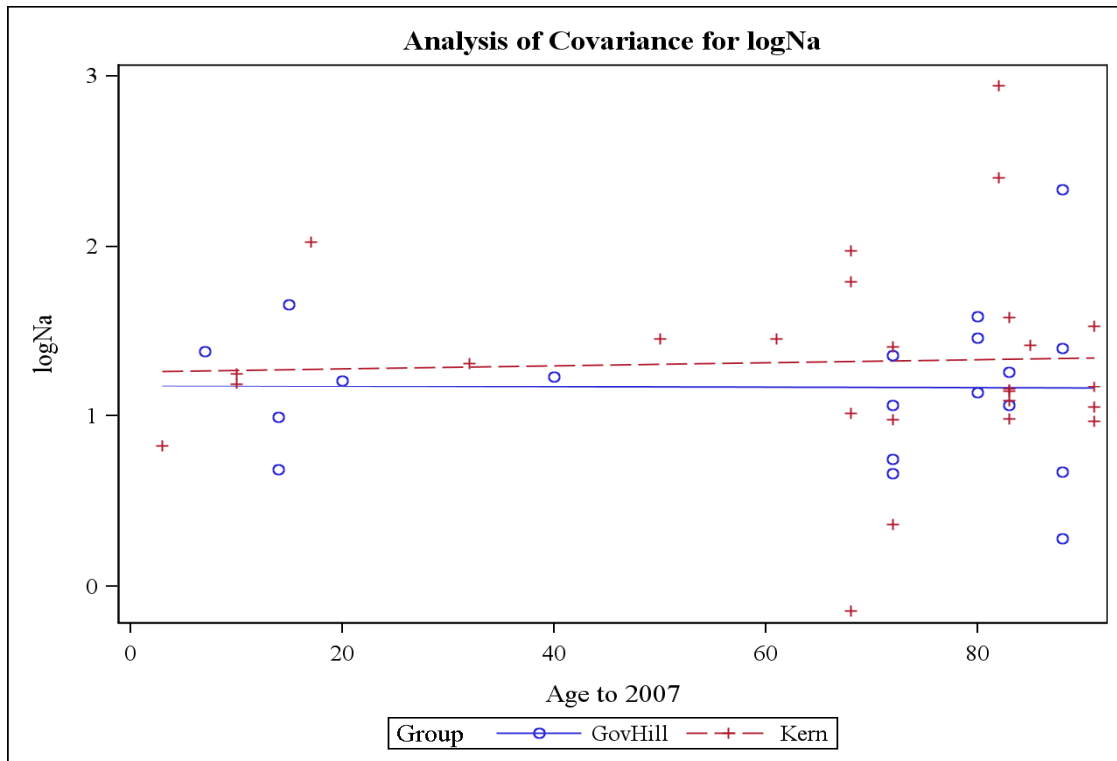


Figure D15: The  $\ln EF_{Na}$  distribution with age of dust in 2 groups (locations of El Paso). The regression lines are fitted according to “Age by Group Interaction” test.

Table D16: Results of “Age effect” and “Group effect” tests for the  $\ln EF_{Na}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	0.06585472	0.03292736	0.12	0.8910
Error	44	12.52080021	0.28456364		
Corrected Total	46	12.58665493			

R-Square	Coeff Var	Root MSE	logNa Mean
0.005232	36.38292	0.533445	1.466196

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	0.00141497	0.00141497	0.00	<b>0.9441 ns</b>
Age_to_2007_	1	0.06288044	0.06288044	0.22	0.6406

**ns = no significant Group effect at the 0.05 alpha level**

Group	logNa LSMEAN	H0:LSMean1=LSMean2 Pr >  t
GovHill	1.45952057	0.9441
Kern	1.47072640	

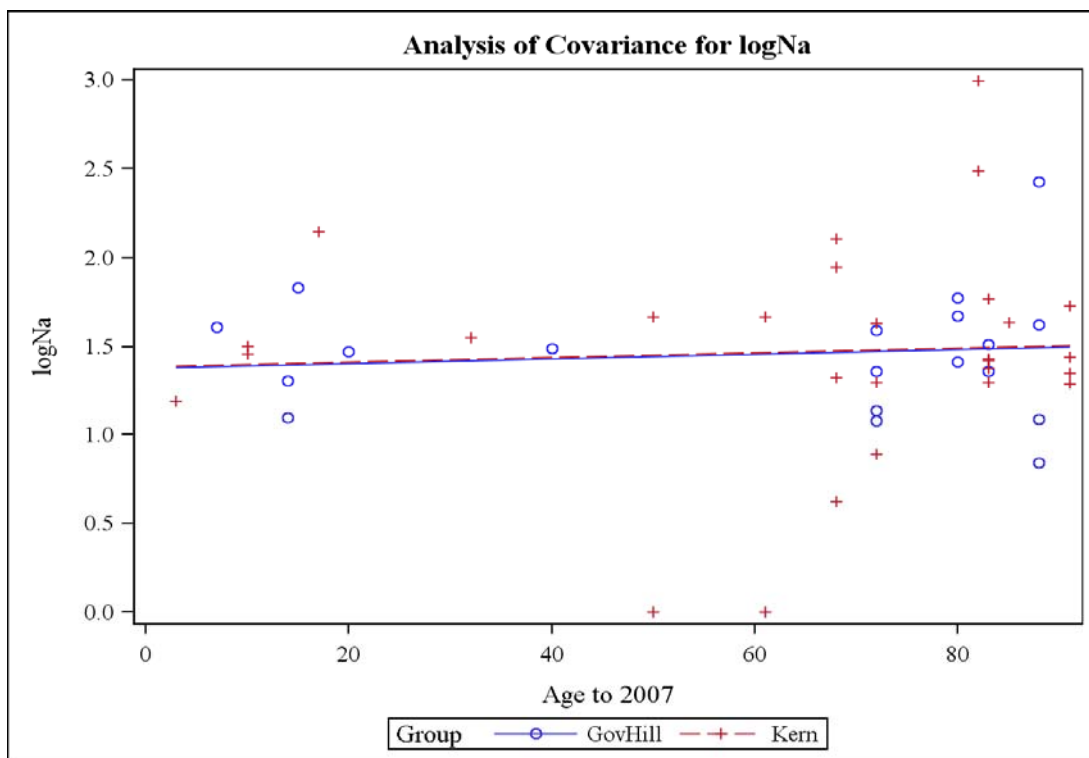


Figure D16: The  $\ln EF_{Na}$  distribution with dust age in 2 groups (locations of El Paso). The fitted parallel lines illustrate non significant Group effect.

Table D17: Results of “Age by Group Interaction” test for the  $EF_{Mg}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	5.10442316	1.70147439	21.04	<.0001
Error	41	3.31507938	0.08085559		
Corrected Total	44	8.41950254			

R-Square	Coeff Var	Root MSE	Mg Mean
0.606262	15.66270	0.284351	1.815467

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	0.70730743	0.70730743	8.75	0.0051
Age_to_2007_	1	0.04142766	0.04142766	0.51	0.4782
Age_to_2007_*Group	1	0.01082587	0.01082587	0.13	<b>0.7163 ns</b>

**ns = no significant interaction so can use Age as covariate**

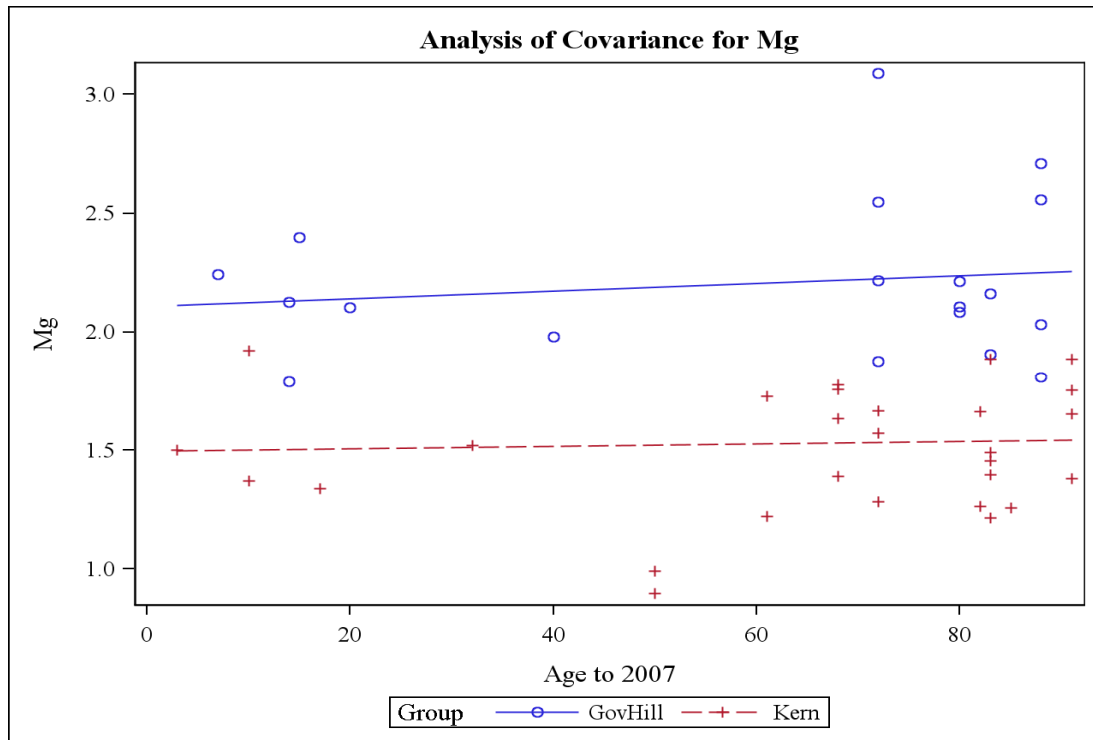


Figure D17: The  $EF_{Mg}$  distribution with age of dust in 2 groups (locations of El Paso). The regression lines are fitted according to “Age by Group Interaction” test.

