

BIOGEOCHEMISTRY OF ISOTOPICALLY-DISTINCT SOURCES OF LEAD IN A  
FORMER WWII AERIAL GUNNERY RANGE

A Thesis

by

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## ABSTRACT

Isotopic composition and concentrations of Pb are used to identify sources of anthropogenic and natural Pb and to assess Pb bioavailability in soils and native plants at a former military installation that served as a WWII era aerial gunnery range. Surficial soil and plant samples are obtained both in target practice areas where copious amounts of bullets persist and areas unaffected by target practice that are devoid of bullets. A selective sequential extraction procedure is used to determine the distribution of Pb amongst different soil components: soil carbonates and ion-exchangeable minerals, organics, oxide and hydroxide minerals, and leachate of residual silicate clays. Plants samples are obtained by sampling multiple species within 1 m square area for each soil sample location. Isotopic compositions of samples directly reflect the presence or absence of bullets in the sample area.

Anthropogenic Pb in sample locations with abundant bullets display a wide range of  $^{206}\text{Pb}/^{207}\text{Pb}$  values (1.140–1.234), but relatively less variation in  $^{206}\text{Pb}/^{208}\text{Pb}$  values (0.473–0.488), which is hypothesized to be reflective of ore-mixing in the manufacture of bullets. Plant samples exhibit a distinction between anthropogenic and natural Pb similar to soil samples, but consistently display lighter  $^{206}\text{Pb}/^{207}\text{Pb}$  values than soil samples, which is inferred to be representative of the influence of regional atmospheric deposition of contaminant Pb.

## DEDICATION

To my parents, my husband, and my son; my past, my present, and my future.

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## NOMENCLATURE

BCR	Community Bureau of Reference
DoD	(United States) Department of Defense
HF	Hydrofluoric Acid
HNO <sub>3</sub>	Nitric Acid
HR-ICP-MS	High Resolution Inductively Coupled Plasma Mass Spectrometer
ICP-MS	Inductively Coupled Plasma Mass Spectrometer
MC-ICP-MS	Multi-Collector Inductively Coupled Plasma Mass Spectrometer
LANWR	Laguna Atascosa National Wildlife Refuge
USFWS	United State Fisheries and Wildlife Service
WWII	World War II

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## CHAPTER I

### INTRODUCTION

Legacy lead (Pb) contamination at former military installations persists as a source of potential hazards for ecological health. Sources of heavy metal contaminants typical to military installations include manufacture of ammunition, weaponry, aircraft, etc., the exploding of ordnances, and numerous other applications<sup>1</sup>. Pb contamination at U.S. military installations predominantly arises from spent ammunition at artillery and small arms firing ranges, though contamination can arise from sources other than ammunition such as leaded paint<sup>1-3</sup>. The legacy of Pb contamination in sensitive ecosystems has become a significant world-wide environmental problem.

Recent emphasis has been placed on both military and civilian shooting ranges as a source of bioavailable heavy metal contaminants particularly in coastal environments. Pb is historically a component in ammunition, and Pb contamination from shooting ranges can be a significant, localized contamination of Pb and other metals. Due to this, guidelines have recently been set forth for small arms firing ranges<sup>4,5</sup>. An example of this is the uptake of Pb by primary producers at a former military shooting range at Fort Ord, California<sup>6</sup>. The bioavailability of Pb from legacy munitions is strongly correlated to the chemistry of Pb in soils, specifically the mechanism by which Pb may be adsorbed and to which soil fraction it may be adsorbed<sup>6</sup>. Identification of the influence of Pb source and soil environment characteristics on Pb bioavailability can improve the prediction of the environmental impact and biomagnifications of Pb at the food web scale. However, due to natural variability in soil chemistry and plant uptake rates, it has

been difficult to pinpoint defined mechanisms of Pb uptake from spent munitions at macroscopic scales<sup>7</sup>.

### **Pb Isotopes as Environmental Tracers**

Pb released into the environment bears the isotopic signature of the ore from which it was derived<sup>8,9</sup>. Early Pb isotope studies show that the  $^{206}\text{Pb}/^{207}\text{Pb}$  radiogenic isotope ratios can successfully be employed as an emissions tracer of atmospheric pollution from leaded gasoline<sup>8</sup>. Ore bodies of Pb used in industrial applications typically yield a lower  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic ratio than naturally sourced Pb in soils and sediments, which exhibit a  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic ratio of approximately 1.21<sup>10</sup>. A distinction between pre-1970's and post 1970's North American ore  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic ratios (1.137-1.197 and 1.28-1.33, respectively) reflects the influence of change of ore on the  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic ratios of atmospheric aerosols<sup>10-12</sup>. Characterization of the Pb isotopic composition of ores used in industry can, therefore, enable their use as a proxy for pollution chronology where significant changes in ore production and industry usage can be traced in anthropogenically influenced atmospheric deposition. Pathway identification can be used to determine environmental fate of heavy metal contaminants and to assess ecological exposure<sup>13</sup>. Mixing models of Pb isotope composition ratios of both anthropogenic and natural end-members have been identified in natural systems, which demonstrates the effect of anthropogenic Pb dispersing through ecosystems on human timescales<sup>14</sup>.

The use of  $^{206}\text{Pb}/^{207}\text{Pb}$  stable isotope ratios as tracers has expanded to use in other media such as in aqueous environments and in macrophytes and as well as for other



sources of pollution like point and nonpoint sources<sup>8, 15, 16</sup>. Analysis of several media e.g. atmospheric bulk deposition, soils, freshwater, and plant materials shows that <sup>206</sup>Pb/<sup>207</sup>Pb stable isotope composition ratios are also useful in identifying biogeochemical pathways of Pb in the environment<sup>15</sup>. Pathway identification can be used to determine environmental fate of heavy metal contaminants and to assess ecological exposure<sup>13</sup>. Mixing models of Pb isotope composition ratios of both anthropogenic and geogenic end-members have been identified in natural systems<sup>14</sup>.

Only in recent times has Pb from spent ammunitions within and surrounding shooting ranges been identified as a known source of contaminants, and research conducted shows elevated concentrations of bioavailable metals are associated with shooting range sites<sup>17</sup>. Recent investigations have evidenced the threat of Pb ammunition persisting in the environment to avian species, mainly through ingestion of Pb shot used in hunting<sup>18, 19</sup>. Biomagnification of Pb through the food chain has been observed at a factor of 100 times greater in horn snails than plants at skeet shooting range at Naval Weapons Station Seal Beach, which raises concerns over health of organisms on the ecosystem scale<sup>20</sup>.

### **Preliminary Assessment**

Five flora samples were obtained from plants that were growing in contact or nearby bullets. Sample sites are shown in figure 1. In some instances, leaching of metal from the bullet into the soil is evident, leaving a halo of copper patina surrounding the bullet. The five flora samples were ashed in a 70C oven for 72 hours. Samples were diluted 100 times, and analyzed through HR-ICP-MS without undergoing column

chemistry as were samples in this study. Preliminary data of the isotopic signature of Pb extracted from five plant samples from LANWR indicates four samples with similar isotopic ratios from approximately 1.170 - 1.190 and an outlier at 1.135 (Fig. 2). The first possible explanation is that the four similar isotopic ratios share a similar source and the samples with a lower concentration (higher inverse concentration value) have been diluted with a greater fraction of coarse-grained material that contains little Pb. The outlier with a distinct and lower Pb isotope ratio originates from a different source, and has a much higher concentration of Pb than those measured in the other four samples. An alternative scenario is that there are more than two sources of Pb, each with different isotopic ratios and concentrations.

CHAPTER II  
IDENTIFICATION AND DISTRIBUTION OF ANTHROPOGENIC AND NATURAL  
PB IN A FORMER WWII AERIAL GUNNERY RANGE

**Introduction**

Owing to the soft, malleable yet dense nature of Pb as a material, Pb was commonly incorporated into ammunition<sup>2</sup>. Excess ammunition in post-war periods has resulted in dumping, stockpiles, and widespread ammunition detritus in and around military installations, and these munitions are often left with little to no effort to remediate or mitigate environmental impacts<sup>6, 21</sup>.

Several investigations have highlighted the forensic capability of mass spectrometry to distinguish type of bullet and to identify the wide range of Pb isotopic composition variability of differing types of bullets<sup>22, 23</sup>. The study of historical Pb inputs from atmospheric sources and Pb ores facilitates the ability to distinguish Pb additives to gasoline and from metal alloys used in WWII era bullets. Only recently has Pb from spent ammunitions within and surrounding shooting ranges been identified as a known source of contaminants, and research conducted shows elevated concentrations of bioavailable metals are associated with shooting range sites<sup>17</sup>. Recent investigations have evidenced the threat of Pb ammunition persisting in the environment to avian species, mainly through ingestion of Pb shot used in hunting, which can result in death via Pb poisoning<sup>18, 19</sup>.

Numerous studies analyze Pb at such sites in total concentrations of soils, plants, fauna, etc.<sup>2, 7, 17</sup>. Additionally, a smaller number of studies address the distribution or

partitioning of Pb within the ecological system i.e. in constituent soil fractions, in specific parts of plants<sup>6, 24, 25</sup>. Selective sequential extraction procedures are common, though aptly debated, procedures to identify associations of an element of interest in operationally defined soil mineral fractions<sup>26, 27</sup>. Few studies utilize isotopic analysis to determine source of contamination at military installations or firing ranges or forensic use in ammunition<sup>23</sup>. Pairing isotopic analysis with selective sequential extractions enables a more precise understanding of distribution of Pb within soil mineral fractions. This, in turn, enables the identification and differentiation of isotopically distinct sources of Pb and their distribution within the soil mineral fractions than solely bulk analysis<sup>28-30</sup>. Isotopic analysis of soil mineral fractions and plants serves as a tool to differentiate distinct sources of Pb, to determine distribution of Pb in the soil<sup>29</sup>.

This study seeks to identify and differentiate isotopically distinct sources of Pb and their distribution in an area known to contain point source pollution. The objectives of this study are to employ isotopic analysis to soil mineral fractions determined by a selective sequential extraction and plants within a former WWII aerial gunnery range and current national wildlife refuge in coastal South Texas. Laguna Atascosa National Wildlife Refuge provides an interesting research location in that it contains legacy small munitions while its close proximity to the United States/Mexican border may result in observable differences in non-point source pollutant Pb isotopic compositions.

### **Research Location and Background**

Laguna Atascosa National Wildlife Refuge is the largest protected area of natural habitat in the Lower Rio Grande Valley with 45,187 acres<sup>31</sup>. LANWR's

ecological prominence is predicated on its unique location as a confluence point where a bottleneck of the Central portion of the North American Flyway is exhibited (Fig. 3). As a result, LANWR serves as a habitat for 10 federally endangered or threatened species, and has the most bird species documented (411 species) of any national wildlife refuge<sup>31</sup>. Geographically, LANWR is approximately 34 miles north-northeast of Brownsville, TX in the southernmost tip of Texas (Fig. 3). LANWR is the permanent home to unique species, including the aplomado falcon and the endangered ocelot, and is also the transient home to nearly half of all migratory bird species in continental United States<sup>31</sup>. LANWR's geographical features vary widely with only minor topographic relief. Habitats include freshwater wetlands, thorny forests, coastal prairies, mudflats and beaches<sup>31</sup>. LANWR also contains unique clay dunes called "lomas"<sup>31</sup>. Plant communities in this area are strongly influenced by minor topographic changes ranging from barren salt flats in topographic lows, grasslands, and to thorny-scrub with yucca plants in topographic highs (Fig. 4).

