Pollution of surface soils in Escambia and Santa Rosa Counties, FL.

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FOREWORD

This study is a component of the "Assessment of Environmental Pollution and Community Health in Northwest Florida" supported by a USEPA Cooperative Agreement award X-9745502 to The University of West Florida (Project Director: Dr. K. Ranga Rao). The contents of this report are solely the responsibility of the authors and do not necessarily represent the official views of the USEPA. The study was undertaken because of the increasing concern for environmental pollution and potential impacts on human health in Northwest Florida. It was designed to assess environmental impacts of toxic pollutants in surface soils. Kristal Flanders managed the spatial databases for the project and drafted the maps. Her assistance has been invaluable. Michael Somerville helped with the fieldwork and some laboratory procedures.

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ABBREVIATIONS and ACRONYMS

ACC - American Creosote Company
ATSDR - Agency for Toxic Substances and Disease Registry
CCA - Chromated copper arsenate
ECUA - Emerald Coast Utilities Authority
ETC - Escambia Treating Company
DGPS - Differential GPS
FDEP - Florida Department of Environmental Protection
FLAAS - Flame atomic absorption spectrometry
GFAAS - Graphite furnace atomic absorption spectrometry
GIS - Geographical Information Systems
PAH - Polycyclic Aromatic Hydrocarbon or Polynuclear Aromatic Hydrocarbon
PCA - Principal component analysis
PCB - Polychlorinated biphenyl
PEL - Probable effects level (concentration above which adverse effects on biota are probable)
PERCH - Partnership for Environmental Research and Community Health
PLI - Pollution load index
r - Correlation coefficient, reflects the degree of linear relationship between two variables.
RSCTL - Residential soil cleanup target level
TEL - Threshold effect level (concentration above which adverse effects on biota are possible)
TEQ - Toxic equivalents
USACE - United States Army Corps of Engineers
USEPA - United States Environmental Protection Agency

EXECUTIVE SUMMARY

The part of the physical environment in Escambia and Santa Rosa Counties that has not yet been addressed by PERCH, or other studies, is surface soils. The only investigations that examined pollution of surface soils in the area were spatially very limited studies at or near superfund sites. In other media (sediments, biota) in the area pollution levels sometimes exceed national and state guidelines, as demonstrated by previous PERCH tasks and other studies. In many other urban areas surface soils have been shown to be polluted and to have the potential to affect the health of humans, especially that of children. One of the authors of this report analyzed a limited number of surface soils from Escambia County as part of a previous study. Results showed that some of the soils had Pb levels above Florida Clean Soil Criteria and all sites had As levels above EPA Soil Screening Levels. These observations indicate that a systematic survey of pollution of surface soils in Escambia and Santa Rosa Counties is warranted. Given the emphasis of PERCH on health implications, we focused the project on soils in public places such as parks, playgrounds and sports fields where most interaction takes place between people and soils.

Studies of pollution of urban soils usually assess pollution by trace metals because of the presence of multiple sources for these metals in an urban setting. The most commonly identified sources are vehicular traffic, road infrastructure, power plants, and industrial activities. Several studies have found trace metal concentrations above national and international regulatory limits. Some studies have specifically examined pollution resulting from the use of wood treated with chromated copper arsenate (CCA). Most of these studies find highly elevated concentrations of Cr, Cu, and As close to the treated wood but the concentrations typically decrease rapidly with distance from the wooden structures. Few studies have employed Geographic Information Systems (GIS), like the present one does, to help identify potential sources of the pollution.

Even though this project focused on a survey of soils throughout the study area we used a stratified sampling approach to collect a relatively high proportion of samples from the Palafox Industrial Corridor where soils have locally been evaluated and have been found to be polluted with dioxins/furans, polycyclic aromatic hydrocarbons (PAHs) and trace metals. For instance, at the Escambia Treating Company (ETC) site the US EPA and FL DEP have found elevated levels of creosote, pentachlorophenol, and dioxin/furan in the soil. In 1995, US EPA contractors analyzed soil samples from neighborhoods around ETC and found elevated levels of dioxins/furans, PAHs, As, and Pb. These findings led to the relocation of the residents of these neighborhoods. About 10 years later another neighborhood, the Clarinda Triangle, was found to have As, Pb, dioxins/furans, and PAH levels above FL DEP soil cleanup target level (SCTL) for residential areas. Soils at the nearby Agrico Chemical Company (ACC) site have been found to be contaminated with Pb, F, Cr, As, Mn, V, and PAHs by government agencies. As a result, soils and sediments at the site were capped. In 2003 the FL DEP sampled soils at the Brown Barge Middle School, located across the street from ACC, and found PAHs and As above their Florida DOH health-based screening values.

The overall goal of this project is to assess if soils in public places in Escambia and Santa Rosa Counties have pollution characteristics that necessitate specific management actions. The project has two components, one that evaluates dioxins/furans and PAHs in the Palafox

Industrial Corridor in the context of known local pollution issues and regional background concentrations, and one that assesses trace metal concentrations throughout the study area. As part of this overall goal the project will compare pollutant concentrations with regulatory guidelines, shed light on potential human and natural sources for the pollutants by using multiple methodological approaches, and evaluate the likelihood that the pollutants will affect other parts of the environment based on a sequential extraction.

Preselection of potential sampling sites took place in a GIS using data provided by local government agencies. Field evaluation of the preselected sites resulted in a total of 126 locations being sampled. Twelve of these locations were located in or near the Palafox Industrial Corridor. At nineteen of the 126 locations 3 to 4 samples were collected to examine the influence of proximity to a road on trace metal levels. At twenty-two of the 126 locations a second sample was collected to study the speciation of the trace metals. Only five of the locations had CCA-treated wood structures. An additional sample was collected near these structures. All samples were analyzed for trace metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn), the 12 from the Palafox Industrial Corridor were also analyzed for dioxins/furans and PAHs.