Table D18: Results of “Age effect” and “Group effect” tests for the  $EF_{Mg}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	5.80311799	2.90155899	33.92	<.0001
Error	44	3.76424346	0.08555099		
Corrected Total	46	9.56736145			

R-Square	Coeff Var	Root MSE	Mg Mean
0.606554	16.40179	0.292491	1.783287

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	5.79486083	5.79486083	67.74	<.0001 *
Age_to_2007_	1	0.06346667	0.06346667	0.74	0.3937

**\* = significant Group effect at the 0.05 alpha level**

Group	Mg LSMEAN	H0:LSMean1=LSMean2 Pr >  t
GovHill	2.21050731	<.0001
Kern	1.49338821	

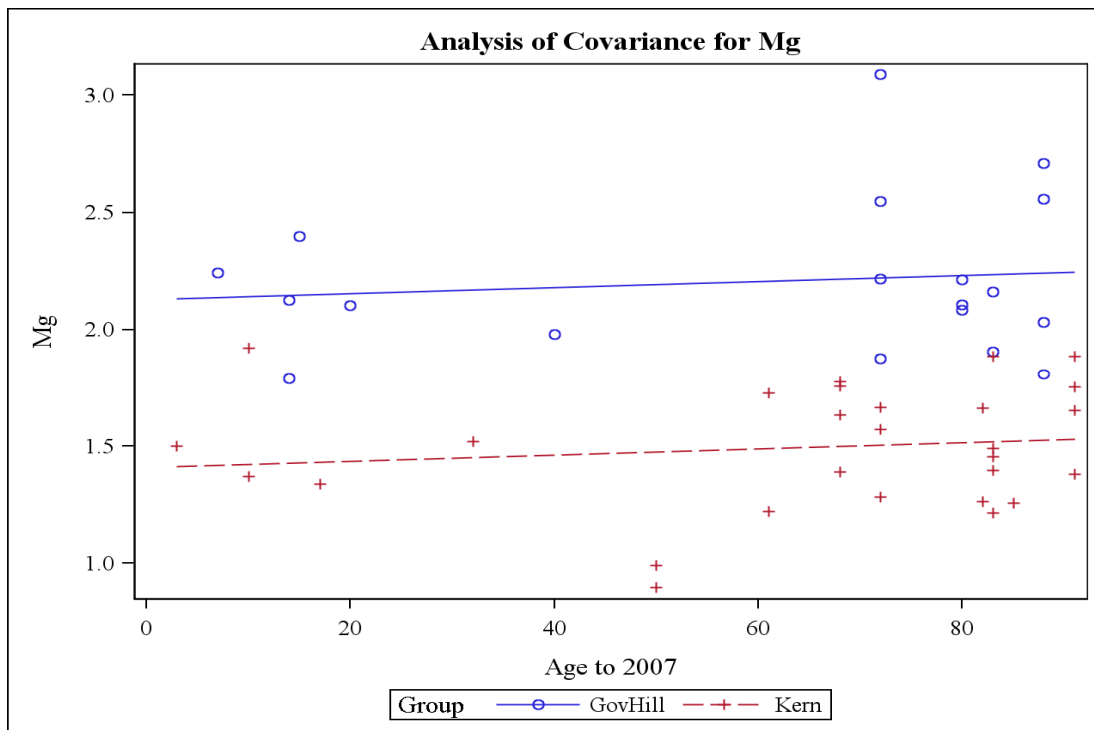


Figure D18: The  $EF_{Mg}$  distribution with dust age in 2 groups (locations of El Paso). The fitted parallel lines illustrate significant Group effect.

Table D19: Results of “Age by Group Interaction” test for the EF<sub>V</sub>.

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	144.8146206	48.2715402	22.15	<.0001
Error	41	89.3534906	2.1793534		
Corrected Total	44	234.1681112			

R-Square	Coeff Var	Root MSE	V_51 Mean
0.618422	24.69763	1.476263	5.977349

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	32.43787628	32.43787628	14.88	0.0004
Age_to_2007_	1	3.50596827	3.50596827	1.61	0.2118
Age_to_2007_*Group	1	0.65062518	0.65062518	0.30	<b>0.5878 ns</b>

**ns = no significant interaction so can use Age as covariate**

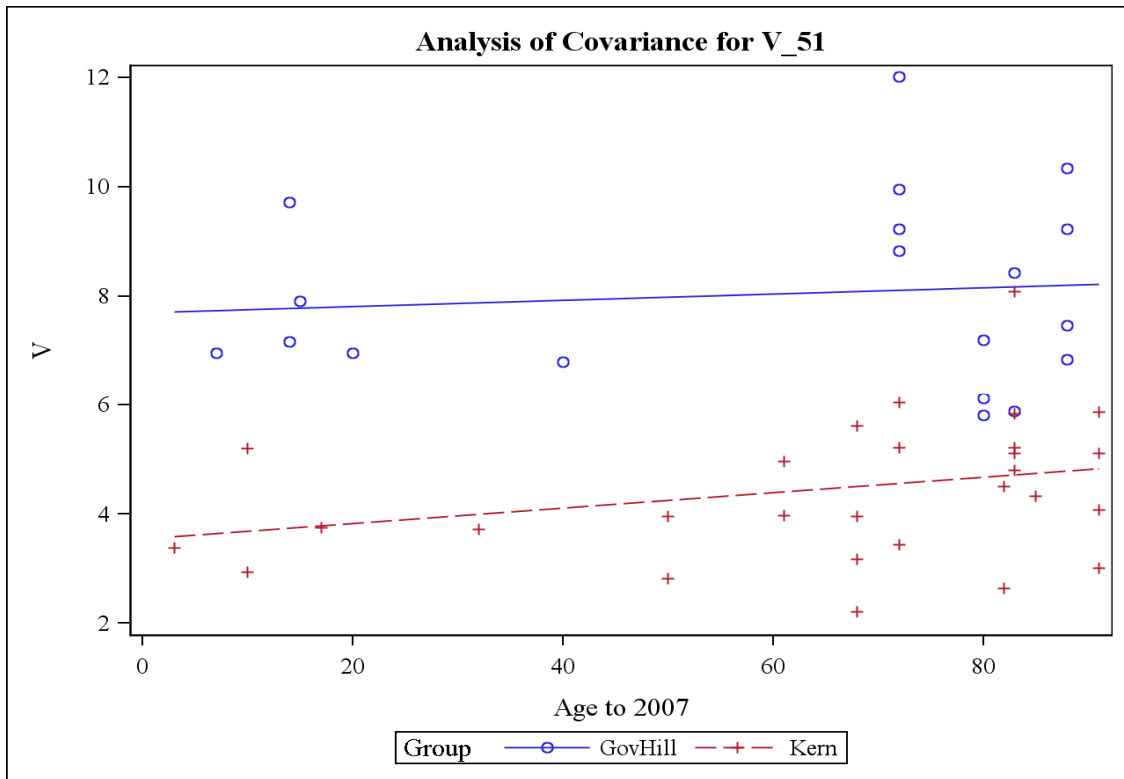


Figure D19: The EF<sub>V</sub> distribution with age of dust in 2 groups (locations of El Paso). The regression lines are fitted according to “Age by Group Interaction” test.