#### *History of LANWR*

The plot of land along the coast of South Texas was obtained by the Department of Defense (DoD) in the 1940's<sup>31</sup>. Figure 7 displays oval shaped berms were constructed to serve as target practice for air-to-surface combat and as a bombing range with some berms even containing railroad tracks that facilitated moving target practice<sup>31</sup>. The berms are located along a curvilinear path that roughly parallels the coastline (Fig. 5). Berms are artificial topographic highpoints, and rise from approximately 12 to 20 feet above the surrounding topography (Fig. 4). The berms are oval in shape and are elevated

from the surrounding topography in the perimeter only, which serve as artificial topographic highs with topographic lows in the interior of each oval. The interior portions of the berms are generally level with the natural topography or slightly lower, and are often filled with water during the wet season.

#### *Input of Pb into LANWR*

Identifying potential sources of natural Pb deposition are extremely difficult to constrain to more specific than broad, regional isotopic averages due to the dynamic deposition setting of LANWR. The Rio Grande once flowed through LANWR, which could have potentially introduce sediments that originated from as far away as Southern Colorado (Fig. 6)<sup>32</sup>. LANWR is located in a semi-arid coastal environment, which is likely influenced by atmospheric deposition of sediments as well as marine deposits. Complete characterization of sediment deposition in LANWR is beyond the scope of this study, but a generalized natural Pb end-member isotopic composition was obtained through analysis of Pb-containing Texas coastal sediments in this study and comparison of published values.

Several uranium-bearing stratigraphic units lie parallel to the Texas coastline approximately 100-150 mi inland (Fig. 6). These formations include the Goliad (Pliocene), the Fleming and Oakville (Miocene), Catahoula (Oligocene), and the Jackson and Rio Grande Embayment (Eocene)<sup>33</sup>. The average  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{208}\text{Pb}$  stable isotopic compositions associated with these formations ranges from 1.19 to 1.237 and 0.48 to 0.496, respectively<sup>34, 35</sup>. These stratigraphic units are composed of uranium-bearing volcanic ash and volcanic-glass rich mudstones and siltstones<sup>33, 36</sup>.

Possible sources of anthropogenic Pb include abundant bullets and the resulting *in situ* metal leaching from spent munitions that are abundant near target practice berms and in areas where sediments (and bullets) that were drained away from the artificial topographic highs have deposited. Observed munitions range in size and caliber, but the 0.50 caliber bullet is the most commonly observed munition. Bullets display a distinct copper patina with some examples displaying an interesting metal precipitate at the base of the bullet (Fig. 7). Many of the bullets in LANWR display copper patina ‘halos’ around the bullet in the soil, which result from *in situ* weathering and display the influence of water in leaching of metals (Fig. 8). Additionally, many bullets are fragmented, thus enabling the leaching of metals contained in the alloy core of each bullet (Fig. 9).

Additionally, a wide array of deposited atmospheric particulate matter may be present due to LANWR’s proximity to industrial activities in the region and pollution from Mexico, which phased out leaded gasoline as recently as the late 1990’s. Due to the regional wind direction, it is plausible that particulate matter, particularly from the Matamoros and Reynosa metropolitan areas, is depositing in LANWR (Fig. 10). The semi-arid climate with strong winds likely redistribute fine grained particulate matter that has been deposited over human time scales.

## **Methodology**

### *Study Area and Sample Locations*

Samples were semi-randomly collected in two general categories: those deliberately sampled near the target practice berms, herein referred to as ‘anthropogenic’ samples, and others randomly sampled in areas not located near berms where no bullets were observed, referred to as ‘natural’ samples (Fig. 11). Anthropogenic samples tend to occur in and around the berms as well as in wash out areas of topographic lows.

### *Environmental Sample Collection*

#### **Soil Sampling**

Samples were collected with plastic trowel that was cleansed with deionized water after each sampling. Approximately 0.75 to 1 kg of soil per sampling location was obtained. Samples were placed in polyethylene (PE) bags for shipment and storage. Samples were stored wet in PE bags at 4°C to minimize geochemical changes due to microbial degradation<sup>37, 38</sup>.

#### **Plant Sampling**

Plant samples were collected from a 1 m<sup>2</sup> at each sample location. Each species present in the sample area was deliberately sampled in order to obtain a representative, though potentially diluted, isotopic composition for plants in each sample area. Samples were collected and placed in polyethylene bags, and stored in a styrofoam cooler in the field. Upon arrival to the laboratory, plant samples were placed in a refrigerator at a temperature of 60°F<sup>39</sup>.



### *Sample Treatment*

End-member analysis for the natural source consists of sample preparations and extractions executed in accordance to methods previously developed, and were executed at the Glenn T. Seaborg Institute at Lawrence Livermore National Laboratory and at the Williams Radiogenic Isotope Laboratory at Texas A&M University. Soil samples were sequentially leached for Pb analysis using a modified version of a previously published optimized BCR 3-step sequential extraction<sup>40, 41</sup>. Pb column chemistry was performed in a class-100 clean lab in order to purify samples for improved ICP-MS analysis.

### *End-member Identification*

Identification of the anthropogenic isotopic ratio end-member was completed through chemical analysis of a spent bullet collected at LANWR, and a potential natural Pb isotopic composition was obtained from a sediment sample of the Catahoula formation. Bulk analysis of the bullet was completed by leaching in 2% nitric acid to mimic natural leaching, and purified through lead column chemistry. This deliberately varies from procedures developed to completely dissolve (25% HNO<sub>3</sub> containing 0.5% HF at 80°C) ammunition for forensic testing because complete dissolution will not approximate natural weathering conditions, which are being approximated by a 2% HNO<sub>3</sub> leach<sup>42</sup>. The Catahoula sediment sample was ground with mortar and pestle to homogenize the sample. A mass of approximately 0.25 g of Catahoula volcanic ash sediment was placed in a 50 mL centrifuge tube and placed in an oven 90°C for 48 h. The Catahoula sediment was leached with *aqua regia*, and purified through lead column chemistry.

### *Sequential Extraction Procedure for Soils*

Soil samples were homogenized through manual mixing, and a representative sample of approximately 1 g of soil was ground with mortar and pestle. A sample of approximately 0.25 g of ground material was placed in a 50 mL centrifuge tube for each sample and placed in an oven to dry at 55°C for 72 h. Three samples from Site 2, 6, and 10 are selected for analytical duplicates.

The sequential extraction procedure performed is modified from the modified BCR 3-step sequential extraction<sup>41</sup>. The dried and homogenized 0.25 g samples are treated with a four step sequential extraction. This sequential extraction procedure sequentially dissolves the exchangeable and acido-soluble, the reducible, the oxidizable, and the leachable residual soil mineral fractions (Table 1)<sup>25</sup>. 0.11 M acetic acid is used to extract the exchangeable and acido-soluble fractions, and 0.5 M hydroxylamine hydrochloride is used to extract the reducible fraction. The oxidizable fraction is extracted with 8.8 M hydrogen peroxide followed by 1.0 M ammonium acetate. The residual fraction is extracted with *aqua regia*.

### *Plant Sample Treatment*

Plant samples were obtained by sampling leaves and stems of different species of plants. Plant samples were composited to obtain an average Pb concentration and to account for differences in inter-species Pb uptake due to variation of plant species throughout the refuge<sup>43</sup>. Plant samples were dried at 55°C for 72 h, and dissolved using concentrated nitric acid, centrifuged, and the supernatant analyzed by ICP-MS<sup>10</sup>.

### *Analytical Techniques*

Pb was separated and purified using anion exchange column (100 µl column and Dowex AG1-X8 anion exchange resin) with 1.8 M HCl and 6 M HCl to elute Pb. Samples were analyzed for Pb using high resolution, inductively-coupled plasma mass spectrometer (Element XR HR-ICP-MS) at Texas A&M University. One (of two bullet potential end-member identification samples) was analyzed using multi-collector inductively-coupled plasma mass spectrometer (NuPlasma MC-ICP-MS) at Lawrence Livermore National Laboratory.

### **Differentiation of Natural and Anthropogenic Sources of Pb**

The Pb isotopic compositions of samples display two distinctive trends, and the dataset can almost completely be divided into two categories: samples collected in areas visibly devoid of bullets and exhibit a more ‘natural’ or geogenic Pb isotopic composition range and samples collected in the close vicinity of bullets and bear what is considered to be an anthropogenic Pb isotopic composition range (Fig. 12). Two samples, 8b and 11, are excluded from this general trend, which denotes the absence of the at least a predominant anthropogenic source of Pb within those samples, however no natural samples’ isotopic compositions fall below the division. The outliers likely represent samples obtained in localized areas of minimal influence from bullet leaching.

In general, samples characterized as natural bear a narrower range of  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic compositions and  $^{206}\text{Pb}/^{208}\text{Pb}$  isotopic compositions that are heavier than those observed in anthropogenic samples with  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{208}\text{Pb}$  values ranging from 1.191 to 1.235 and 0.479 to 0.496, respectively. The likely explanation for this

observation is that anthropogenically influenced samples have been exposure to multiple sources of Pb that display lower  $^{206}\text{Pb}/^{208}\text{Pb}$  values than most North American geogenic samples<sup>44</sup>.

### *Pb Isotopic Composition in Soils*

#### **Soluble/Ion-exchangeable, Reducible, and Oxidizable Fractions**

The soluble/ion-exchangeable, reducible, and oxidizable fractions in natural samples exhibit a similar Pb isotopic composition with  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{208}\text{Pb}$  values ranging from 1.207 – 1.224 and 0.486 – 0.494, respectively (Table 3). Natural samples within these three fractions exhibit a more clustered trend, which suggests a common source of Pb (Fig. 13).

The soluble/ion-exchangeable, reducible, and oxidizable fractions in anthropogenic samples exhibit a greater range of Pb isotopic compositions with  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{208}\text{Pb}$  values ranging from 1.131 – 1.229 and 0.471 – 0.491, respectively (Table 2). Again, samples 8b and 11 resemble the isotopic composition of natural samples, while the remaining samples range from relatively clustered around the trend line to isotopic compositions that resemble the residual clays. The wide range of isotopic compositions, particularly in  $^{206}\text{Pb}/^{207}\text{Pb}$ , suggests a higher degree of end-member mixing, which likely results from mixing of multiple anthropogenic and geogenic sources of Pb so as to somewhat obscure the geogenic Pb isotopic composition range but not completely overwhelm the geogenic isotopic composition with anthropogenic compositions (Fig. 13)<sup>29</sup>.

## Leachate of Residual Mineral Fraction

The Pb isotopic compositions of samples treated with leach 4 are inferred to be representative of a partial extraction and not a full digestion. Leach 4 consists of a hot *aqua regia* treatment, which is essentially a strong leach<sup>45, 46</sup>. Others have employed *aqua regia* as a leach to characterize alumino-silicate clays<sup>44</sup>. Pb isotopic compositions in the natural residual silicate leachate differ significantly from those of the remaining fractions. These samples are noticeably offset from the general trend where Pb isotopic compositions of the initial three leaches are more or less clustered, and exhibit isotopic compositions of 1.222 – 1.235 and 0.479 – 0.487 for  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{208}\text{Pb}$ , respectively (Table 2; Fig. 14). This suggests that Pb leached with *aqua regia* represents a different source of Pb within LANWR. Others observe a similar trend where natural Pb isotopic ratios associated with their alumino-silicate fraction are also offset from the general trend of the data<sup>29</sup>. It was concluded that the Pb in the alumino-silicate represents a different mineral source than Pb in the residual leach fraction<sup>29</sup>.