Chemical analyses of the samples were carried out by a contracted NELAP certified commercial laboratory with standard US EPA methods and QA/QC procedures. For the sequential extraction of trace metals a true standard method does not seem to exist and we arranged for the contracted lab to perform an extraction often described in the scientific literature. Physical analysis of the samples were performed in-house at UWF. To better express the toxicity of the dioxins/furans and PAHs we transformed their raw concentrations into toxic equivalents with methods promulgated by national and international government agencies. For some aspects of the project the trace metal concentrations were transformed into indexes (index of geoaccumulation, enrichment factor, pollution load index) that are a better measure of the pollution level than the raw concentrations.

Results for the Palafox Industrial Corridor show that the dioxin/furan TEQs remain below the US EPA screening level for children of 50 ng/kg, but exceed the FL DEP SCTL of 7 ng/kg in half of the samples from that area. This suggests that, depending on which guideline is followed, the dioxins/furans in the surface soils of the Palafox Industrial Corridor may deserve further scrutiny. The TEQ values are comparable to those found by EPA contractors in the same general area but have minor variations that can be explained by small scale spatial variations. The TEQ values in the industrial corridor are statistically higher than elsewhere in the study area, which illustrates the influence of the local (former) industry on the soils in the industrial corridor. The zone of elevated TEQs is limited to the Palafox Industrial Corridor and quickly drops off to background levels outside the industrial corridor. PAHs show a very similar pattern with elevated benzo(a)pyrene equivalent concentrations being limited to the Palafox Industrial Corridor. Five of the 12 samples in the corridor exceed the FL DEP residential SCTL (RSCTL) of 0.1 mg/kg TEQ, and thus may justify further study, especially because the highest value (1.06 mg/kg) was observed in a residential area near a school. On the other hand, benzo(a)pyrene equivalent concentrations as high as 1.3 mg/kg have been described as regional background values in the scientific literature.

Trace metal concentrations are generally below the respective RSCTLs. Arsenic, however, exceeds its RSCTL of 2.1 mg/kg at 33 of the 126 sites and thus is of environmental concern. These 33 samples are from locations throughout the study area in both rural and urban settings and do not show a clear spatial pattern. This indicates that there is no specific local point source for the As and suggests that the relatively high values are due to a regionally high background concentration. The average As concentration of 1.38 mg/kg is between the averages obtained in urban settings elsewhere in Florida (Gainesville and Miami) and, consequently, can not be considered to be exceptionally elevated in the study area. Concentrations for Pb and Zn, two trace metals that often have been linked to transportation sources, are somewhat higher in urban areas than in rural areas. Chromium and Ni, two metals that are also often thought to derive from anthropogenic sources in urban areas, are statistically significantly higher in rural areas than in urban areas in the present study. Principle component analysis (PCA) shows that these metals derive mainly from the parent material of the soils, which is more metal bearing in the rural northern parts of the study area.

To evaluate if the trace metals originate from anthropogenic activities we applied two indexes that compare observed concentrations to background concentrations. Even though many studies use general crustal values for the backgrounds, we determined local background concentrations that provide a much better basis for comparison. The two indexes yield consistent results and show that Pb and Zn have the largest anthropogenic component. However, levels described by the indexes as "strongly polluted" are reached at 4% to 6% of the sites only for these two trace metals. Most of these sites are in the Palafox Industrial Corridor. Sites characterized as "polluted" by the indexes are along the Escambia River and in the urban parts of the study area. In spite of it exceeding the RSCTL, As reaches "pollution" levels at relatively few sites, indicating that its local background level is high compared to the RSCTL. GIS-based hot spot analysis corroborates some of these observations and clearly shows that trace metal concentrations are elevated in the Palafox Industrial Corridor, as compared to the rest of the study area.

The average concentration of all analyzed trace metals (As, Cd, Cr, Cu, Ni, Pb, Zn), with the exception of Hg, decreases between 2 m and 20 m from the edge of a road. This decrease is statistically significant. The higher concentrations near the road are due traffic activities and originate from the wearing of tires and brake pads, tire weights that fall off, oil drips, and emissions. Arsenic has rarely been associated with traffic activities but in the current study follows the trend of the other trace metals. Beyond 20 m the influence of traffic on trace metal concentrations becomes minimal. Only Pb and Zn show signs of further decrease beyond 20 m. Based on the pollution indexes these two metals have higher pollution levels and at proportionally more sites near a road than in the total dataset. Arsenic is still the only element that exceeds its RSCTL.

Trace metal concentrations in soil materials at the base of structures made of CCA-treated wood had not been previously studied in the study area. Results of the current project show that the concentrations of Cr, Cu, and As are markedly higher near CCA-treated wood than in the whole dataset. The other trace metals have below average concentrations near CCA-treated wood, most likely because of the very high quartz sand content of the soils near the structures. Arsenic concentrations are substantially higher than the RSCTL but Cr and Cu do not exceed their respective RSCTLs. In principle, the As exceedances may warrant further assessment but this option has to be considered in light of the very limited spatial extent of the pollution and the limited number of CCA-treated structures in the study area (5). Nevertheless, it seems best to avoid contact with soils in very close proximity to these CCA-treated structures.