Table D20: Results of “Age effect” and “Group effect” tests for the  $EF_v$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	155.3308546	77.6654273	37.03	<.0001
Error	44	92.2906886	2.0975156		
Corrected Total	46	247.6215432			

R-Square	Coeff Var	Root MSE	V_51 Mean
0.627291	24.68373	1.448280	5.867349

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	153.8385191	153.8385191	73.34	<.0001 *
Age_to_2007_	1	4.2014853	4.2014853	2.00	0.1640

**\* = significant Group effect at the 0.05 alpha level**

Group	V LSMEAN	H0:LSMean1=LSMean2 Pr >  t
GovHill	8.06856372	<.0001
Kern	4.37366681	

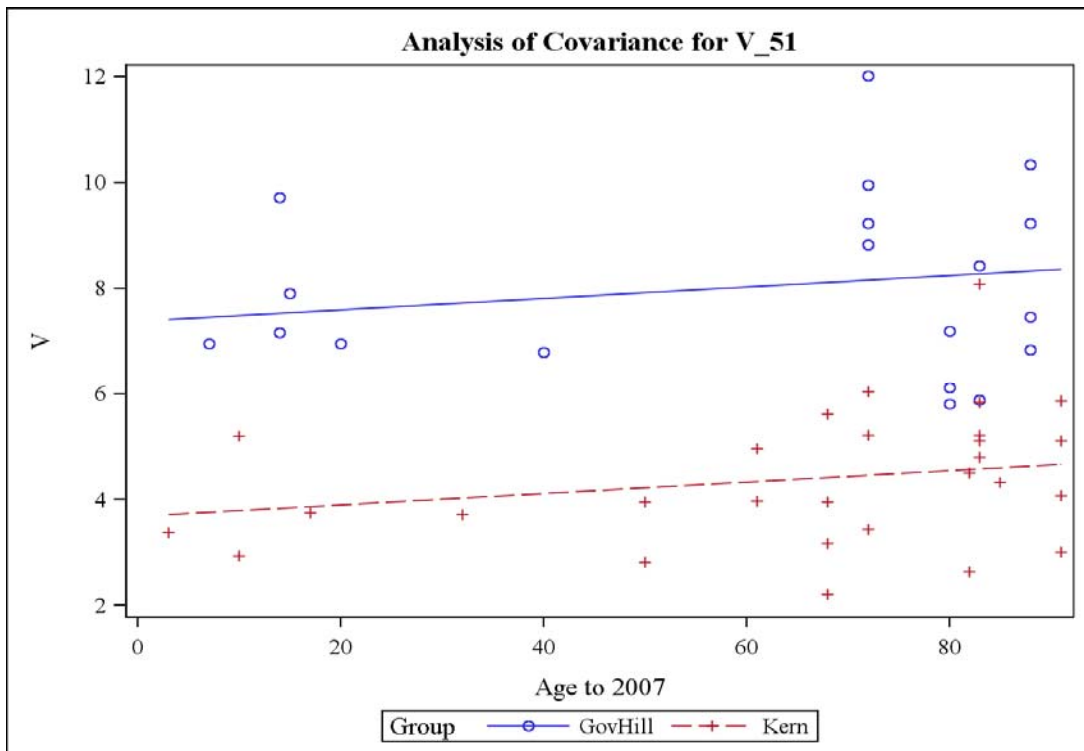


Figure D20: The  $EF_v$  distribution with dust age in 2 groups (locations of El Paso). The fitted parallel lines illustrate significant Group effect.

Table D21: Results of “Age by Group Interaction” test for the  $\ln EF_{Se}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	2.31757696	0.77252565	6.67	0.0009
Error	41	4.74632343	0.11576399		
Corrected Total	44	7.06390039			

R-Square	Coeff Var	Root MSE	logSe Mean
0.328087	22.21319	0.340241	1.531707

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	0.05094859	0.05094859	0.44	0.5108
Age_to_2007_	1	0.23299314	0.23299314	2.01	0.1635
Age_to_2007_*Group	1	0.59981524	0.59981524	5.18	<b>0.0281 *</b>

**\* = significant interaction so cannot use Age as covariate**

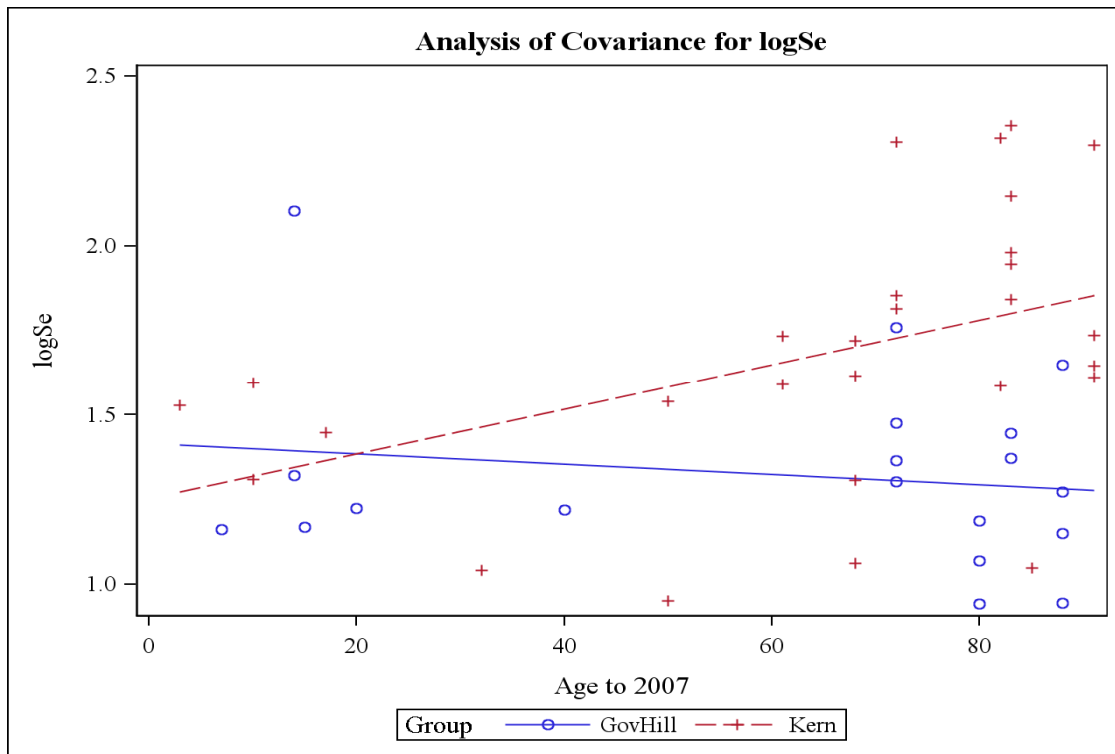


Figure D21: The  $\ln EF_{Se}$  distribution with age of dust in 2 groups (locations of El Paso). The regression lines are fitted according to “Age by Group Interaction” test.

Table D22: Results of the ANOVA test “Group effect” for the  $\ln EF_{Se}$ .

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	1.41689857	1.41689857	11.28	0.0016
Error	45	5.65049298	0.12556651		
Corrected Total	46	7.06739155			

R-Square	Coeff Var	Root MSE	logSe Mean
0.200484	23.11260	0.354354	1.533162

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	1.41689857	1.41689857	11.28	<b>0.0016 *</b>

**\* = significant Group effect at the 0.05 alpha level**

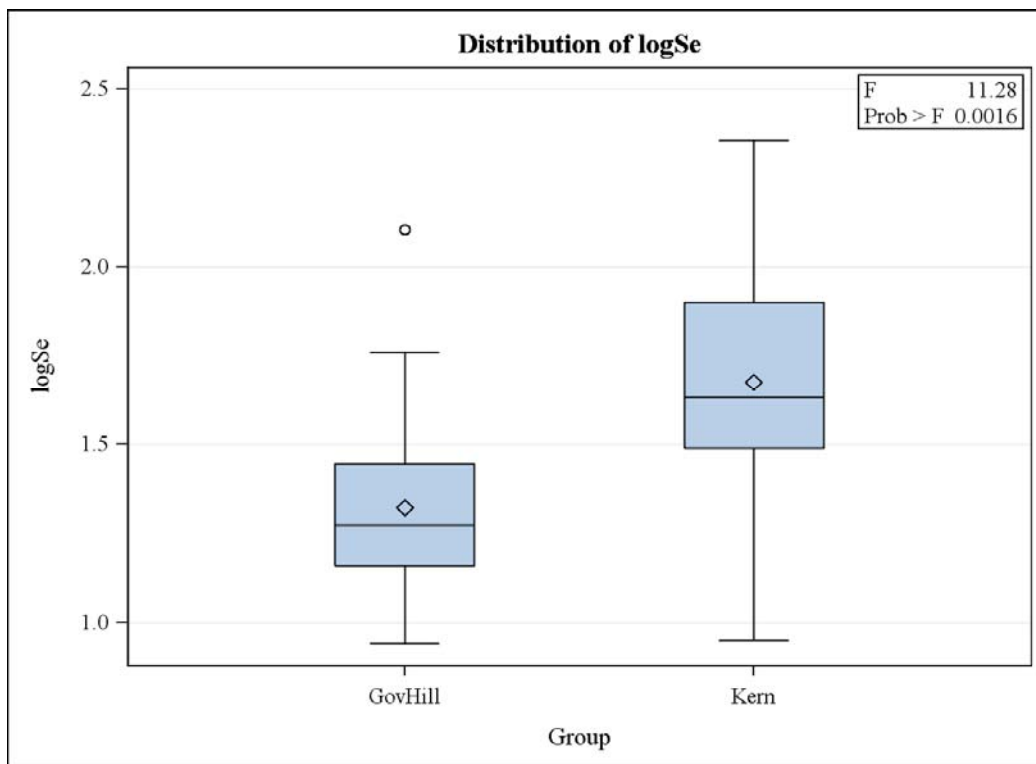


Figure D22: Box plots of  $\ln EF_{Se}$  distribution in 2 groups (locations of El Paso).