The volcanic ash standard is not strongly related to the alumino-silicate leachate. Given that the isotopic ratios are lower for both  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{208}\text{Pb}$  than the Catahoula ash, it may be plausible to use the Catahoula Ash sample as a coarse proxy for natural Pb. Also given the depositional setting of LANWR, the Rio Grande River deposited sediments that could potentially originate at any point from Southern Colorado to mouth of river (Fig. 6). The Rio Grande also incises outcrops of several uranium-bearing in the South Texas coastal plain, thus it is plausible that the leachable residual fraction bears a different isotopic composition than the ash sample because of the age of

the parent sediments<sup>36,47</sup>. The ash sample is from the Oligocene aged Catahoula formation. Other uranium-bearing formations (both older and younger than the Catahoula) outcrop in the Texas coastal plains, and likely exhibit a range of isotopic compositions that vary accordingly to age (Fig. 6)<sup>33,36</sup>. The leachable residual fraction likely does represent a natural source of Pb because the isotopic composition is somewhat similar to the Catahoula ash sample, and it is well documented in the literature that anthropogenic sources of lead are strongly correlated to the more labile fractions<sup>48</sup>. Though provenance of sediments cannot be constrained, the homogeneity exhibited in natural samples strongly suggests a natural source.

Anthropogenic samples exhibit a shift towards lower  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic compositions from an average of 1.214 to 1.229 and a much lower  $^{206}\text{Pb}/^{208}\text{Pb}$  isotopic compositions of 0.472 to 0.485. Leachable residual fraction samples exhibit the same division between anthropogenic and natural as observed in the initial three leaches (Fig. 14). The consistent pattern of the differentiation of anthropogenic and natural samples where natural samples' isotopic compositions are generally lighter for both  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{208}\text{Pb}$  is observed in the more resistant soil mineral fraction in addition to the more labile fractions.

Teutsch et al. observed a peculiar trend that the natural Pb isotopic composition associated with their alumino-silicate fraction was shifted towards a more anthropogenic composition in areas of high Pb contamination<sup>29</sup>. It was concluded that anthropogenic Pb was incorporated into alumino-silicate minerals via exchange with natural Pb over a timescale of 40 years, which suggests the residual fraction in samples collected in areas

where bullets are abundant may be displaying a similar mechanism of incorporation of anthropogenic Pb over short time scales. The samples in Teutsch et al. contained much higher concentrations of Pb than samples in this study, thus the influence of any natural Pb component in the isotopic composition was overwhelmed and masked by the anthropogenic Pb<sup>29</sup>. At LANWR, the contaminant concentration is sufficiently high enough to affect isotopic ratios, but low enough as to not overwhelm the natural isotopic ratios, which gives rise to a dataset that displays a degree of mixing that is consistent with intermediate concentration ranges as observed in Teutsch et al.<sup>29</sup>. <sup>206</sup>Pb/<sup>207</sup>Pb isotopic ratios of the residual fraction are consistently lower for both unaffected and affected samples.

*Isotopic Composition Range of Anthropogenic Pb – Evidence of Ore-mixing?*

The wide range of <sup>206</sup>Pb/<sup>207</sup>Pb and <sup>206</sup>Pb/<sup>208</sup>Pb isotopic compositions in anthropogenic samples is most likely due to end-member mixing between natural and anthropogenic sources of Pb primarily of bullets in soils and a combination of bullets and atmospheric deposition in plants. The effect of anthropogenic sources of Pb in anthropogenic samples is readily observable; concentrations increase by an order of magnitude, and isotopic compositions in all samples collected in the vicinity of bullets shift towards lower <sup>206</sup>Pb/<sup>207</sup>Pb and <sup>206</sup>Pb/<sup>208</sup>Pb isotopic ratios.

Identification of source of anthropogenic Pb is further confounded by multiple iterations of end-member mixing. The initial end-member mixing likely occurred because of historical policy decisions. LANWR's use as an aerial gunnery range is constrained to the years that World War II was fought. As the threat of war loomed, the

United States began to import larger quantities of foreign Pb to supplement domestic supplies<sup>49</sup>. The mixing of ores (domestic and foreign) in the refining and ammunition manufacturing processes ultimately yields a wide range of isotopic compositions as domestic ores bearing a Mississippi Valley Type (MVT) isotopic composition to much lower, less radiogenic foreign ores (Fig. 15).

#### *Pb Isotopic Compositions of Plants*

Plant samples obtained in areas devoid of bullets display  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic compositions from an average of 1.191 to 1.208 and  $^{206}\text{Pb}/^{208}\text{Pb}$  isotopic compositions of 0.489 to 0.494 (Table 3). Samples collected in areas where bullets are abundant exhibit a shift towards lower  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic compositions from a wide range from 1.140 to 1.199 and lower  $^{206}\text{Pb}/^{208}\text{Pb}$  isotopic compositions of 0.479 to 0.489. Though concentration measurements suggest appreciable quantities of Pb are bioavailable to plants, but isotopic compositions do not directly corroborate this inference because plant isotopic compositions display an offset from the general trend of samples in the bioavailable soil fractions. However, the distinct trend of differentiation between geogenic and anthropogenic sources of Pb where natural samples' isotopic compositions are generally lighter for both  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{208}\text{Pb}$  than samples considered to be more influenced by anthropogenic sources of Pb is observed in all plant samples in addition to soil samples (Fig. 16).

$^{206}\text{Pb}/^{207}\text{Pb}$  isotopic compositions of plant samples are consistently lower than soil samples for both natural and anthropogenic samples, which is a trend consistent with all plant samples. Klaminder et al. observed this trend in disturbed and undisturbed sites



(for atmospheric deposition of anthropogenic Pb and uptake from soils) in Sweden, but only describe this observation as a possible different source of Pb and/or taking up Pb from a deeper/different pool of Pb through deep tree roots, which is extremely unlikely in this context given the surficial sampling scheme of this study<sup>50</sup>.

Notten et al. observe a similar trend of offset in isotopic compositions of plants and snails from the general trend in soils, and attribute the lower isotopic composition of Pb to atmospheric deposition of an anthropogenic source of Pb<sup>51</sup>. Aerosols analyzed in the past 40 years in South Texas and Mexico exhibit isotopic compositions similar to plant samples of LANWR (Fig. 6). It is likely that plant samples from LANWR exhibit isotopic compositions lower than the general leaches 1-3 trend line due to influence from atmospheric deposition of Pb either from leaded gasoline and/or industrial emissions from the U.S. and/or Mexico<sup>11, 52-55</sup>.

The shift from higher to lower Pb isotopic ratios observed in natural and anthropogenic plant samples is attributed primarily to anthropogenic end-member mixing from Pb in bullets. Biotic fractionation is an unlikely mechanism for these observations in that observed isotopic compositions generally increase upon uptake into plants, which is counterintuitive to predict that plants are sequestering isotopically heavier Pb and has never been observed in heavy metals such as Pb. Plant samples were washed with Milli-Pore water prior to digestion, which reduces the influence of airborne particles that may have accumulated on the surface of plant leaves.

Given LANWR's semi-arid coastal setting with moderate to strong winds that vary from predominantly N-NE to S-SE in direction, it is likely aerosols are transported

via eolian processes throughout the region, though the determination of extent of transport and provenance is beyond the scope of this study (Fig. 10).

## CHAPTER III

### BIOAVAILABILITY OF PB IN LANWR

Recent emphasis has been placed on both military and civilian shooting ranges as a source of bioavailable heavy metal contaminants, particularly in biomagnifications through the food chain<sup>20, 56</sup>. The bioavailability of Pb from legacy munitions is strongly correlated to the chemistry of Pb in soils, specifically the mechanism by which Pb may be adsorbed and to which soil fraction it may be adsorbed<sup>6</sup>. Many bullets are fragmented, thus enabling the leaching of metals contained in the alloy core of each bullet into the soil (Fig. 4). Due to LANWR's ecological significance, there is a critical need to investigate the geochemical behavior and bioavailability of contaminants such as Pb. Mobilization of metals from Pb-cored ammunition present from the former use of LANWR as a WWII firing range constitutes an unquantified ecological risk.

This study seeks to determine an approximate measure of the bioavailable Pb for each isotopically distinct source of Pb to plants by comparing concentrations of Pb in various operationally defined soil mineralogical groups through a selective sequential extraction procedure.

#### **Distribution of Pb in Soils – Concentrations**

The sum of Pb of each leach for a given sample represents the summed concentrations of Pb from each leach. These are not considered to be representative of total Pb concentrations in soils as a final HF dissolution was not performed. Summed Pb concentrations from the four leaches in soils range from 316 to 2,333 ppb (Table 3). Pb concentrations in soils are relatively low throughout LANWR, ranging from one to

hundreds of parts per billion. Concentration measurements vary by an order of magnitude in samples obtained in areas devoid of bullets versus areas near target practice berms where bullets are widely dispersed or concentrated in topographic lows.

A significant portion of Pb in soil fraction is contained in the soluble/acid-extractable fraction, which constitutes 18.4% to 59.2% of the summed Pb concentration. Due to poor data quality, most concentration measurements for the soluble/acid-extractable fraction could not be used for analysis. Concentrations of the soluble/acid-extractable fraction for natural samples range from 309 to 348 ppb, whereas concentrations for anthropogenic samples range from 1,663 to 2,316 ppb. The reducible fraction contains the highest observed concentrations and percentage of Pb with concentrations ranging from 133 to 6,822 ppb, constituting 39.7% to 75.3%. The smallest concentrations of Pb are found in the oxidizable soil fraction with concentrations ranging from 0.1 to 1.4 ppb. The leachable residual fraction contains minute concentrations of Pb, ranging from 1.9 to 8.5 ppb.

Though the dataset is limited due to poor concentration results in leach 1, the bulk of Pb in soils is contained in the soluble/acid-extractable and reducible fractions, ranging from 18 to 57% for the soluble/acid-extractable fraction and 39% to 75% for the reducible fraction. This is particularly interesting due to the implications of Pb bioavailability. Two of the dominant pathways of Pb enrichment in plants is via uptake through the roots from the soil solution and uptake of aerosol particulate matter via respiration<sup>39, 48, 57</sup>. With the majority of Pb contained in more labile soil fractions, the amount of potentially solubilized Pb increases the potential for Pb to be bioavailable to

plants via root uptake. Additionally, Pb may be absorbed through uptake of aerosol particulate matter via respiration, which could represent a mix of locally sourced airborne sediments from within the refuge to sediment sourced from outside the refuge. By comparing the summed concentration of Pb in soils to the concentration in plants, it is observed that appreciable quantities of Pb are bioavailable to plants given that total Pb concentrations in plants range from 2 to 180 ppb where summed soil leach concentrations range from 316 to 2,333 ppb.

Within LANWR, bullets accumulate in large quantities in localized washout areas near fire range berms. Given that berms seasonally fill with water and thus serve as transient wetlands and habitats for wildlife, the potential of the introduction of Pb in the food chain exists via release of Pb contained in more readily leached soil minerals and introduction to the food chain through primary producers.

### **Bioavailability of Pb in Plants**

Plant samples obtained in areas devoid of bullets exhibit low concentrations, ranging from 3.2 to 7.9 ppb (Table 3). Samples collected in areas where bullets are abundant concentrations up to two orders of magnitude greater than those of natural samples, and range from 13.4 to 180.4 ppb (Table 3). In comparison to concentrations of Pb in soils, it appears that an appreciable quantity of Pb, particularly in plants growing in the proximity of bullets, is bioavailable to plants.

## CHAPTER VI

### CONCLUSIONS AND IMPLICATIONS

The effects of anthropogenic sources of Pb within LANWR are observed both in concentration and isotopic measurements. Pb concentrations in soil and plant samples increase by up to several orders of magnitude in areas where bullets are abundant. Pb concentrations observed are well below published EPA values (over 5,000 ppm is considered hazardous for human health), therefore Pb is unlikely to be a major concern to the ecological health of LANWR<sup>58</sup>. The majority of Pb is observed in the soluble/ion-exchangable and reducible soil fractions. A significant, consistent distinction is observed in the isotopic compositions of all samples, i.e. all soil mineral fractions and plants, obtained in areas affected by bullets versus areas devoid of bullets. In areas devoid of bullets, three general trends are present. Pb in the soluble/ion-exchangeable, reducible, and oxidizable fractions bear a similar isotopic composition range, clustering around the general trend line. The isotopic composition of Pb in leach four, which is inferred to be associated with leachable residual mineral fraction, varies from the other soil mineral fractions. Pb isotopic compositions in the residual mineral fraction appear to be influenced by mixing of natural more resistant minerals, as evidenced from the isotopic composition of the volcanic ash and other mineral fractions analyzed in this study. Influence of the incorporation or adsorption of anthropogenic Pb into/onto more resistant minerals may be a possible mechanism that is responsible for lowering the  $^{206}\text{Pb}/^{208}\text{Pb}$  in the leachable residual fraction where bullets are present. Plant samples obtained in both areas display isotopic compositions that are consistently more enriched in  $^{207}\text{Pb}$  than all

other samples. This is inferred to be an influence of atmospheric deposition potentially via respiration of airborne particulate matter originating from industrial sources of Pb or leaded gasoline, which may be attributed to emissions from the United States and/or Mexico (Fig. 15).