Trace metal speciation extracts gradually more tightly bound fractions of the metals from the soil materials. This speciation allows for a better evaluation of the potential for transfer of the trace metals to other parts of the environment than do total trace metal concentrations. Arsenic and Zn have the largest proportions in the two most loosely bound fractions of the metals, often considered to be the bioavailable fractions, (16.15% and 24.03% respectively). This implies that because of the magnitude of their concentrations and their availability these two trace metals have the greatest potential to negatively affect other parts of the environment. The other metals have relatively low bioavailable fractions. Lead, Cr, and Cu have relative large organic matter-bound fractions. These fractions are relatively stable but can be released into the rest of the environment by changes in Eh or pH that affect the organic matter. Arsenic and Cr have about 70% in the stable residual fraction, indicating that this portion is unlikely to influence the environment on a human time scale. Evaluating the radioactivity was a secondary objective of this task and results of our pilot study indicate that the radioactivity of the soils in the study area is near background levels and does not exceed levels reported in the literature for unpolluted locations.

In summary, the present study is the first systematic survey of soil pollution in Escambia and Santa Rosa Counties. Results show that most trace metals in the soils we examined have a clear anthropogenic component but with the exception of As do not exceed the respective RSCTLs. Arsenic deserves most attention in follow-up studies, but as shown by this and other studies, may be elevated because of high regional background concentrations. The PAH benzo(a)pyrene equivalent concentration exceeds the RSCTL in the Palafox Industrial Corridor and may also warrant further consideration.

1. Introduction

Other PERCH projects have shown that pollutants are present in the air, water, and biota of Escambia and Santa Rosa Counties. In some instances the levels of pollution exceed national and state guidelines. The part of the physical environment that has not yet been addressed by PERCH is surface soils. Other studies in the area that examined pollution of surface soils were exclusively related to superfund sites and were very limited in spatial extent. A general survey of the pollution of surface soils in Escambia and Santa Rosa County is not known to us. Surface soils in many other urban areas have been shown to be polluted (e.g. Pfeiffer et al., 1991; Kelly et al., 1996; Sanchez Martin et al., 2000). The influence of this pollution on human health, especially that of children, is strong and well documented (Simpson, 1996; Dor et al., 1998; Mielke et al., 1999). Therefore, a systematic survey of pollution of surface soils in Escambia and Santa Rosa Counties was warranted. This survey ties in with the health aspect of PERCH and makes PERCH a more complete endeavor that examines all four components of the environment (air, water, biota, soils). Given the emphasis on health implications, we choose to focus our sampling campaign on soils in public places such as parks, playgrounds and sports fields where much interaction takes place between humans and soils.

2. Background

Environmental research in the two-county area has rarely focused on pollution of surface soils. The only studies of surface soils known to us are related to superfund sites. These studies usually concentrated on on-site pollution but in some cases off-site locations were examined. For instance, between 1982 and 1992 the US EPA and the FL DEP conducted several soil investigations at the Escambia Treating Company (ETC) site. They found elevated levels of creosote, pentachlorophenol and dioxin in the soil and as a result directed soil excavations to prevent further groundwater contamination (US EPA, 1991). In 1995, US EPA contractors analyzed soil samples from neighborhoods around ETC and found elevated levels of dioxins/furans, PAHs, As, and Pb (Black and Veatch Waste Science, 1995). These findings led to the relocation of the residents of these neighborhoods. CDM Federal collected soil samples in 1998 from other locations in the vicinity of ETC and identified elevated levels of trace metals, PAHs, pesticides, and dioxins/furans (CDM Federal, 1998). The soils in one residential neighborhood, the Clarinda Triangle, had As, Pb, dioxins/furans, and PAH levels above FL DEP SCTL for residential areas (ATSDR, 2005a). Soils at the Agrico Chemical Company (ACC) site have been studied since 1983. They were found to be contaminated with Pb, F, Cr, As, Mn, V, and PAHs (ATSDR, 2005b). As a result, EPA contractors remediated and capped soils and sediments at the site. Off-site soil samples were analyzed for PAHs, pesticides and trace metals but none had concentrations likely to cause adverse health effects. In 2003 the FL DEP sampled soils at the Brown Barge Middle School, located across the street from ACC, for radionuclides, trace metals, pesticides, fluoride, PAHs and polychlorinated biphenyl (PCBs). The PAHs and As were measured above their Florida DOH health-based screening values (ASTDR, 2005b). One of the authors of this report has analyzed a limited number of surface soils from Escambia County for trace metals as part of a study of stormwater treatment systems (Liebens, 2001). Samples were collected from sites that were thought to be relatively unaffected by direct release of pollutants and thus should represent background levels of pollution. Results showed that some of these sites had Pb levels above Florida Clean Soil Criteria and all sites had As levels above EPA Soil Screening Levels. Recently, very high levels of elemental mercury were identified in soils in McIntosh, AL, just NW of Escambia and Santa Rosa County. The mercury is present in materials from a superfund site that were used for road improvement and as fill in public and private places (Mobile Register, March 11 2005). Because of the increased public awareness of the potential adverse effects of mercury resulting from the media coverage of the situation in McIntosh, we felt it was pertinent to include mercury in the present study.