Table D23: Results of “Age by Group Interaction” test for the  $EF_{Pb}$  (before 1966).

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	542347.953	180782.651	11.98	<.0001
Error	32	482954.731	15092.335		
Corrected Total	35	1025302.684			

R-Square	Coeff Var	Root MSE	Pb Mean
0.528964	55.69311	122.8509	220.5854

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	4614.32439	4614.32439	0.31	0.5841
Age_to_2007	1	12381.42675	12381.42675	0.82	0.3718
Age_to_2007*Group	1	18365.00594	18365.00594	1.22	0.2782

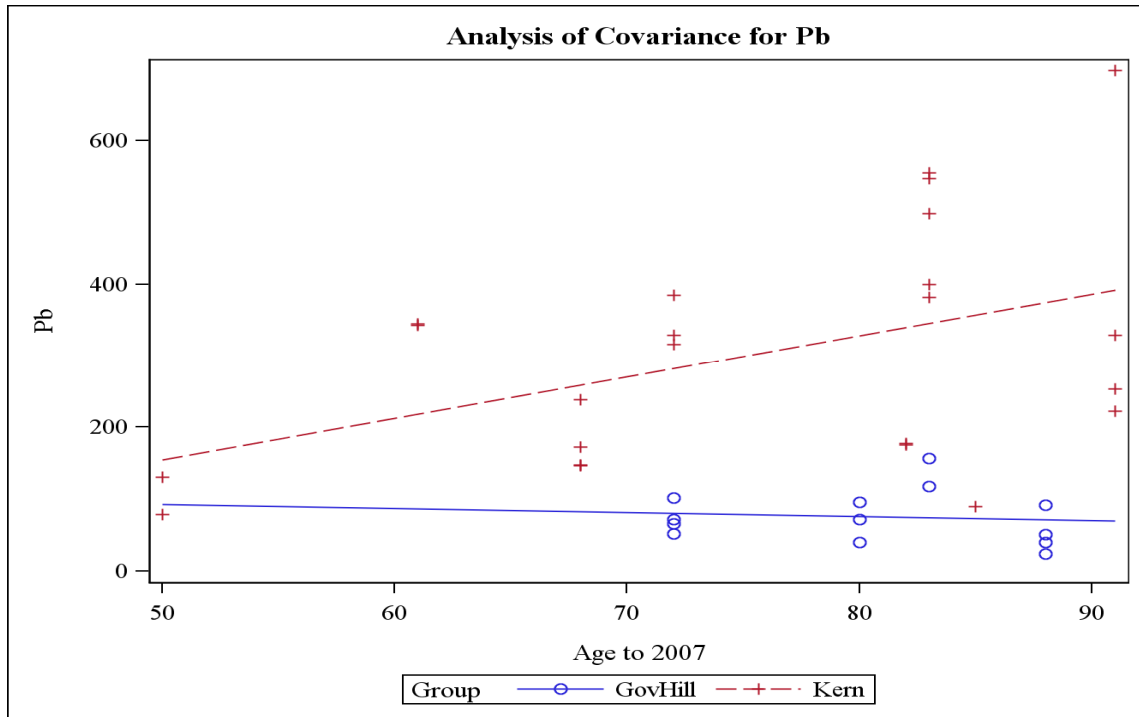


Figure D23: The  $EF_{Pb}$  distribution with age of dust (50-90 years) in 2 groups (locations). The regression lines are fitted according to “Age by Group Interaction” test.

Table D24: Results of “Age by Group Interaction” test for the  $EF_{Pb}$  (post 1966).

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	5501.00939	1833.66980	1.01	0.4306
Error	9	16270.44203	1807.82689		
Corrected Total	12	21771.45142			

R-Square	Coeff Var	Root MSE	Pb Mean
0.252671	56.64123	42.51855	75.06642

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	138.733103	138.733103	0.08	0.7880
Age_to_2007	1	25.569902	25.569902	0.01	0.9079
Age_to_2007*Group	1	2024.472904	2024.472904	1.12	0.3175

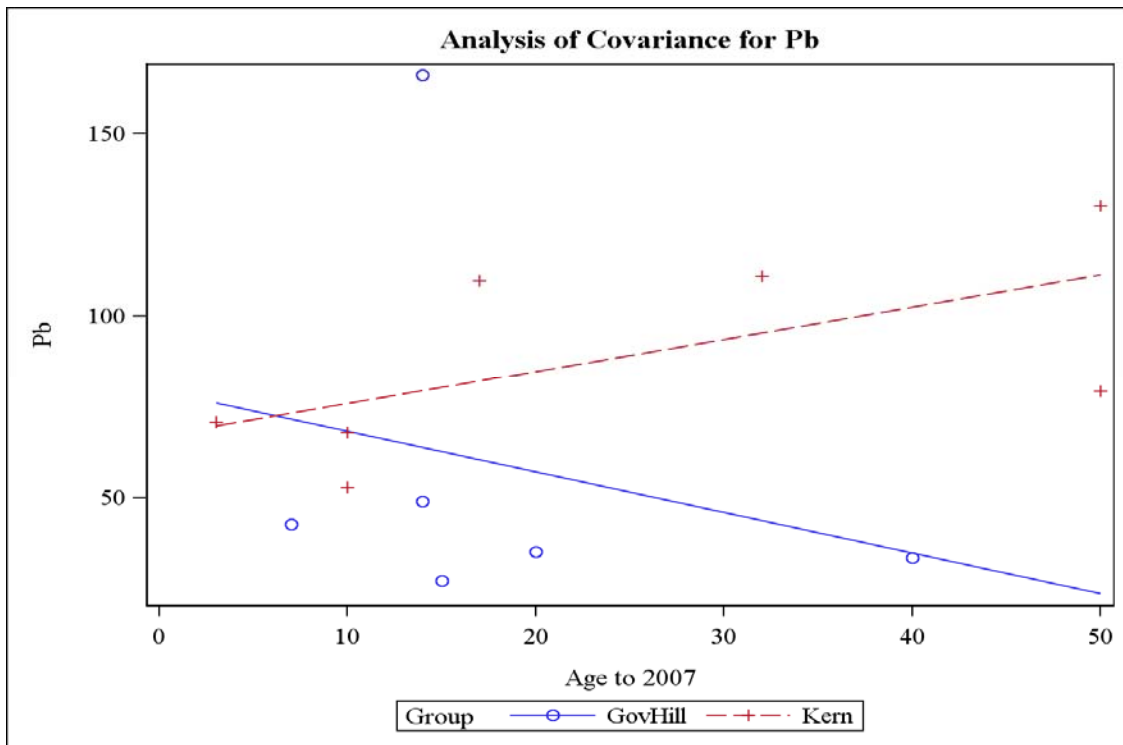


Figure D24: The  $EF_{Pb}$  distribution with age of dust (0 - 50 years) in 2 groups (locations). The regression lines are fitted according to “Age by Group Interaction” test.

Table D25: Results of “Age by Group Interaction” test for the  $EF_{As}$  (pre 1966).

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	50621.16081	16873.72027	12.63	<.0001
Error	32	42747.14503	1335.84828		
Corrected Total	35	93368.30584			

R-Square	Coeff Var	Root MSE	As Mean
0.542166	55.35229	36.54926	66.03026

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	342.283958	342.283958	0.26	0.6162
Age_to_2007	1	1083.812136	1083.812136	0.81	0.3745
Age_to_2007*Group	1	1541.638440	1541.638440	1.15	0.2907