Pb isotopic compositions of samples obtained in areas where bullets are present display a similar distinctions between the soluble/ion-exchangeable, reducible, and oxidizable fractions, the leachable residual fraction, and plant samples. However, the pattern is less distinct and displays a wider degree of mixing as evidenced by the wide range of  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic compositions. This phenomenon likely results from multiple iterations of end-member mixing i.e. ore bodies were mixed in bullet manufacture, metal leachate in the soil may be influenced by deposition of particulate matter, which may be sourced from local to region sediments, thus causing further mixing. Isotopic compositions of bullet samples displayed a wide range of  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios, but similar  $^{206}\text{Pb}/^{208}\text{Pb}$  ratios. The wide variation in  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic compositions likely represents end-member mixing of different ores used in the manufacture of bullets during WWII as the U.S. shifted from more domestic to an increasingly larger amount of foreign ores as the U.S. prepared for war<sup>49</sup>. Additional mixing likely occurred as bullets become physically dispersed throughout LANWR and bullets began to leach into sediments. Atmospheric industrial or automotive emissions is most evident in plant samples, and likely constitutes an additional source of anthropogenic Pb into the refuge. Natural Pb in sediments are likely to be influenced by a wide variety of processes, including fluvial sediments carried by the Rio Grande when

its path flowed through the refuge, atmospheric deposition, and coastal erosion and deposition processes.

Legacy Pb contamination at former military installations persists as a source of potential hazards for ecological health. Numerous studies analyze Pb at such sites in total concentrations of soils, plants, fauna, etc.<sup>2, 7, 17</sup>. Additionally, a smaller number of studies address the distribution or partitioning of Pb within the ecological system i.e. in constituent soil fractions, in specific parts of plants<sup>6, 24, 25</sup>. Few studies utilize isotopic analysis to determine source of contamination at military installations or firing ranges or forensic use in ammunition<sup>23</sup>. Isotopic analysis of soil mineral fractions and plants serves as a tool to differentiate distinct sources of Pb, to determine distribution of Pb in the soil, and to serve as a measure of the bioavailability of Pb in a habitat<sup>29</sup>. Such research can directly benefit wildlife officials to better target problematic areas and prioritize areas of concern to maximize benefit for wildlife.

Plant samples were composited during this study in order to provide a general isotopic profile for a given sample area. Such a process obscures the Pb isotopic signature variations that may exist from species to species as well as provides no information regarding uptake mechanism. In order to better characterize plant uptake, and perhaps demonstrate the effect of aerosol particulates on plants, it would be advantageous to analyze plant roots, stems, and leaves separately. Additionally, collection and analysis of particulate matter in LANWR would provide valuable information regarding the influence of local and/or regional source of aerosols on plants and surficial soil sediments.



Throughout the course of this research, the water cycle in LANWR is drastic. Many low-lying areas serve as transient wetlands in the winter months, but are completely dry in the summer. Further research into the effects of water on biogeochemistry on a temporal scale could yield fascinating insight into the importance of water, not as a biologic necessity, but a driving mechanism of localized geochemistry.

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## APPENDIX A



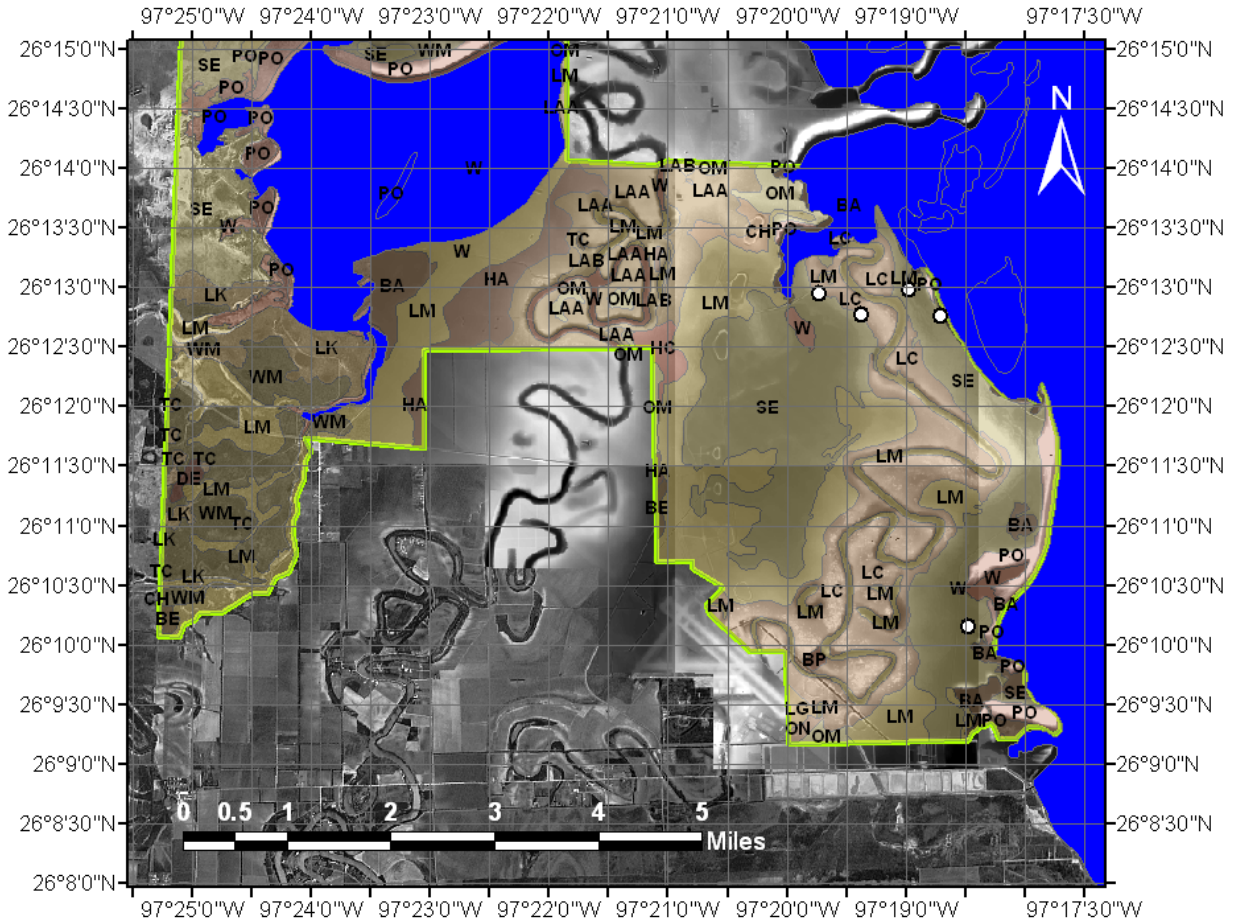


Figure 1. Location of preliminary plant samples indicated by white circles with black outline on soil units map. Samples were obtained in the Lomalta clay soil units, which are generally composed of silty clay loams and clays. Plant samples were obtained from individual plants of differing species.

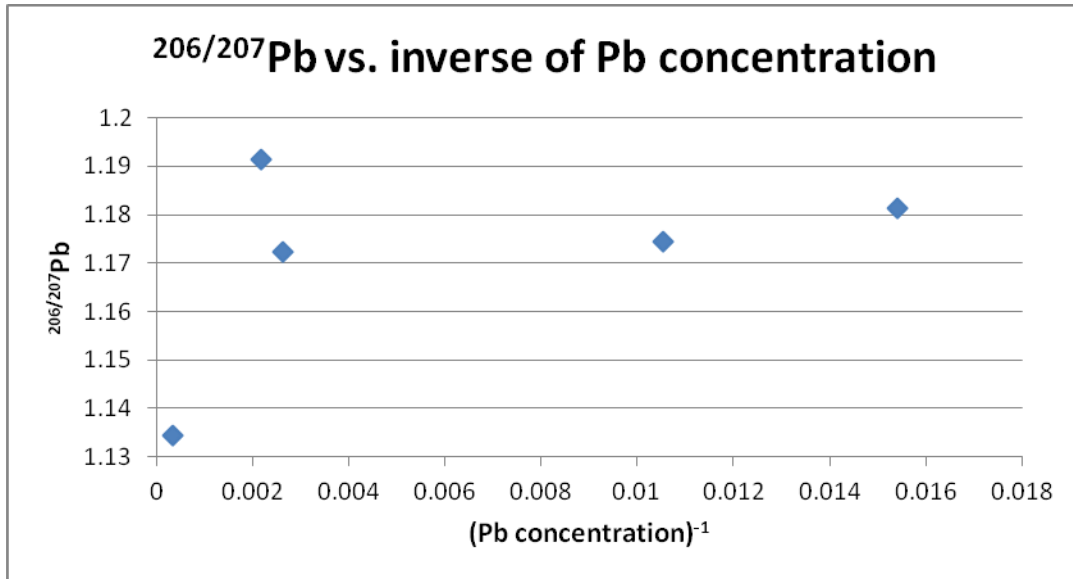


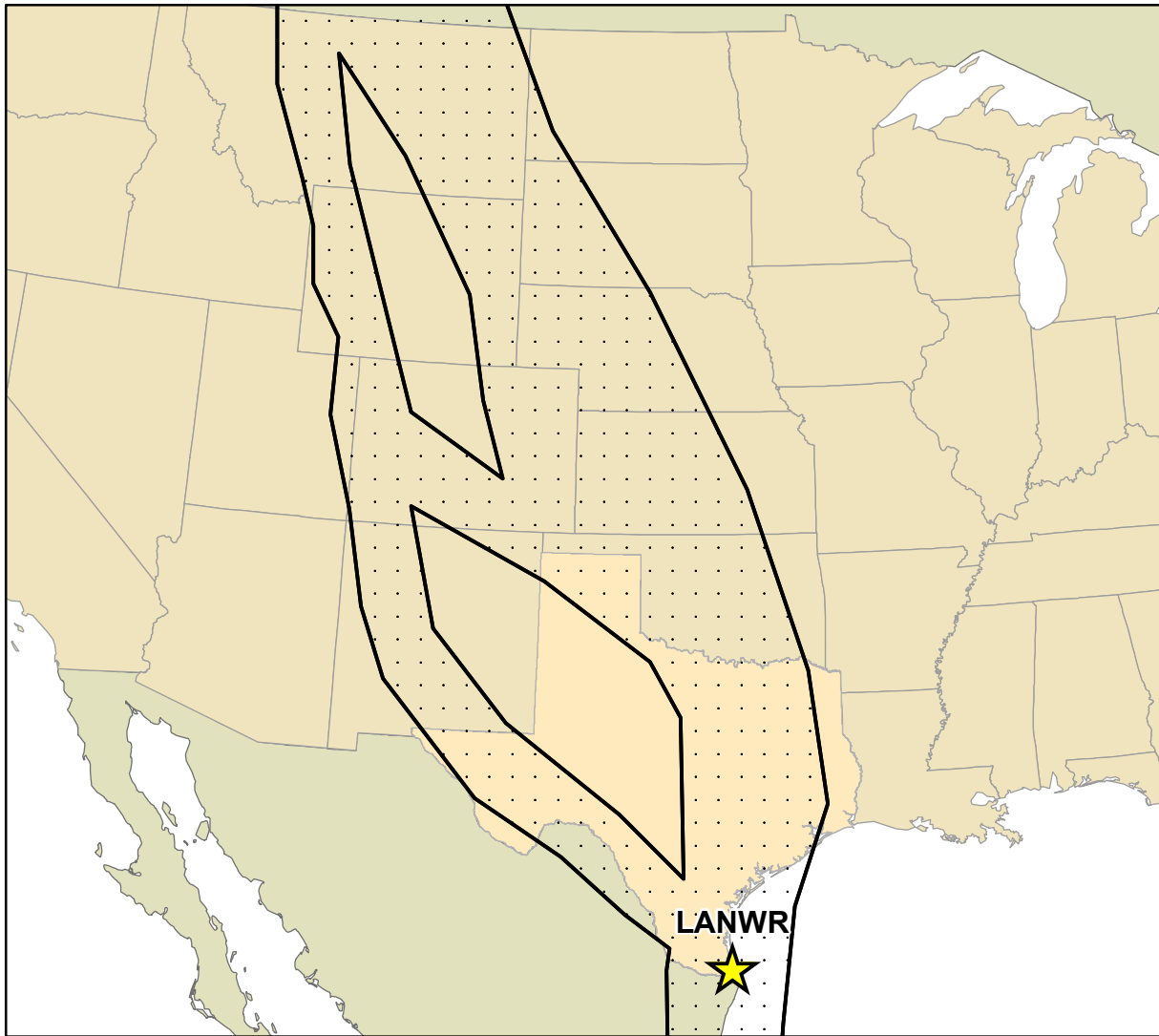
Figure 2. Inverse of total Pb concentration vs. ratio of <sup>206</sup>Pb/<sup>207</sup>Pb isotopes, illustrating <sup>206</sup>Pb/<sup>207</sup>Pb isotopic composition dissimilarities primarily between samples of the highest and lowest concentrations.