Most studies of pollution of urban soils elsewhere focus on pollution by trace metals (Harrison et al., 1981; Chirenje et al., 2004; Datta and Sarkar, 2005) although PAHs and other pollutants have also been studied (Dierkes and Geiger, 1999; Krauss et al., 2000; Motelay-Massei et al., 2004; Priha et al., 2005). Several of these studies have found trace metal concentrations that exceed national and international regulatory limits (Madrid et al., 2002; Imperato et al., 2003). Geographic Information Systems (GIS) have been employed in some studies, but not many, to help identify potential sources of the pollution (Imperato et al., 2003; Li et al., 2004). The most commonly identified sources are vehicular traffic, road infrastructure, power plants, and industrial activities (Ritter and Rinefierd, 1983; Banat et al., 2005; Moller et al., 2005). Emissions from these sources reach soils mainly via atmospheric deposition (Simonson, 1995; Nicholson et al., 2003). Increased surface soil pollution has been linked to city centers and historic districts, probably because human activities are more intense and older in these areas (Kahle, 2000; Madrid et al., 2002; Chen et al., 2005). Natural variations in soil characteristics and differences in human activities among cities result in varying levels of pollution in urban soils and several researchers have indicated the continued need for a better understanding of urban soil pollution, including the role of atmospheric transport of metals (De Kimple and Morel, 2000; Manta et al., 2002). Some studies have focused specifically on surface soil pollution resulting from the use of wood treated with chromated copper arsenate (CCA). Most of these studies find highly elevated levels of Cr, Cu, and As close to the treated wood (<0.5 m from structure). The levels of Cr, Cu, and As typically decrease rapidly with distance from the wooden structures, in deeper layers, and with age of the structure (Chirenje et al., 2003b; Gezer et al., 2005). Soil characteristics such as organic matter content and pH have also been shown to effect the Cr, Cu, and As level in CCA contaminated soils (Balasoiu et al., 2001; Gezer et al., 2005). Because of the well documented adverse health effects of Cr, Cu and As the US EPA has worked with pesticide manufacturers to voluntarily phase out CCA use for wood products around the home and in children's play areas.

3. Objectives

The general objective of this project is to support management of soils in Escambia County and Santa Rosa County by assessing the level and spatial extent of pollution of surface soils in the area. The specific objectives are:

- to determine the concentrations and spatial pattern of trace metals in the two-county area
- to determine the concentrations and spatial distribution of PAHs and dioxins/furans in surface soils in the Palafox industrial corridor where ETC and ACC are located
- to identify potential origins and source areas for the trace metals by using geospatial and statistical techniques
- to assess the influence of the proximity of a major road on the pollution of the soils

- to evaluate if structures made of treated wood at playgrounds affect local soil pollution
- to assess the potential threat of the trace metals to the rest of the environment by determining the speciation of the metals
- to evaluate concentrations of the various pollutants with regards to regulatory limits

4. Site Selection

To facilitate sampling in the field, a map of potential sampling sites was constructed. To construct the map, data on the location and the type of public places were obtained from Engineering Departments at Escambia County, Santa Rosa County, City of Pensacola, and City of Milton and entered into a GIS. The obtained data included a total of 270 public places. The greatest concentration of public places was found to be present in the two cities (Pensacola and Milton). Outside the cities the density of public places decreased rapidly. The map of the public places was overlaid in the GIS on a map of major roads to determine if any of the public places were near a major road.

Because of the lower density, all public places outside the cities were retained as potential sampling sites. In the cities potential sampling sites were manually selected in the GIS from among all public places. Selection criteria included creation of a more-or-less homogeneous spatial distribution of potential sampling sites and retention of sufficient sites in each of the categories “near road”, “playground”, and “others”. These specific categories were needed to address the specific objectives (see above). Figure 1 is the resulting map of potential sampling sites. The potential sites included 17 playgrounds, 32 sites near major roads, and 78 other sites (Figure 2). All sites were visited and visually evaluated for recent disturbance of the surface. After rejecting some of the sites, a scarcity of sites was observed in the central and eastern portions of the study area. In consultation with EPA personnel it was decide to collect an additional 11 samples (PSS119 - PSS129) at publicly accessible places in the central and eastern portions of the study area to obtain a spatially more homogeneous sampling design. Ultimately, we sampled 126 locations (Figure 3). Twelve of these sites were located in the Palafox Industrial Corridor, in and beyond areas analyzed by previous studies (Figure 4).

Additionally, three to four samples were collected at 19 of the public places that were near major roads. One of the samples at each site was located at the edge of the road, or as close to it as safely and practically possible, and depending on the size of the site two or three more samples were collected at 20 m intervals. To examine the speciation of the metals an additional sample was also collected at 22 sites that had been found to have high trace metal concentrations in the initial phase of the study. The description of the exact original sampling location and the collected GPS coordinates were used to obtain a sample as close as possible to the original location. At each of five playgrounds a sample was collected at the base of structures made of CCA-treated wood. This latter data set is limited in size because no other treated wood play structures could be found in public places in the study area.

The soil samples were collected from 0 - 5 cm depth with a stainless steel scoop after removal of grass, weeds and any loose surficial material. Within the general area of interest for each sample (the public place) an attempt was made to determine the area of least disturbance for sampling. Care was used to avoid areas that might have had anthropogenic influences and thus might yield unrepresentative pollution levels. Samples were preserved in precleaned glass jars on ice and shipped within 24 hours to the analytical lab.

5. Analysis and Data Processing

All samples were analyzed for trace metals. Because of the pollution history of the Palafox Industrial Corridor the 12 samples from that area were also analyzed for dioxins/furans and PAHs. Ten samples from outside the corridor were analyzed for dioxins/furans and PAHs to serve as reference values. At all initial 126 sampling sites the radioactivity of the surface soil was measured with a Geiger-Mueller counter that detects alpha, beta and gamma radiation. The Geiger counter had a Geiger-Mueller tube with a thin mica window and detected alpha, beta, gamma, and X-rays. Alpha and beta radiation was measured with an efficiency of 80% by the counter, as per the manufacturer. Dose rate conversion is calculated internally using a conversion factor that is optimized for Cs-137. The total radioactivity was determined in the field by placing the Geiger counter on the surface of the soil after removing grass, weeds and any other loose debris.