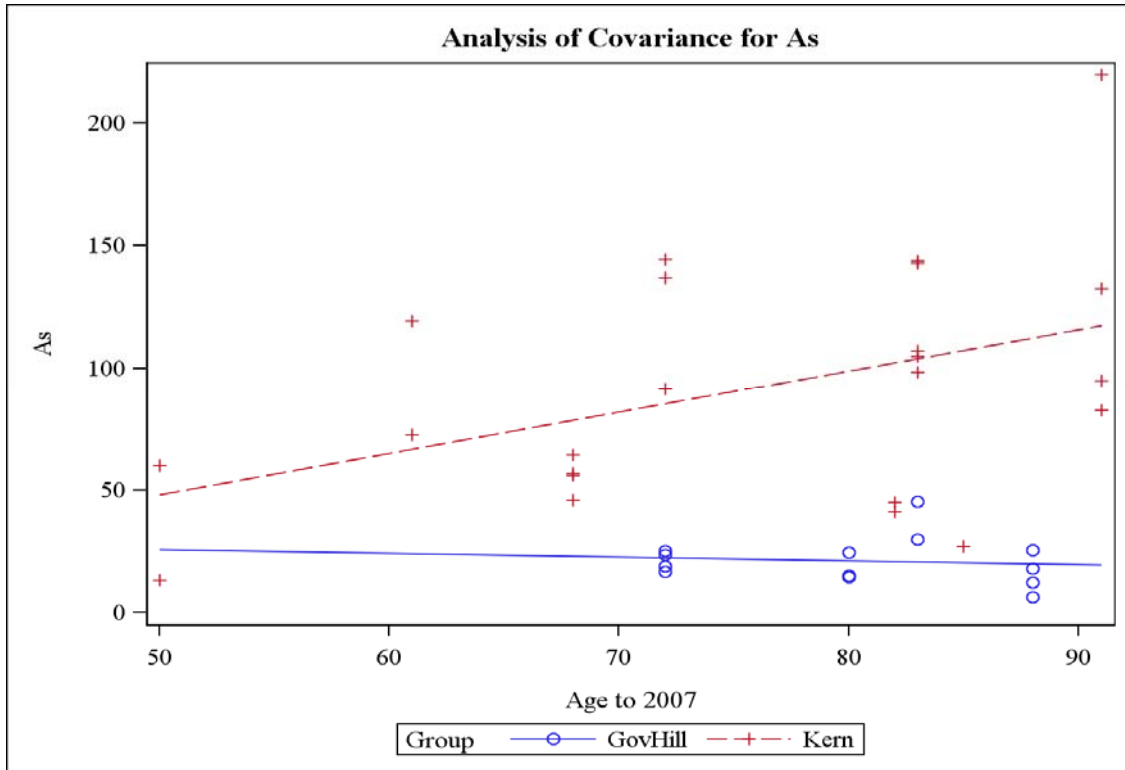


Figure D25: The  $EF_{As}$  distribution with age of dust (50- 90 years) in 2 groups (locations). The regression lines are fitted according to “Age by Group Interaction” test.

Table D26: Results of “Age by Group Interaction” test for the  $EF_{As}$  (post 1966).

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	766.900707	255.633569	1.37	0.3132
Error	9	1679.640687	186.626743		
Corrected Total	12	2446.541394			

R-Square	Coeff Var	Root MSE	As Mean
0.313463	51.91888	13.66114	26.31247

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	9.4305830	9.4305830	0.05	0.8272
Age_to_2007	1	11.1707269	11.1707269	0.06	0.8122
Age_to_2007*Group	1	135.0449852	135.0449852	0.72	0.4170

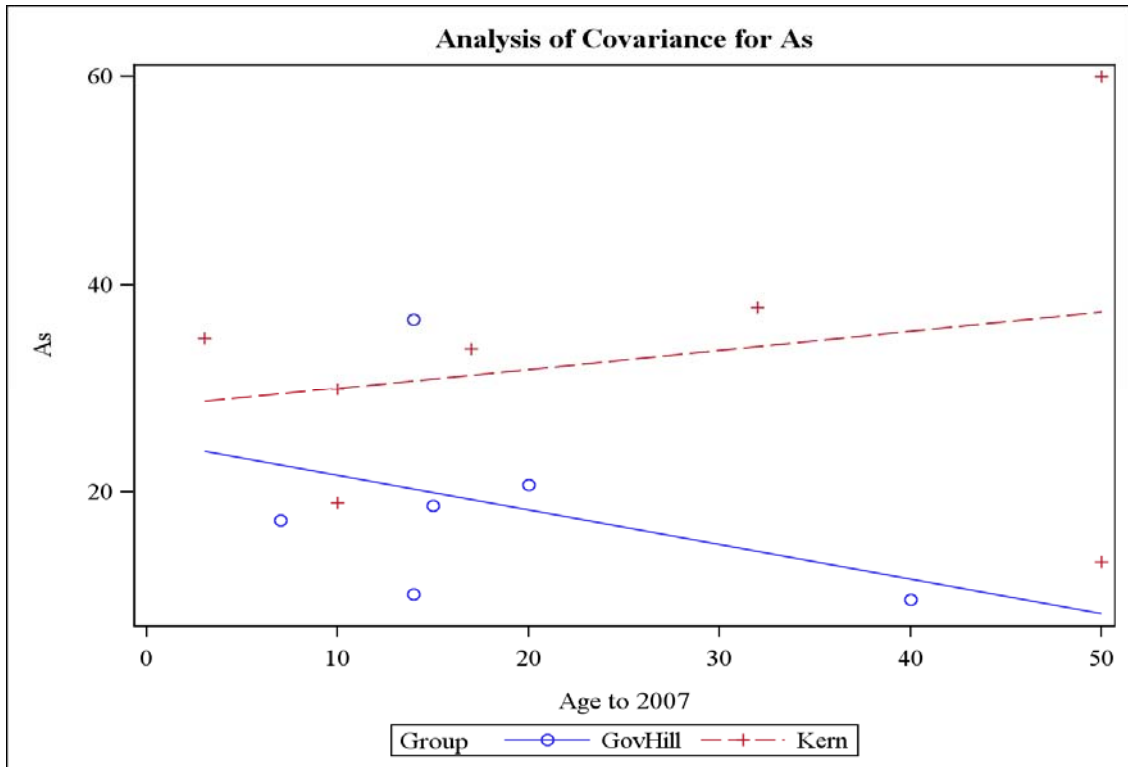


Figure D26: The  $EF_{pb}$  distribution with age of dust (0 -50 years) in 2 groups (locations). The regression lines are fitted according to “Age by Group Interaction” test.

Table D27: Results of “Age by Group Interaction” test for the EF<sub>Cd</sub> (pre 1966).

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	26.45698194	8.81899398	26.09	<.0001
Error	32	10.81793751	0.33806055		
Corrected Total	35	37.27491944			

R-Square	Coeff Var	Root MSE	logCd Mean
0.709780	11.28087	0.581430	5.154120

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	0.17555975	0.17555975	0.52	0.4764
Age_to_2007	1	0.00003967	0.00003967	0.00	0.9914
Age_to_2007*Group	1	0.81510683	0.81510683	2.41	0.1303

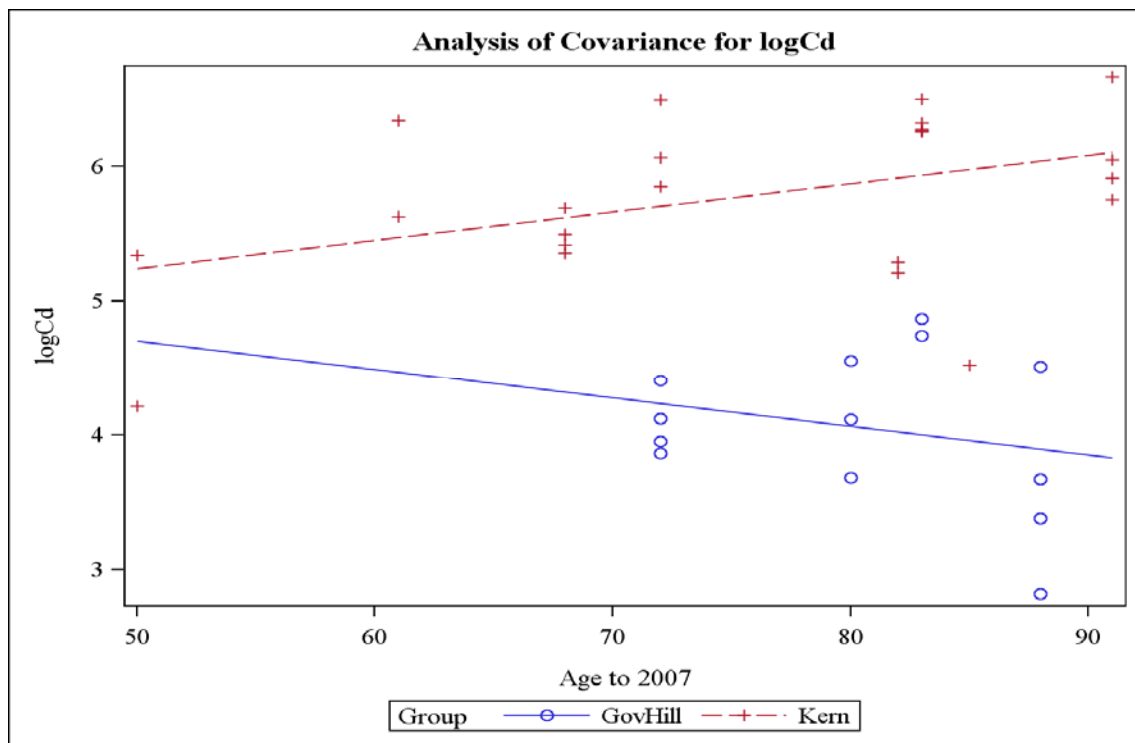


Figure D27: The EF<sub>Cd</sub> distribution with age of dust (50-90 years) in 2 groups (locations). The regression lines are fitted according to “Age by Group Interaction” test.