Figure 3. Example of bullet weathered *in situ*. Copper patina is apparent in surrounding soil, and large metal oxide nodules are commonly precipitated around the base of the bullet where the bullet core is exposed.



Figure 4. Bullet fragments in a washout near a target practice berm. Intactness of bullets range from pristine, unexploded with copper patina to shards. A range of intactness is observed in topographic lows, which function as washout areas that drain to the Laguna Madre.



**LEGEND**

- ★ Laguna Atascosa National Wildlife Refuge (LANWR)
- Central Portion of North American Flyway

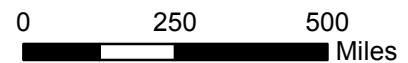


Figure 5. Location of LANWR, South Texas and its proximity to the Central Portion of the North American Flyway. Modified from Natural Resources Conservation Service.

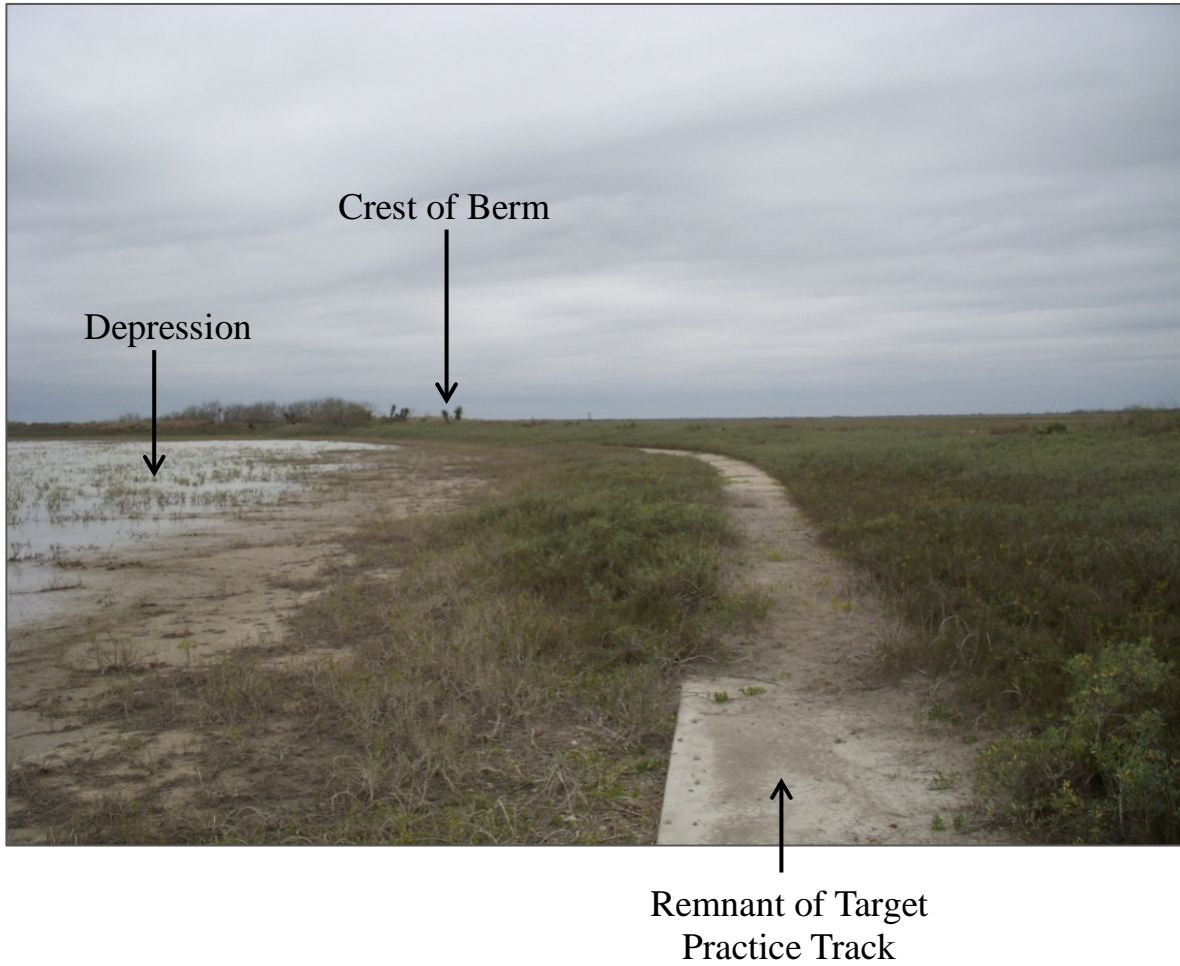




Figure 6. View of berm morphology with remnant target practice track. Vegetation varies along a topographic gradient. Yuccas are observed along local topographic highs, and denote the crest of the target practice berms. Here, an example of the man-made target structures persisting in environment is observed.



Source: USGS, NASA

**LEGEND**

-  Target Practice Berm Locations
-  LANWR Boundary

**Digital Elevation Model (Re. MLLW, m)**

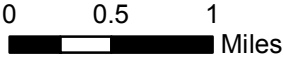
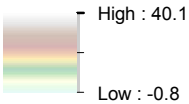


Figure 7. Locations of target practice berms outlined in yellow ovals in LANWR. Target practice berms are oriented in curvi-linear trend that roughly parallels the coastline.

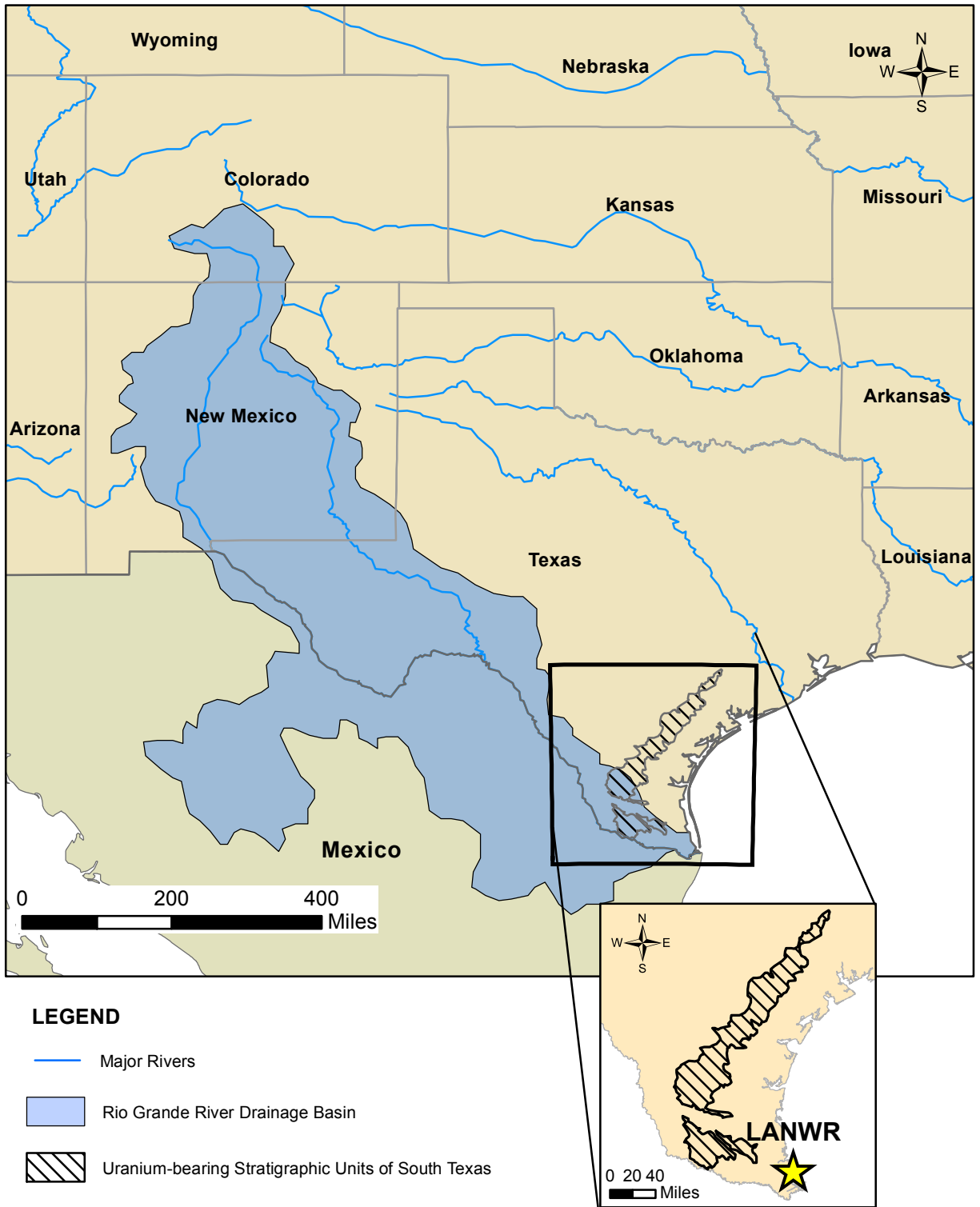
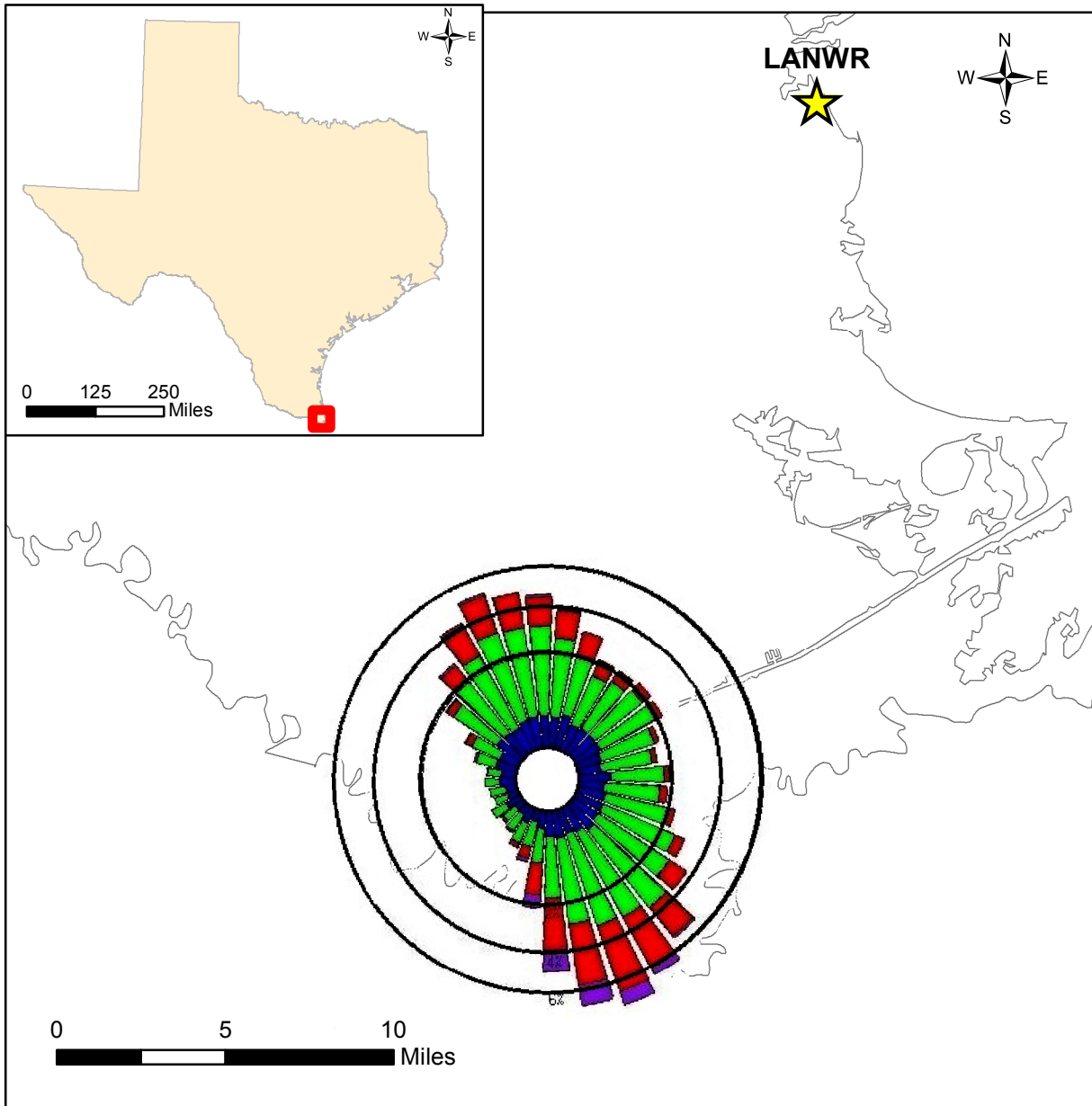