The chemical analyses of the samples were carried out by a contracted NELAP certified commercial laboratory (Columbia Analytical Services, Jacksonville, FL) with standard USEPA procedures. The data were subjected to data validation procedures and QA/QC procedures in accordance with the project's QAPP. USEPA SW-846 methods were used for dioxin/furans (method 1613B) and PAHs (method 8270). Mercury was determined by Method 7471A for sediments by cold vapor atomic absorption. The other project metals (Al, As, Cd, Cr, Cu, Fe, Pb, Hg, Ni, Zn) were analyzed on an ICP-MS (method 6010, Acid Digestion of Sediments, Sludges, and Soils).

In the literature many similar yet different methods have been reported over the years for sequential extractions. They all apply, in a step wise fashion, gradually more aggressive compounds to extract progressively tighter held metals from the soil. Currently, two general approaches seem to exist, one based on the method pioneered by Tessier et al. (1979) and one based on recommendations by the European Community (Lopez-Sanchez et al., 1993; Fiedler et al., 1994; Ramos et al., 1999). Because of its relative simplicity, we made arrangements with the contracted analytical laboratory to employ the latter method, as modified by Wasay et al. (1998). The method extracts five metal fractions consecutively from any given sample: water extractable, exchangeable, oxide bound, organic matter bound, and residual fraction. Quality control samples, including laboratory control samples, matrix spikes, matrix spike duplicates, and standard reference materials were run for this procedure as for the other samples.

The particle size distribution, organic matter content, and pH of the samples were determined in the Soils Lab of the Department of Environmental Studies at the University of West Florida. Samples were manually mixed and homogenized in the lab while being air dried. After air drying, samples were crushed with mortar and pestle to break up aggregates. The pipette method was used for clay and dry ro-tap sieving for the sand fractions (procedure 3A1 of Burt (2004)). Organic matter was determined with the loss-on-ignition method by heating at 400°C for 6 hrs. pH was measured in a 1:1 soil - water solution (method 4C1a2 of Burt (2004)).

The dioxin/furan analytical data were converted to TEQ adjusted concentrations using equivalency factors relative to 2,3,7,8-tetrachlorodibenzo(p)dioxin that have been adopted by WHO and were taken from Van Den Berg et al. (1998). Dioxin/furan congeners with non-detects were assigned a value of ½ the detection limit if the congener was found in any of the samples. The only congener to be completely excluded from the TEQ by this procedure, because it was not detected in any of the samples, was '2,3,7,8-Tetrachlorodibenzofuran (TCDF).

PAH concentrations were converted to benzo(a)pyrene equivalents using FL DEP guidelines for direct exposure soil cleanup target levels (Chapter 62-777, F.A.C). The method uses seven of the 18 PAHs tested for because they pose a significant risk to human health. The seven PAHs and their conversion factors are benzo(a)anthracene (0.1), benzo(a)pyrene (1.0), benzo(b)fluoranthene (0.1), benzo(k)fluoranthene (0.01), chrysene (0.01), dibenz(a,h)anthracene (1.0), and indeno(1,2,3cd-)pyrene (0.1).

The converted dioxin/furan and PAH data and the analytical data for the trace metals were entered into a GIS for visual interpretation and geostatistical analysis. Sampling points from previous studies in the Palafox industrial corridor, mostly by USEPA and FL DEP contractors, were entered into the GIS using digital aerial photographs for reference.

For the trace metal data three indexes were calculated to aid in the assessment of the pollution levels. Two of these indexes, the index of geoaccumulation and the enrichment factor, compare observed concentrations with background concentrations and thus are a measure for the degree of anthropogenic pollution. The index of geoaccumulation (Muller, 1969) is calculated as:

$$\text{Igeo} = \log_2 (\text{Conc. metal}_{\text{sample}} / 1.5 * \text{Conc. metal}_{\text{background}})$$

The factor of 1.5 is intended to account for variations in background values and minimizes overestimation of pollution levels. Interpretation of index values in descriptive terms is challenging but generally values are interpreted as listed in Table 7 (Ntekim et al., 1993; Banat et al., 2005; Gonzalez at al., 2007).

The enrichment factor also employs a ratio of observed to background concentrations but standardizes the trace metal concentrations with a stable metal of natural origin. It is in concept a combination of the other two indexes. For the standardization Al is often used (Covelli and Fontolan, 1997) as it is usually unaffected by anthropogenic inputs and relatively immobile in most common soils. The enrichment factor is calculated as follows:

$$\text{EF} = (\text{Conc. metal}/\text{Conc. Al})_{\text{sample}} / (\text{Conc. metal}/\text{Conc. Al})_{\text{background}}$$

Descriptive terminology for EF based on a survey of the literature is listed in Table 7 (Banat et al., 2005; Wang et al., 2006). Background concentrations for these indexes were established by statistically separating the bimodal distribution of the trace metal concentrations from the present study. A K-means cluster analysis with Euclidean distances between the concentrations was used to separate the concentrations into two groups, one group of presumable background values and one of sites with concentrations significantly above these background values, presumably due to anthropogenic influences. The mean concentration of the background group for each metal was used in the calculation of the indexes. These local background values are more appropriate than the general crustal background concentrations that have often been employed in other studies (Covelli and Fontolan, 1997; Ray et al., 2006; Gonzalez et al., 2007). The background concentration was also used as a class break on the GIS maps showing the spatial distribution of the trace metals. The midpoint between the highest value of the background group and the lowest value of the anthropogenic group was used for the second class break of the maps.