Table D28: Results of “Age by Group Interaction” test for the  $\ln EF_{Cd}$  (post 1966).

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	3.81348409	1.27116136	7.42	0.0083
Error	9	1.54091959	0.17121329		
Corrected Total	12	5.35440367			

R-Square	Coeff Var	Root MSE	logCd Mean
0.712215	9.449424	0.413779	4.378884

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	2.36725735	2.36725735	13.83	0.0048
Age_to_2007	1	0.67256940	0.67256940	3.93	0.0788
Age_to_2007*Group	1	0.63662807	0.63662807	3.72	0.0859

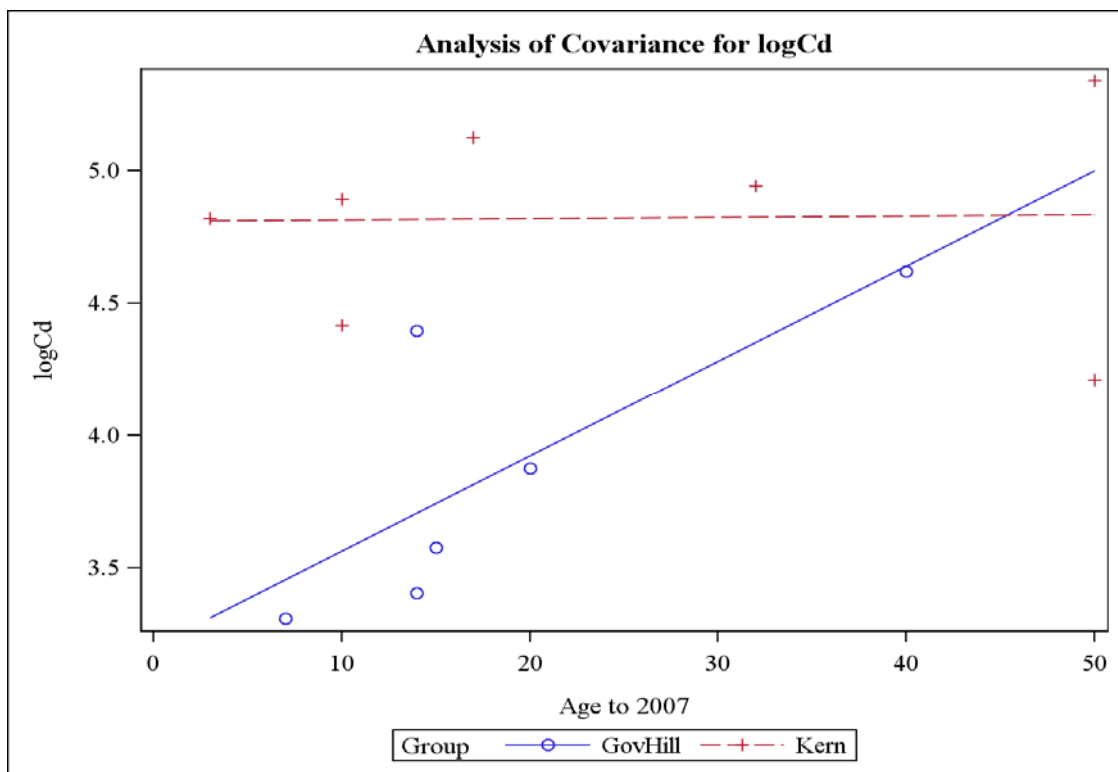


Table D28: The  $EF_{Cd}$  distribution with age of dust (0 -50 years) in 2 groups (locations). The regression lines are fitted according to “Age by Group Interaction” test.

Table D 29: Results of “Age by Group Interaction” test for the  $\ln EF_{Cu}$  (pre 1966).

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	12.95068661	4.31689554	13.30	<.0001
Error	32	10.38677448	0.32458670		
Corrected Total	35	23.33746109			

R-Square	Coeff Var	Root MSE	logCu Mean
0.554931	10.07503	0.569725	5.654825

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	0.14295651	0.14295651	0.44	0.5117
Age_to_2007	1	0.00191982	0.00191982	0.01	0.9392
Age_to_2007*Group	1	0.51205876	0.51205876	1.58	0.2182

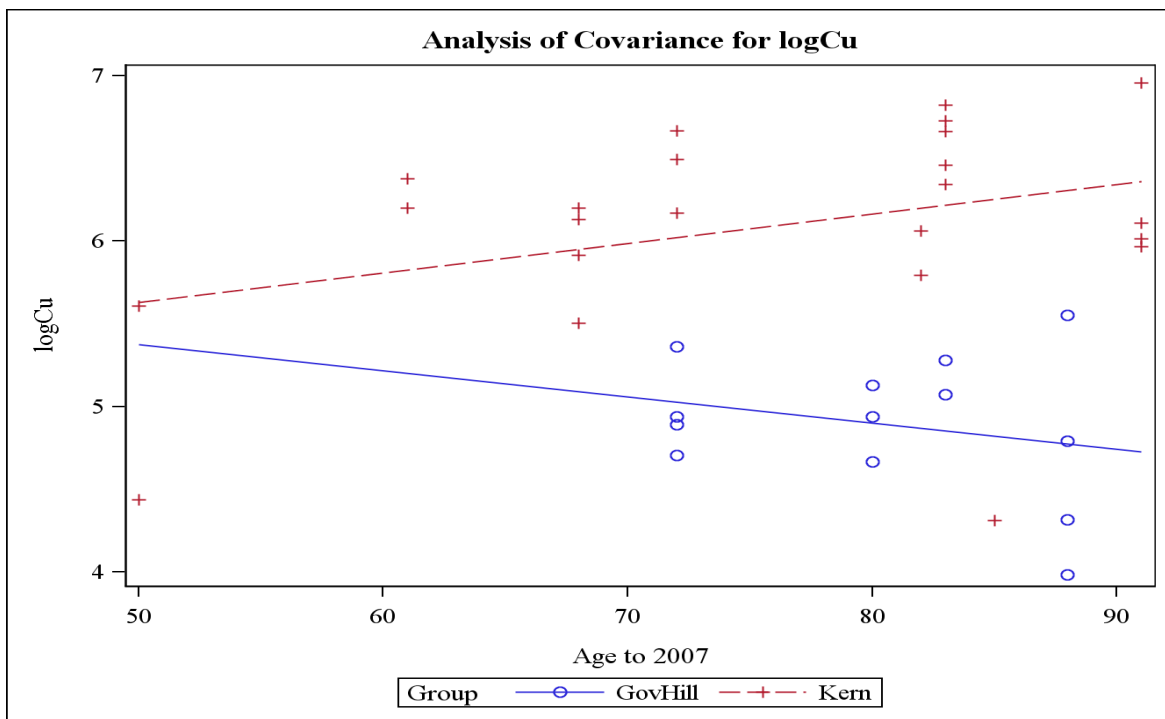


Figure D29: The  $\ln EF_{Cu}$  distribution with age of dust (50- 90 years) in 2 groups (locations). The regression lines are fitted according to “Age by Group Interaction” test.

Table D30: Results of “Age by Group Interaction” test for the  $\ln EF_{Cu}$  (post 1966).

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	0.91395054	0.30465018	0.94	0.4600
Error	9	2.91018435	0.32335382		
Corrected Total	12	3.82413489			

R-Square	Coeff Var	Root MSE	logCu Mean
0.238995	10.95484	0.568642	5.190786

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	0.20896458	0.20896458	0.65	0.4422
Age_to_2007	1	0.05784459	0.05784459	0.18	0.6823
Age_to_2007*Group	1	0.00525853	0.00525853	0.02	0.9013