Figure 8. Rio Grande River drainage basin with major uranium-bearing outcropping formations of South Texas and their proximity to LANWR, which was formerly a mouth of the Rio Grande river. Modified from Stanley, 1999 and Ambrose, 2007.





Figure 9. Example of abundant 0.50 caliber legacy munitions observed in LANWR. Note metal precipitates around base of bullet.



**LEGEND**

★ Laguna Atascosa National Wildlife Refuge (LANWR)

**Wind Speed (knots)**

■ 20+	■ 5 - 12
■ 12 - 20	■ 0 - 5

Figure 10. Wind rose diagram for Brownsville - South Padre Island International Airport from 1973 to 2004. Note the predominant wind directions are from S-SE and N-NW. From NOAA Aviation Forecast Preparation System (AvnFPS), 2007.



Source: USGS, NASA

**LEGEND**

- Sample collected in area devoid of bullets
- Sample collected in area with observed bullets
- LANWR Boundary

**Digital Elevation Model (Re. MLLW, m)**

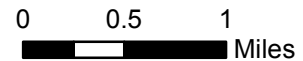
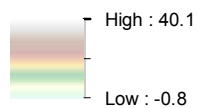


Figure 11. Sample Locations. Samples are symbolized by the presence (black dots) or absence (white dots) of bullets.

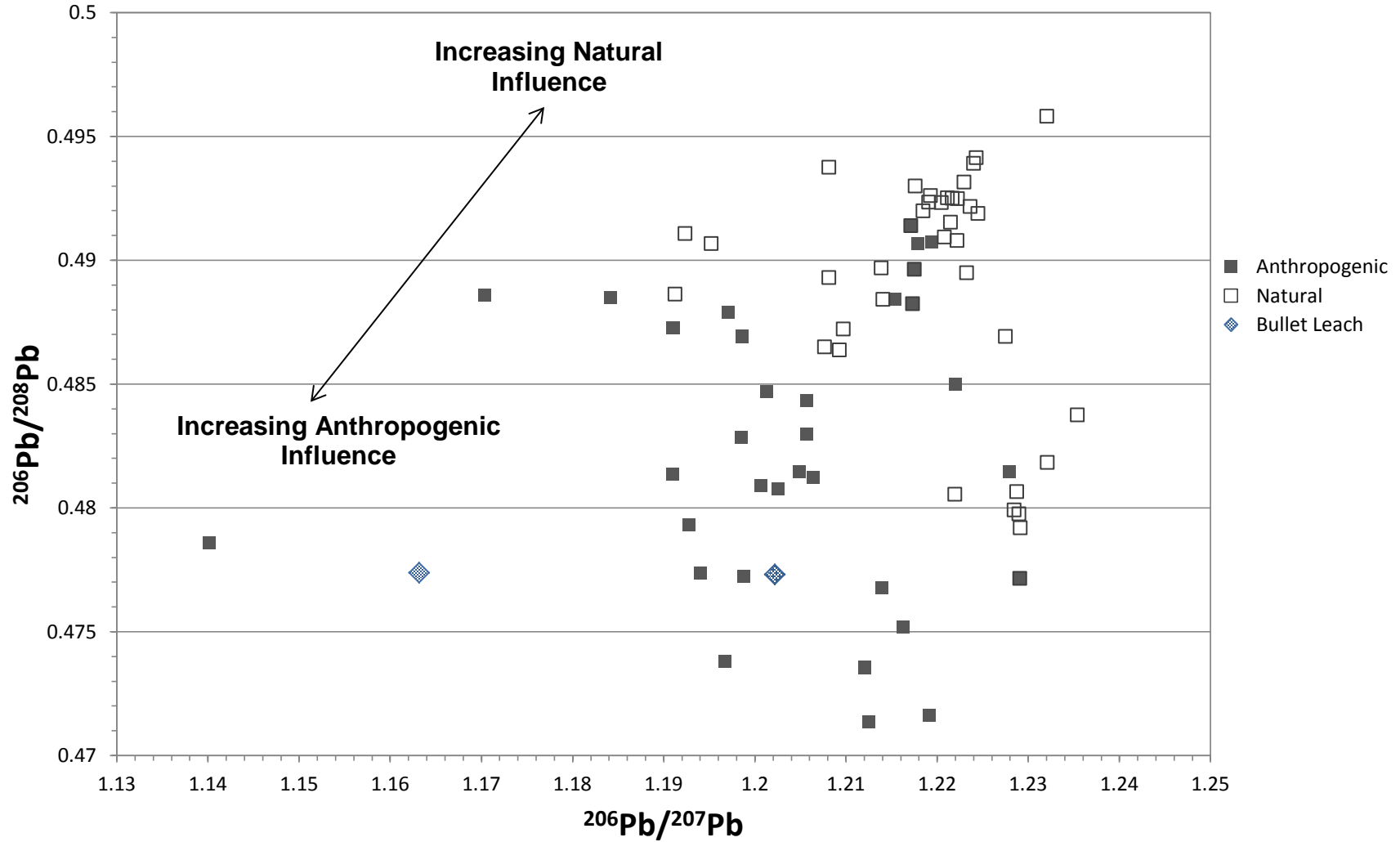


Figure 12. Distinction between natural and anthropogenic isotopic compositions. Samples clustered around higher  $^{206}\text{Pb}/^{208}\text{Pb}$  isotopic compositions reflect the influence of predominantly natural Pb, whereas samples of increasingly anthropogenic Pb isotopic compositions display a wider range of  $^{206}\text{Pb}/^{207}\text{Pb}$  and lower  $^{206}\text{Pb}/^{208}\text{Pb}$  isotopic compositions

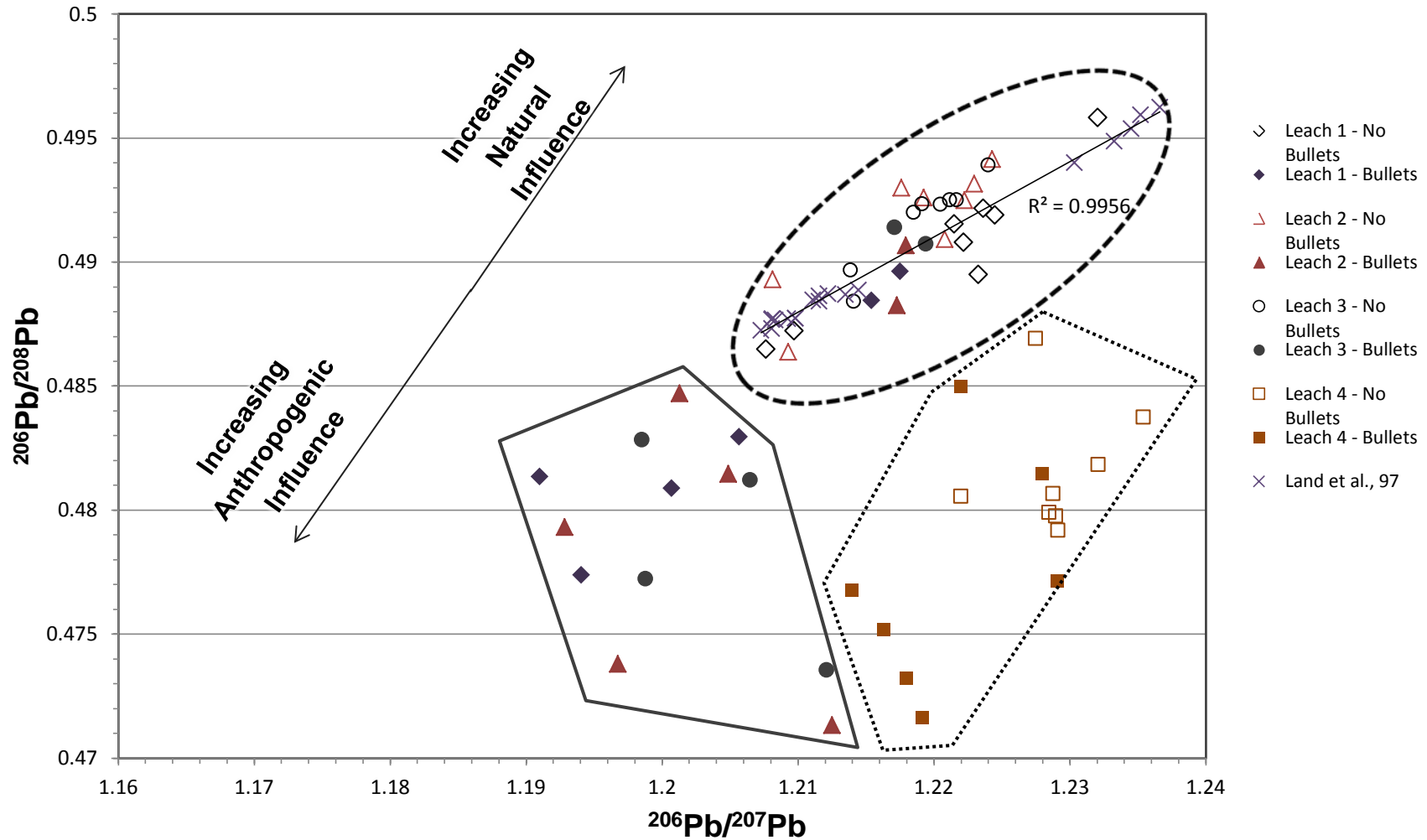


Figure 13. Distribution of anthropogenic and natural Pb in soil samples. Samples are symbolized by leach and by the presence or absence of observable bullets. Labile fraction samples, represented by leaches 1-3, display two patterns: samples with a more natural influenced isotopic composition are more clustered around South Texas volcanic ash isotopic compositions (black dashed oval) whereas anthropogenically influenced samples display more variation in  $^{206}\text{Pb}/^{207}\text{Pb}$  and lower  $^{206}\text{Pb}/^{208}\text{Pb}$  compositions (gray box). The residual mineral fraction (dotted line) displays distinct isotopic variation from the labile fractions.