The pollution load index (PLI) (Tomlinson et al., 1980) standardizes the observed trace metal concentration with the Al concentration but does not take into account a background value. It is a measure for the overall level of all trace metals combined. The PLI is calculated as

$$PLI = (CF_1 * CF_2 * CF_3 * \ldots CF_n)^{1/n}$$

in which CF = Conc. metal $_{sample}$ /Conc. Al $_{sample}$ for all n metals in a sample.

This PLI was used for hot spot analysis in the GIS to evaluate if samples with high levels of trace metals are concentrated in any given part of the study area. Hot spot analysis assesses the value at each site within the context of values at neighboring sites. If a site's value is high, and the values for all of its neighboring sites are also high, it is part of a hot spot. The local sum of the values at a given site and its neighbors is compared proportionally to the sum of values at all sites in the study area. When the local sum is very different from the statistically expected local sum, and that difference is too large to be the result of random chance, a statistically significant Z score for the given site is the result.

As one of the approaches to assess the origin of the metals we performed a principle component analysis (PCA) with varimax rotation on a trace metal dataset that included Al and Fe. These two metals are typically of geogenic origin and any trace metal that has component loadings similar to those of these two metals most likely also derived from the soil parent material. This approach to identify the potential origin of trace metals in soils and sediments has often been reported on in the literature (Kumru and Bakac, 2003; Loska and Wiechula, 2003; Boruvka et al., 2005). Results showed that three components had eigenvalues >1 and together explained 78.5% of the variance.

6. Results

6.1. Dioxins and PAHs in the Palafox Industrial Corridor

Dioxin/furan TEQs in the Palafox Industrial Corridor are between 1.15 ng/kg and 38.21 ng/kg and have a mean of 10.45 ng/kg (Table 1). None of these values exceed the EPA screening level for children of 50 ng/kg, which is used to determine whether further site-specific evaluation is to occur. However, the direct exposure based FL DEP SCTLs for dioxin/furan TEQ are lower than the EPA screening level and are exceeded by some of the observed TEQs. Six out of 12 sites in the Palafox Industrial Corridor exceed the RSCTL (7 ng/kg) and one site (PSS6) exceeds the commercial/industrial SCTL (30 ng/kg). PSS6 and one of the sites that exceed the RSCTL (PSS5) are located in the Clarinda Triangle just west of the ETC site, indicating that the dioxins/furans in soils in that area are of environmental concern and justify continued evaluation. The TEQ values observed in the current study are comparable to those found by EPA contractors in the same general area (Figure 5, Figure 6). The EPA contractors found a concentration above the EPA screening level (74.83 ng/ kg) in the Clarinda Triangle west of the ETC site. The highest value of the current study was found at approximately the same location but it is below the screening level (PSS6, 38.205 ng/kg TEQ). The difference in magnitude between the EPA result and our result is possibly due to local variations in the dioxin/furan concentrations. A cluster of elevated concentrations was found by EPA contractors just north of the ETC site (Figure 6) and this is currently a restricted area. Three samples taken by us to the northeast of the general area where EPA contractors collected samples have low dioxin/furan TEQs (< 3.05 ng/kg). Samples taken just south of the Clarinda Triangle (PSS15) and the ETC site (PSS14) in areas previously not studied have intermediate TEQs (16.90 ng/kg and 13.80 ng/kg respectively) that exceed the FL DEP RSCTL.

Elsewhere in the study area dioxin/furan TEQs are between 0.16 ng/kg and 20.5 ng/kg and have an average of 3.84 ng/kg (Table 1, Figure 7). The high value of 20.5 ng/kg is an outlier and is much higher than the second highest TEQ value (8.41 ng/kg). The sample with the maximum concentration was collected relatively close to a natural gas processing plant and a boat launch and may potentially represent local contamination (Figure 3). In any case, the TEQ values in the Palafox corridor (Figure 5, Table 1) are higher than those in other parts of the study area, including other parts of the city of Pensacola (Figure 7, Table 1). A rank sum test shows that the difference is statistically significant (p=0.001). This shows that even though the TEQs are below the screening level in the Palafox Industrial Corridor they are above (informal) local background levels and thus represent anthropogenic enrichment. TEQs just north and northeast of the Palafox corridor are more in-line with those found elsewhere in the study area, indicating that the dioxin/furan pollution in the Palafox Industrial Corridor quickly drops of in the surrounding areas to the (informal) local background levels (Figure 5, Figure 7).

Benzo(a)pyrene equivalent concentrations in the Palafox Industrial Corridor exceed the FL DEP residential SCTL of 0.1 mg/kg in 5 out of the 12 samples (Table 1). One of these samples (PSS04) also exceeds the industrial/commercial SCTL of 0.7 mg/kg. This sample was collected in a vacant lot in a residential area near Brown Barge Middle School (Figure 8). Just east of there, on school property, E&E (2004) also found elevated benzo(a)pyrene equivalent concentrations at two sites (Figure 10). Literature on the Agrico Chemical Superfund site, which is located just north of these sampling sites, indicates that a drainage ditch ran south from Agrico to approximately the area where we sampled (Geraghty and Miller, 1992) but future work will have to determine if a link exists between the high benzo(a)pyrene equivalent concentrations and the drainage ditch. Our three samples to the northeast of the general area where EPA contractors sampled have low benzo(a)pyrene equivalent concentrations (Figure 8, Table 1). Our sample just south of the Clarinda Triangle exceeds the residential SCTL but is located in an industrial/ commercial setting. The range of benzo(a)pyrene equivalent concentrations found by the current study is comparable to that of the previous studies (Figure 8, Figure 10). Even though the values are elevated in some of our samples, their ranges are not very unusual. ATSDR's estimate of U.S. background concentrations of benzo(a)pyrene range from 0.002 mg/kg to 1.3 mg/kg and maximum background concentrations as high as 2.1 mg/kg have been found in metropolitan Chicago (ATSDR, 1995).