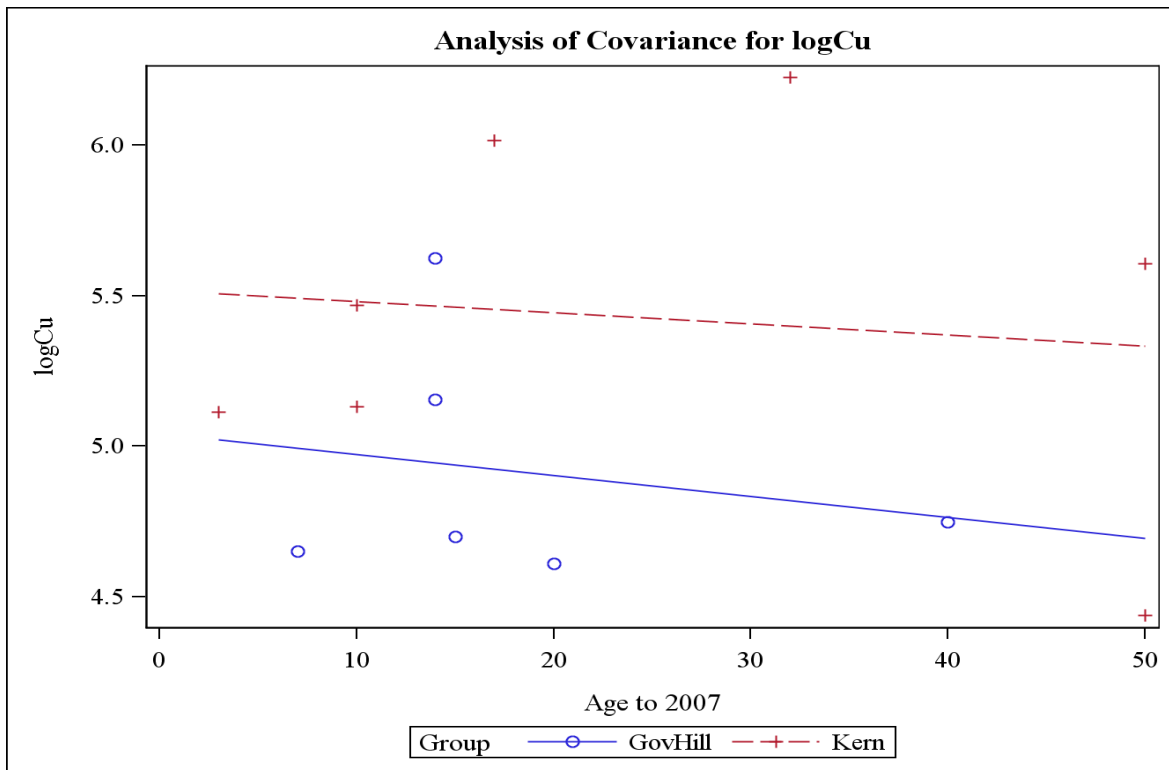


Figure D30: The  $\ln EF_{Cu}$  distribution with age of dust (0 -50 years) in 2 groups (locations). The regression lines are fitted according to “Age by Group Interaction” test.

Table D31: Results of “Age by Group Interaction” test for the  $\ln EF_{se}$  (pre 1966).

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	2.32786553	0.77595518	7.07	0.0009
Error	32	3.51435018	0.10982344		
Corrected Total	35	5.84221571			

R-Square	Coeff Var	Root MSE	logSe Mean
0.398456	20.95188	0.331396	1.581702

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	0.18194312	0.18194312	1.66	0.2073
Age_to_2007	1	0.00126785	0.00126785	0.01	0.9151
Age_to_2007*Group	1	0.31275551	0.31275551	2.85	0.1012

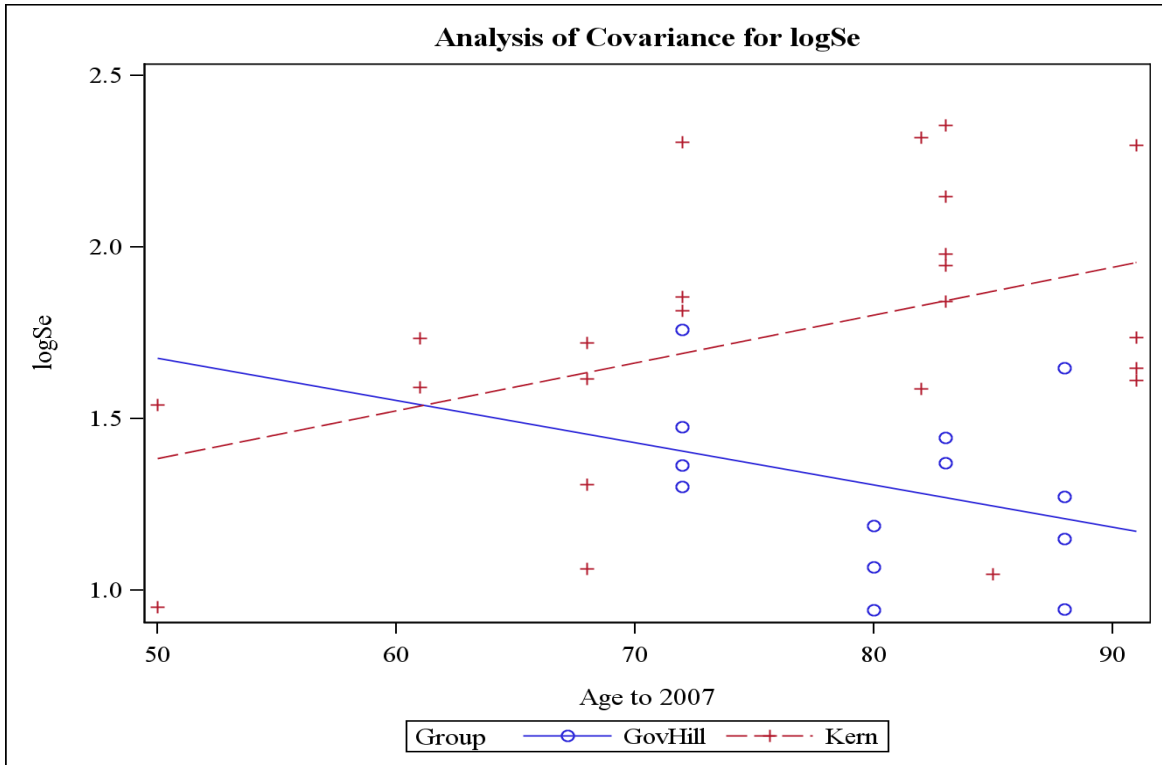


Figure D31: The  $\ln EF_{se}$  distribution with age of dust (50- 90 years) in 2 groups (locations). The regression lines are fitted according to “Age by Group Interaction” test.

Table D32: Results of “Age by Group Interaction” test for the  $\ln EF_{Se}$  (post 1966).

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	0.11967837	0.03989279	0.38	0.7700
Error	9	0.94521838	0.10502426		
Corrected Total	12	1.06489674			

R-Square	Coeff Var	Root MSE	logSe Mean
0.112385	23.92526	0.324074	1.354528

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	0.00176635	0.00176635	0.02	0.8997
Age_to_2007	1	0.07144171	0.07144171	0.68	0.4308
Age_to_2007*Group	1	0.00088885	0.00088885	0.01	0.9287

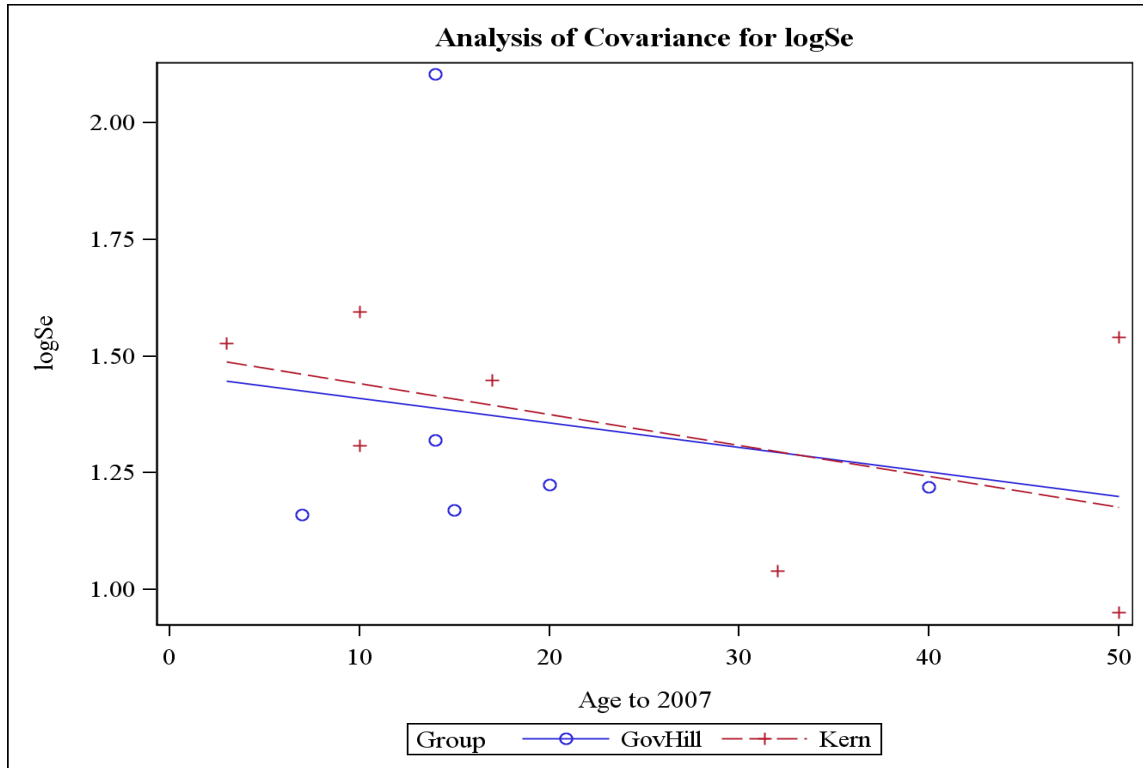


Figure D32: The  $\ln EF_{Se}$  distribution with age of dust (0 -50 years) in 2 groups (locations). The regression lines are fitted according to “Age by Group Interaction” test.