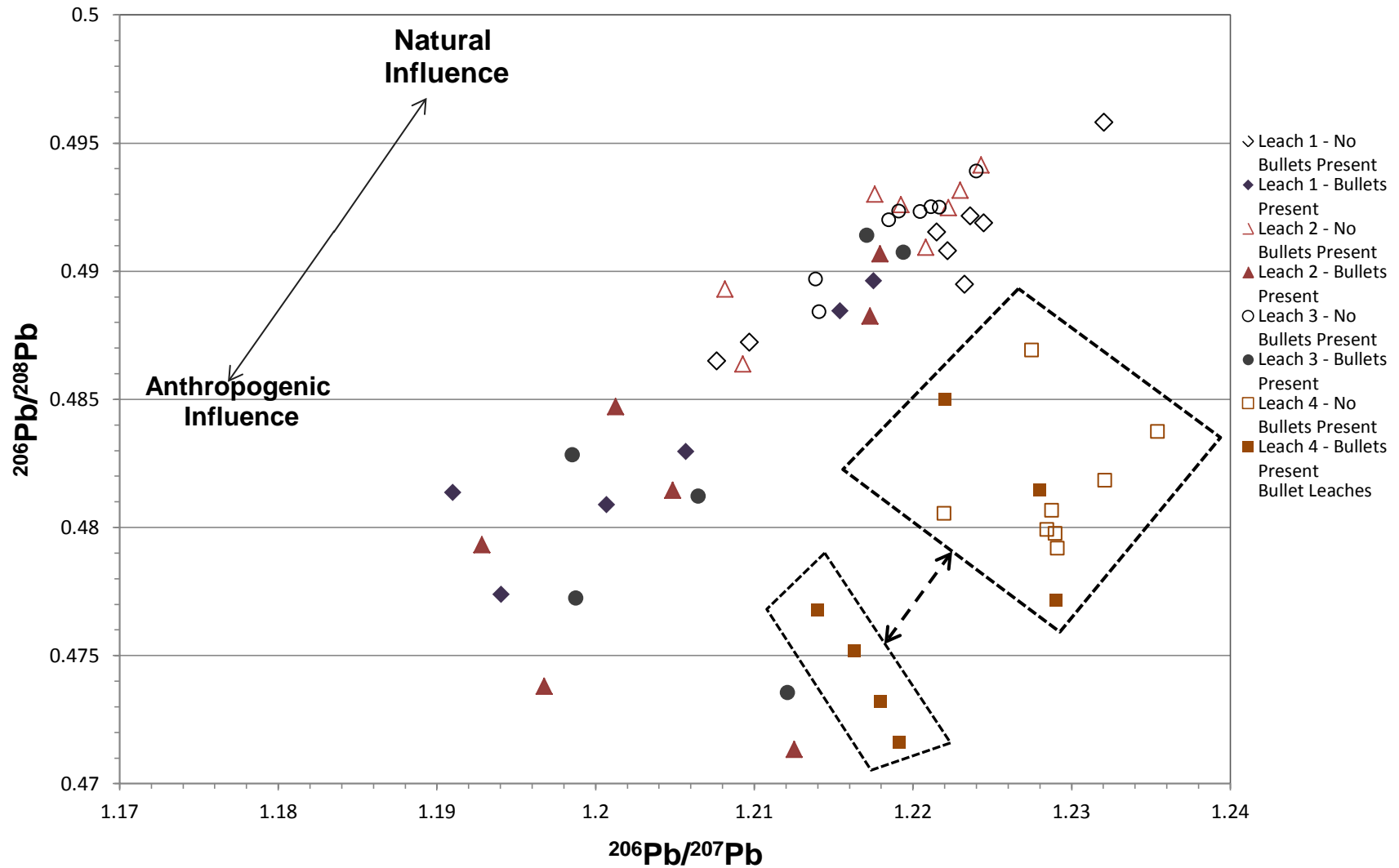


Figure 14. Isotopic composition variation in residual fraction of soils. Two distinct isotopic compositions in more natural Pb and more anthropogenic Pb influenced samples. Similar trend was observed in clays studied by Teutsch et al., and was inferred to represent exchange of anthropogenic Pb with natural Pb (2001).

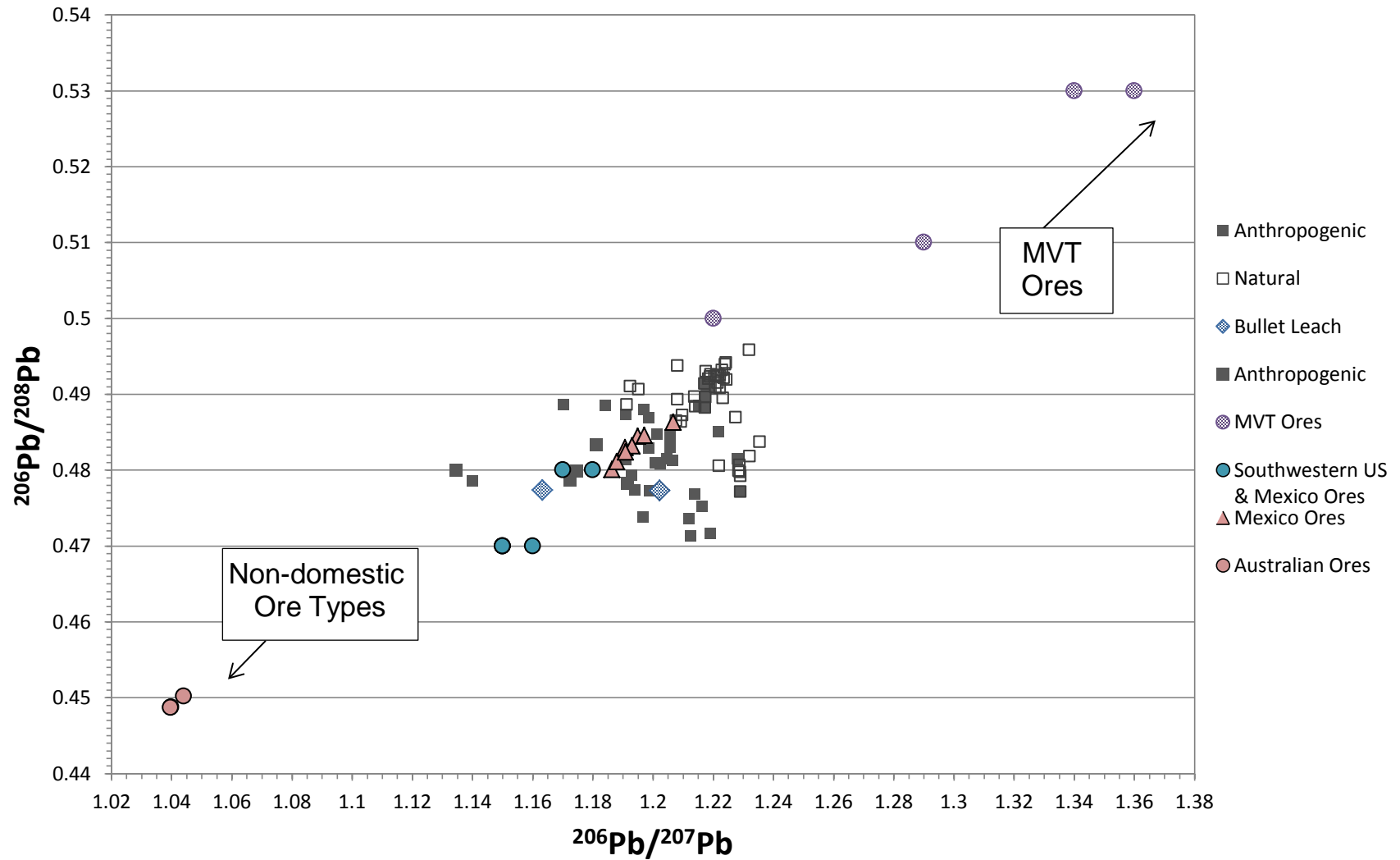


Figure 15. Transition of anthropogenic Pb isotopic compositions from Mississippi Valley Type (MVT) ores to non-domestic sourced ores. MVT Ores and Southwestern & Mexican Ores, Rabinowitz, 2002; Mexico Ores, Cummings, 1979; Australian Ores, Cummings and Richards, 1975.

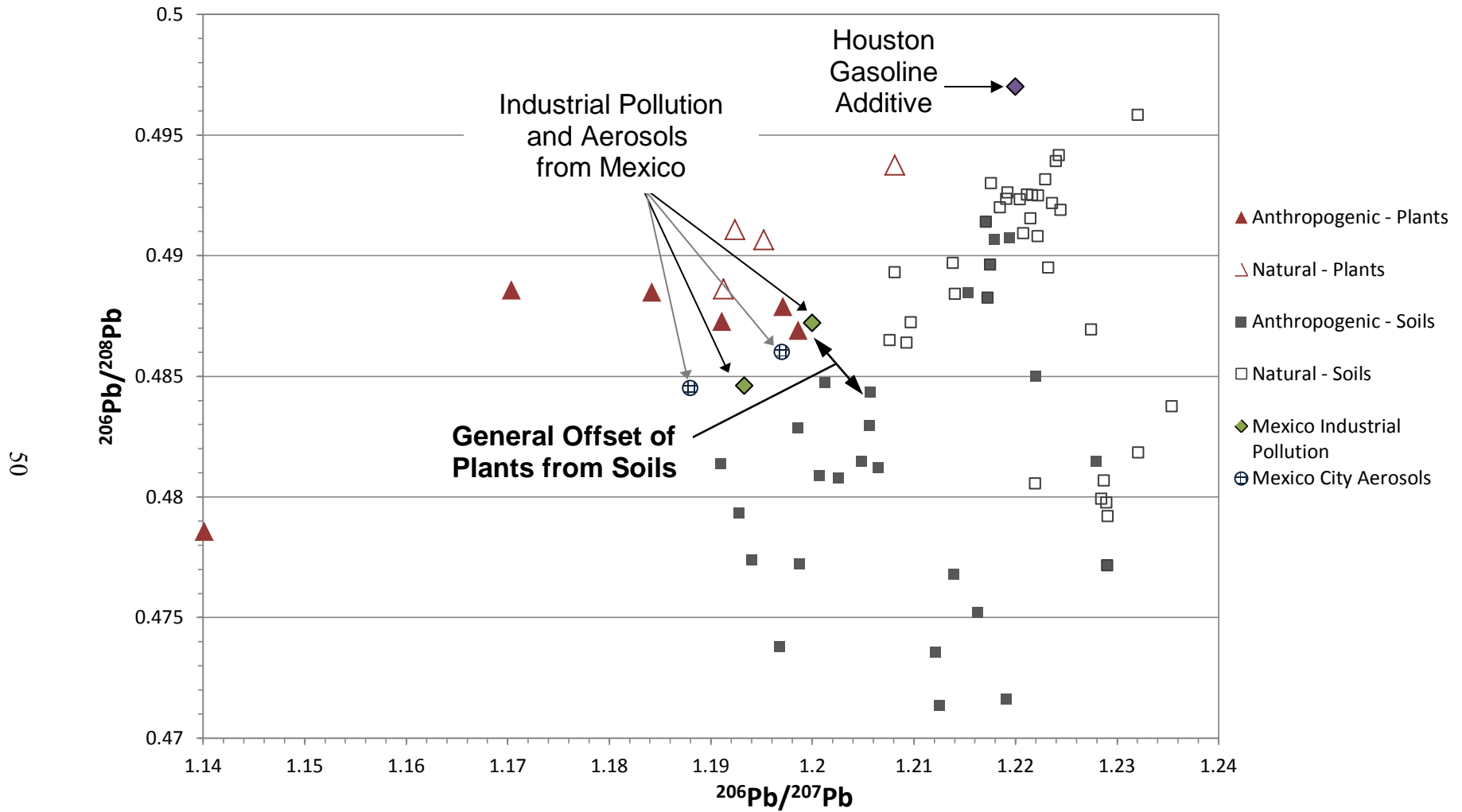


Figure 16. Offset of isotopic composition of plants from soils. All plant samples bear a lower  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic composition relative to soil samples. Industrial pollution from Mexico, Soto-Jimenez, 2006 and Morton-Bermea, 2011; Mexican Aerosols, Bollhofer and Rosman, 2000; Houston Pb emission, Chow et al., 1975.