The benzo(a)pyrene equivalent concentrations remain low throughout the rest of the study area, including other urban areas (Table 1, Figure 11). The maximum equivalent concentration observed outside the Palafox corridor is 0.0274 mg/kg, well below the residential SCTL. Even though SCTL were not designed to determine the likelihood of illness these observations suggest that adverse health effects from PAHs outside the Palafox Industrial Corridor can be expected to be minimal. The maximum benzo(a)pyrene equivalent concentration is more than an order of magnitude lower outside the Palafox Industrial Corridor than inside the corridor (Table 1). This indicates that the PAH pollution is limited to the Palafox Industrial Corridor. Obviously, outside the Palafox corridor a sparser sampling scheme was used and it is possible that in those areas small local nuclei of PAH pollution in surface soils exist.

Table 1. Dioxin/furan TEQ and benzo(a)pyrene equivalents.

Sample ID	dioxin/furan TEQ ng/kg	benzo(a)pyrene equivalents mg/kg
	Palafox industrial corridor and vicinity	
PSS01	3.05	0.0275
PSS02	1.15	0.0114
PSS03	2.64	0.0511
PSS04	15.63	**1.0638**[2]
PSS05	16.45	**0.2309**
PSS06	38.21	**0.2515**
PSS07	7.43	0.0217
PSS08	13.78	**0.1229**
PSS09	3.55	0.0516
PSS10	1.32	0.0371
PSS14	13.89	0.0551
PSS15	16.87	**0.1030**
minimum	1.15	0.0114
maximum	38.21	1.1762
mean	10.45	0.2464
regulatory guideline[1]	50.00	0.1000
# above guideline	0	5
	Sites elsewhere in the study area	
PSS 21	4.49	0.0080
PSS 26	3.07	0.0221
PSS 46	0.70	0.0078
PSS 52	4.45	0.0013
PSS 55	1.69	0.0274
PSS 57	2.18	0.0051
PSS 59	1.13	0.0055
PSS 60	2.32	0.0021
PSS 61	20.5	0.0011
PSS 62	8.41	0.0040
PSS 88	1.26	0.0127
PSS 100	0.95	0.0250
PSS 113	2.39	0.0039
PSS 116	0.16	0.0010
minimum	0.16	0.0010
maximum	20.5	0.0274
mean	3.84	0.0091
regulatory guideline[1]	50.00	0.1000
# above guideline	0	0

[1] Guideline for dioxin/furan TEQ is EPA screening level for children. FL DEP RSCTL is 7 ng/kg. Guideline for benzo(a)pyrene is FL DEP SCTL.
[2] Bold print: Value exceeds guideline.

6.2 Trace Metals

Trace metal concentrations are generally low and with the exception of As do not exceed their respective residential SCTLs (Table 2). For As, 33 of the samples exceed the residential SCTL of 2.1 mg/kg., and thus are of environmental concern. These 33 samples are from locations throughout the study area in both rural and urban settings and do not show a clear spatial pattern (Figure 12). This indicates that there is no specific local point source for the As. High As concentrations in soils and sediments in the region have been reported previously (Chen et al., 1999; Liebens, 2001) and have been ascribed to high geological background values by some. The average As concentration of 1.38 mg/kg is between the averages obtained in the urban settings of Gainesville, FL (0.40 mg/kg) and Miami, FL (2.81 mg/kg) (Chirenje et al., 2003a), and thus is not exceptionally elevated in the study area. The highest As concentration (6.9 mg/kg) was measured in sample PSS04 near Brown Barge Middle School, the same sample that has the highest benzo(a)pyrene equivalent concentration (Figure 9). At the school, a DEP contractor (E&E, 2004) also found As levels above the ATSDR screening value. Sample PSS04 also has the highest concentration for Cu and Hg, and the next-to-highest concentration for Pb and Cr, but the concentrations for these four metals do not exceed the respective RSCTLs in the sample.

A single sample (PSS123) exceeds the residential SCTL for Pb, which is 400 mg/kg. However, nearby samples have considerably lower Pb concentrations (Figure 13) and PSS123 is not near an obvious potential contamination source. Therefore, we verified this elevated concentration for Pb with the results of the sequential extraction procedure (see below) by adding the concentrations of the various fractions. The sum of these fractions is 2.87 mg/kg for Pb. One would not expect the results to be identical, given that samples were collected on different dates and total concentrations were obtained with different procedures, but the difference of 2 orders of magnitude suggests that the initial high concentration of Pb at PSS123 may be erroneous or the result of very localized pollution of unknown origin. A source for an error is not apparent as this sample was collected and analyzed systematically with all other samples. Other relatively elevated Pb concentrations were observed in the Palafox Industrial Corridor only (Figure 13).

Cadmium concentrations are often below the detection limit throughout the two-county area (Figure 14). The highest concentrations are present in the urban areas (Pensacola, Milton). Zinc also generally has higher concentrations in the urban areas but does otherwise not have a distinct spatial pattern (Figure 15). Chromium and Ni present a different pattern with higher concentrations in the rural northern part of the area (Figure 16, Figure 17). Both Cd and Cr are high in PSS123, the sample that may have a localized pollution issue. Copper does not have a distinctive spatial pattern but has intermediate and high concentrations along Escambia River (Figure 18). Unlike the other metals Hg does not have a group of high concentrations but has one outlier at the high end of the concentration scale. This outlier is from the Palafox Industrial Corridor (Figure 19). Intermediate Hg concentrations are mainly from northern Escambia County, the rest of the study area has interspersed intermediate and low Hg concentrations.