Table D33: Results of “Age by Group Interaction” test for the  $\ln EF_{sb}$  (pre 1966).

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	16.22019678	5.40673226	18.87	<.0001
Error	32	9.17061703	0.28658178		
Corrected Total	35	25.39081381			

R-Square	Coeff Var	Root MSE	logSb Mean
0.638821	9.048081	0.535333	5.916540

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	0.00024743	0.00024743	0.00	0.9767
Age_to_2007	1	0.05665253	0.05665253	0.20	0.6596
Age_to_2007*Group	1	0.13385428	0.13385428	0.47	0.4993

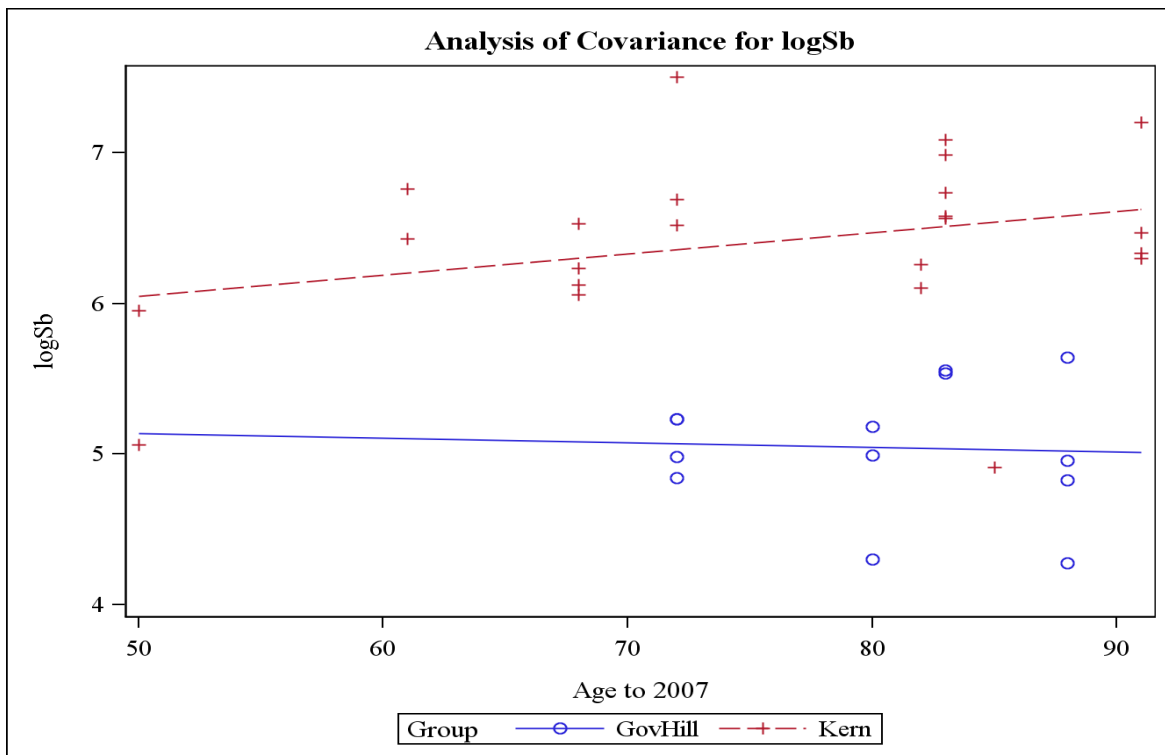


Figure D33: The  $\ln EF_{sb}$  distribution with age of dust (50- 90 years) in 2 groups (locations). The regression lines are fitted according to “Age by Group Interaction” test.

Table D34: Results of “Age by Group Interaction” test for the  $\ln EF_{sb}$  (post 1966).

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	1.62749386	0.54249795	2.19	0.1591
Error	9	2.23136436	0.24792937		
Corrected Total	12	3.85885822			

R-Square	Coeff Var	Root MSE	logSb Mean
0.421755	9.137377	0.497925	5.449321

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	0.84885177	0.84885177	3.42	0.0973
Age_to_2007	1	0.00811077	0.00811077	0.03	0.8605
Age_to_2007*Group	1	0.09038978	0.09038978	0.36	0.5609

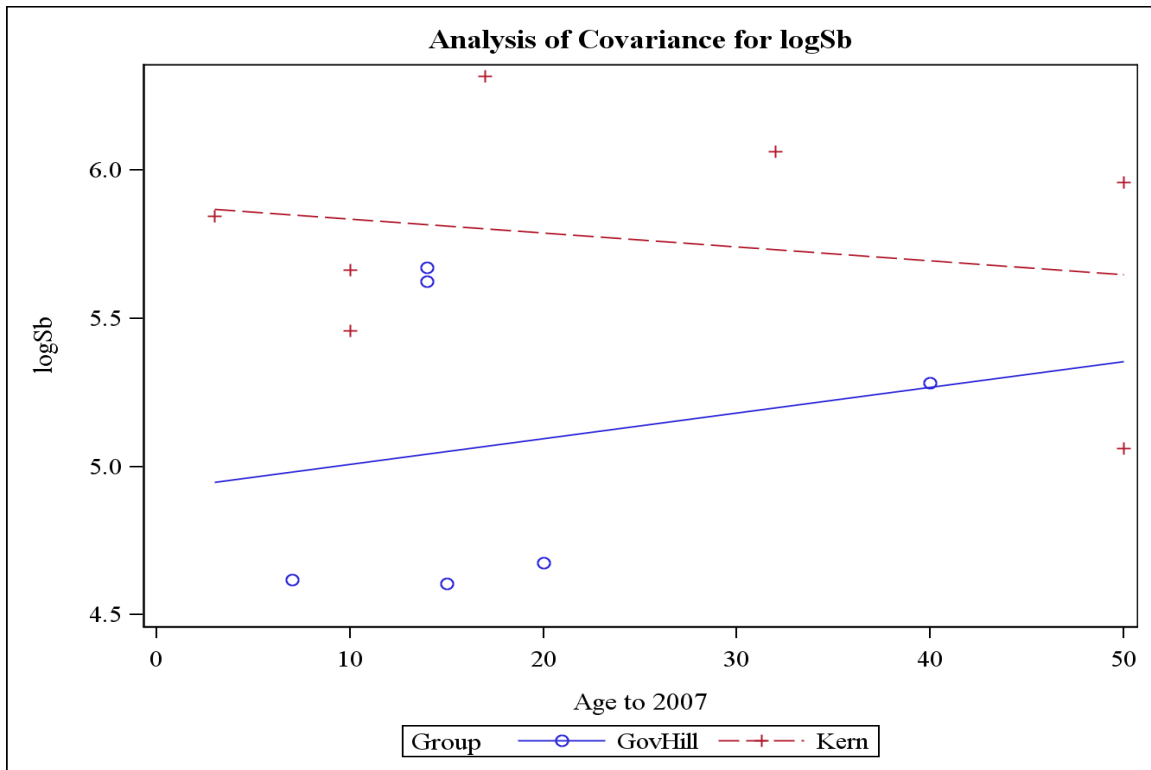


Figure D34: The  $\ln EF_{sb}$  distribution with age of dust (0 -50 years) in 2 groups (locations). The regression lines are fitted according to “Age by Group Interaction” test.

## **CURRICULUM VITA**

Eugenia Shekhter is a native of Kiev (Ukraine). She obtained both her Bachelor and Master of Engineering degrees in Industrial Engineering from the St. Petersburg Technological Institute CPI. Then she earned her Master's degree in Psychology at the St. Petersburg University. She also studied Theology in Paris, France. In 2000, she joined her family in El Paso, Texas. In 2002, she entered the doctoral program in Environmental Science and Engineering at The University of Texas at El Paso.

While pursuing her doctoral degree, Dr. Shekhter worked as a research associate and as an assistant instructor for the College of Science. She was also the recipient of a Welsh Foundation Fellowship.

Dr. Shekhter has presented her research at conferences and workshops, including the International Conference on Aeolian Research (July 2010, Argentina, Santa Rosa, La Pampa) and the 2010 AGU Fall Meeting (San Francisco, California).

Dr. Shekhter's dissertation "Heavy Metal Pollution: Historical Reconstruction and Source Interpretation in the Paso del Norte Region" was supervised by Dr. Keith Pannell.

Dr. Shekhter plans to pursue a position in higher education and to continue her forensic research of complex environmental problems. Dr. Shekhter is also interested in serving as a consultant using her multidisciplinary knowledge and a holistic approach to help educate and benefit the community.