Table 1. Summary of the Procedures Used.

<b>Selective Sequential Dissolution. Modified from Rauret et al. (1999).</b>		
Leach	Conditions	Association of Pb
1	0.11 M Acetic Acid	Adsorbed, Cation Exchangable, and Carbonates
2	0.5 M Hydroxydolamine Hydrochloride	Oxides
3	8.8 M H <sub>2</sub> O <sub>2</sub> buffered to pH of 2-3 at 85°C, 1 M Ammonium Acetate buffered to pH 2	Organic matter
4	<i>Aqua Regia</i>	Residual Silicates

#### **Ash Digestion**

Conditions	Association of Pb
Aqua Regia and HF heated to 90°C for 24 hr	All associations of Pb

#### **Bullet Leach**

Conditions	Association of Pb
Leach bullet in 2% Nitric Acid for 24 hr	Weakly associated, i.e. adsorbed

Table 2. Pb per Unit Mass of Soil Associated with Respective Fractions of LANWR Soil and Plant Samples.

Sample	Adsorbed, Cation Exchangable, & Carbonates		Oxides		Organic Matter		Residual Silicates		Plant Digestion		Ash <sup>d</sup> , Bullet <sup>f</sup>		Summed Soil	
	[ng g <sup>-1</sup> ]	STD	[ng g <sup>-1</sup> ]	STD	[ng g <sup>-1</sup> ]	STD	[ng g <sup>-1</sup> ]	STD	[ng g <sup>-1</sup> ]	STD	[ng g <sup>-1</sup> ]	STD	[ng g <sup>-1</sup> ]	STD
Site 2 (N) <sup>g</sup>	308.6	0.880	367.2	1.250	5.9	1.220	243.2	1.260	b		c		924.9	2.327
Site 3 (N)	a		676.0	0.980	26.0	1.570	366.3	1.600	3.2	4.183	c		a	
Site 4 (N)	a		307.2	1.000	18.5	1.630	262.3	1.220	7.9	3.506	c		a	
Site 5 (N)	a		470.8	1.100	22.5	1.150	225.3	1.280	3.9	3.963	c		a	
Site 6 (N)	a		424.8	1.020	18.6	1.050	234.0	1.150	b		c		a	
Site 7 (N)	a		132.8	1.190	21.1	1.030	143.0	1.340	2.0	6.707	c		a	
Site 8 (A)	a		908.0	0.990	22.6	0.940	340.2	1.210	180.3	3.820	c		a	
Site 9 (A)	a		2839.2	0.880	100.8	0.990	558.3	1.530	18.3	2.099	c		a	
Site 10 (A)	2127.6	5.460	1961.6	0.860	86.7	1.000	592.2	1.380	109.5	1.775	c		4768.1	5.784
Site 11 (A)	1662.8	9.810	6821.6	0.970	155.8	0.890	421.7	1.210	9.0	2.142	c		9061.9	9.972
Site 13 (A)	a		514.0	0.970	28.8	1.000	256.6	1.280	b		c		a	
Site 15 (A)	2285.6	8.170	2224.8	0.930	45.8	0.970	252.3	1.310	b		c		4808.6	8.383
Site 2-2 (N)	347.6	0.607	804.8	1.330	36.5	0.930	296.1	1.120	b		c		1485.0	2.063
Site 6-2 (N)	a		307.6	0.950	16.5	1.110	193.7	1.270	b		c		a	
Site 10-2 (A)	2315.6	4.840	1536.0	0.800	59.2	0.970	400.2	1.050	b		c		4311.0	5.110
Site 8BP (A)	b		b		b		b		13.4	2.424	b		b	
Site 9BP (A)	b		b		b		b		58.3	2.429	b		b	
Ash	c		c		c		c		c		250.4	5.950	c	
Bullet	c		c		c		c		c		895.7	7.420	c	

<sup>a</sup> Sample not reported due to high error measurements

<sup>b</sup> Sample not collected

<sup>c</sup> Not applicable

<sup>d</sup> Full digestion using *aqua regia* and HF

<sup>e</sup> Leach using 2% Nitric acid

<sup>g</sup> N refers to 'natural' sample; A refers to 'anthropogenic' sample

Table 3. Isotopic Compositions of Pb Associated with Respective Fractions of LANWR Soil and Plant Samples

Sample	Adsorbed, Cation Exchangeable, and Carbonates				Oxides				Organic Matter			
	<sup>206</sup> Pb/ <sup>207</sup> Pb	STD	<sup>206</sup> Pb/ <sup>208</sup> Pb	STD	<sup>206</sup> Pb/ <sup>207</sup> Pb	STD	<sup>206</sup> Pb/ <sup>208</sup> Pb	STD	<sup>206</sup> Pb/ <sup>207</sup> Pb	STD	<sup>206</sup> Pb/ <sup>208</sup> Pb	STD
Site 2 (N) <sup>d</sup>	1.208	0.00158	0.486	0.00049	1.208	0.00174	0.489	0.00039	1.214	0.00158	0.490	0.00090
Site 3 (N)	1.223	0.00142	0.489	0.00051	1.221	0.00142	0.491	0.00051	1.221	0.00211	0.493	0.00090
Site 4 (N)	1.224	0.00212	0.492	0.00090	1.219	0.00219	0.493	0.00072	1.219	0.00130	0.492	0.00078
Site 5 (N)	1.221	0.00184	0.492	0.00062	1.222	0.00164	0.492	0.00086	1.220	0.00207	0.492	0.00093
Site 6 (N)	1.222	0.00187	0.491	0.00054	1.223	0.00147	0.493	0.00080	1.222	0.00130	0.492	0.00078
Site 7 (N)	1.232	0.00243	0.496	0.00063	1.218	0.00130	0.493	0.00078	1.218	0.00130	0.492	0.00078
Site 8 (A)	1.218	0.00124	0.490	0.00060	1.217	0.00130	0.488	0.00078	1.217	0.00184	0.491	0.00063
Site 9 (A)	1.191	0.00101	0.481	0.00089	1.193	0.00130	0.479	0.00078	1.199	0.00119	0.477	0.00048
Site 10 (A)	1.201	0.00104	0.481	0.00064	1.201	0.00130	0.485	0.00078	1.206	0.00152	0.481	0.00057
Site 11 (A)	1.206	0.00183	0.483	0.00054	1.213	0.00130	0.471	0.00078	1.212	0.00101	0.474	0.00056
Site 13 (A)	1.215	0.00169	0.488	0.00082	1.218	0.00130	0.491	0.00078	1.219	0.00147	0.491	0.00072
Site 15 (A)	1.194	0.00115	0.477	0.00069	1.197	0.00103	0.474	0.00035	1.199	0.00156	0.483	0.00040
Site 2-2 (N)	1.210	0.00195	0.487	0.00066	1.209	0.00145	0.486	0.00078	1.214	0.00137	0.488	0.00044
Site 6-2 (N)	1.224	0.00192	0.492	0.00063	1.224	0.00187	0.494	0.00060	1.224	0.00145	0.494	0.00067
Site 10-2 (A)	1.203	0.00140	0.481	0.00068	1.205	0.00130	0.481	0.00078	1.206	0.00105	0.484	0.00055
Site 8BP (A)	a		a		a		a		a		a	
Site 9BP (A)	a		a		a		a		a		a	
Ash	c		c		c		c		c		c	
Bullet	c		c		c		c		c		c	

<sup>a</sup> Sample not reported due to high error measurements

<sup>b</sup> Sample not collected

<sup>c</sup> Not applicable

<sup>d</sup> N refers to 'natural' sample; A refers to 'anthropogenic' sample

Table 3. Isotopic Compositions of Pb Associated with Respective Fractions of LANWR Soil and Plant Samples, con't.

Sample	Residual Silicates				Plant Digestion				Bullet Leach & Ash Digestion			
	$^{206}\text{Pb}/^{207}\text{Pb}$	STD	$^{206}\text{Pb}/^{208}\text{Pb}$	STD	$^{206}\text{Pb}/^{207}\text{Pb}$	STD	$^{206}\text{Pb}/^{208}\text{Pb}$	STD	$^{206}\text{Pb}/^{207}\text{Pb}$	STD	$^{206}\text{Pb}/^{208}\text{Pb}$	STD
Site 2 (N) <sup>d</sup>	1.222	0.00227	0.481	0.00088	b		b		c		c	
Site 3 (N)	1.229	0.00198	0.479	0.00064	1.191	0.00397	0.489	0.00275	c		c	
Site 4 (N)	1.229	0.00222	0.481	0.00055	1.208	0.00610	0.494	0.00166	c		c	
Site 5 (N)	1.229	0.00279	0.480	0.00087	1.192	0.00676	0.491	0.00322	c		c	
Site 6 (N)	1.232	0.00283	0.482	0.00087	b		b		c		c	
Site 7 (N)	1.227	0.00172	0.487	0.00056	1.195	0.00467	0.491	0.00260	c		c	
Site 8 (A)	1.229	0.00164	0.477	0.00096	1.140	0.00621	0.479	0.00167	c		c	
Site 9 (A)	1.216	0.00160	0.475	0.00387	1.184	0.00388	0.488	0.00204	c		c	
Site 10 (A)	1.222	0.00148	0.485	0.00492	1.170	0.00235	0.489	0.00107	c		c	
Site 11 (A)	1.219	0.00188	0.472	0.00079	1.197	0.00337	0.488	0.00212	c		c	
Site 13 (A)	1.228	0.00142	0.481	0.00044	b		b		c		c	
Site 15 (A)	1.214	0.00177	0.477	0.00070	b		b		c		c	
Site 2-2 (N)	1.228	0.00158	0.480	0.00080	b		b		c		c	
Site 6-2 (N)	1.235	0.00195	0.484	0.00078	b		b		c		c	
Site 10-2 (A)	1.218	0.00183	0.473	0.00054	b		b		c		c	
Site 8BP (A)	a		a		1.191	0.00368	0.487	0.00213	c		c	
Site 9BP (A)	a		a		1.199	0.00494	0.487	0.00325	c		c	
Ash	c		c		c		c		1.207	0.00190	0.479	0.00047
Bullet	c		c		c		c		1.202	0.00130	0.477	0.00078

<sup>a</sup> Sample not reported due to high error measurements

<sup>b</sup> Sample not collected

<sup>c</sup> Not applicable