To evaluate some of these spatial patterns we statistically compared average concentrations for the various metals in urban and rural areas (Table 3). Mean concentrations for

Pb and Zn, two trace metals that often have been linked to transportation sources, are higher in urban areas than in rural areas. The difference of the means for the two land uses is statistically not significant for Pb and significant for Zn at $\alpha = 8\%$. Chromium and Ni are statistically significantly higher in rural areas than in urban areas (Table 3), even though these two metals are often thought to derive from anthropogenic sources in urban areas. In the current study, however, principle component analysis (PCA) indicates that these two metals are strongly associated with Fe and Al, two geogenic metals (Figure 20). This association suggests that in the study area Cr and Ni may also predominantly be of geogenic origin. Given this contention, the higher levels of Cr and Ni, and Al and Fe, in rural areas (Table 3) can be explained by the presence of older, more intensely weathered soils in the rural northern part of the study area. The urban areas in the south are underlain but younger, less weathered soils that developed in marine sediments with low metal content (USDA-NRCS, 2004). These observations indicate that the higher concentrations of Cr and Ni in rural areas are not due to anthropogenic influences. Strong influence of parent material composition on the concentrations of Cr and Ni have been found elsewhere (Wilcke et al., 1998). Differences between rural and urban areas are small and statistically not significant for As, Cd, Cu and Hg (Table 3).

The contention that Cr and Ni derive from the parent material of the soils, more so than the other trace metals, is consistent with the relatively large and significant correlation coefficients between the concentrations of Cr and Ni and the various particle size fractions of the soils (Table 4). The small correlations between the other trace metals and the particle size fractions is remarkable as in many studies a strong correlation has been found between clay and trace metal content (Banat et al., 2005; Anderson and Christensen, 2006).

Table 2. Trace metal concentrations [mg/kg].

sample	Aluminum	Arsenic	Cadmium	Chromium	Copper
PSS 01	4450	1.1	BDL[1]	3.4	2.6
PSS 02	4900	1.8	BDL	5.9	3.5
PSS 03	13700	3.6	BDL	20.0	8.4
PSS 04	16500	**6.3**	0.55	25	15
PSS 04Dup	16900	**7.5**	0.6	31	20
PSS 05	2900	1.4	0.39	4.9	18
PSS 06	7400	**2.8**	2.6	11	13
PSS 06Dup	6900	**2.4**	0.55	8.3	11
PSS 07	4000	1.2	0.11	3.5	4.4
PSS 08	3200	**2.4**	0.29	6.1	12
PSS 09	4300	**2.6**	0.27	6.2	9.9
PSS 10	3800	1.0	0.200	4.4	12.0
PSS 14	6100	1.5	0.460	8.2	7.0
PSS 15	6900	4.1	0.600	8.8	16.0
PSS 16	6000	1.0	0.085	5.7	4.0
PSS 17	16000	2.2	0.140	12.0	4.6
PSS 18	3800	0.7	BDL	3.1	2.1
PSS 19	3600	1.3	BDL	5.7	1.8
PSS 20	8000	1.8	0.100	10.0	5.3
PSS 21	6800	0.9	0.069	6.6	3.1
PSS 22	13000	3.0	0.065	11.0	3.9
PSS 23	6800	1.1	BDL	6.0	2.5
PSS 24	8100	1.3	BDL	5.9	2.2
PSS 25	7200	2.2	0.150	9.7	4.8
PSS 26	12000	1.7	0.075	9.3	4.3
PSS 27	2600	0.7	0.080	2.8	4.7
PSS 28	7000	3.0	0.091	12.0	3.7
PSS 29	1300	0.7	BDL	1.9	1.4
PSS 30	2900	1.1	0.070	4.0	4.2
PSS 31	15000	2.7	0.110	29.0	6.6
PSS 32	11000	2.8	0.098	17.0	12.0
PSS 33	5600	2.6	0.140	12.0	6.2
PSS 34	3900	1.8	0.078	9.3	6.6
PSS 35	3200	0.7	BDL	3.9	2.6
PSS 36	11000	2.1	0.210	8.9	6.4
PSS 37	16000	1.9	0.130	12.0	6.8
PSS 38	11000	3.5	BDL	33.0	5.4
PSS 39	10000	2.1	BDL	8.3	4.8
PSS 40	6600	4.6	0.086	6.5	5.8
PSS 41	4300	1.1	BDL	4.1	2
PSS 42	11000	2	BDL	8.9	4.1
PSS 43	5900	0.79	BDL	5.5	2
PSS 44	7400	1.6	0.13	6.6	5
PSS 45	8400	2.4	0.18	8.7	7.6

Table 2. Trace metal concentrations [mg/kg] (continued).

sample	Aluminum	Arsenic	Cadmium	Chromium	Copper
PSS 46	5100	1.2	BDL	6	2.45
PSS 47	11000	3.5	0.22	14	11
PSS 48	2800	0.8	BDL	3.3	2.2
PSS 49	2800	BDL	BDL	BDL	BDL
PSS 50	7400	BDL	BDL	BDL	BDL
PSS 51	12000	2.6	BDL	11	5.6
PSS 52	7800	1.8	BDL	8.2	3.8
PSS 53	2000	1.1	0.12	2.7	1.6
PSS 54	2700	4.7	0.085	5.9	8.1
PSS 55	8520	1.7	0.31	11	10
PSS 56	14000	2.8	0.11	12	4.8
PSS 57	22000	3.4	0.19	16	9.5
PSS 58	10500	1.6	0.089	8.3	4.7
PSS 59	5970	1.4	BDL	7.5	3.7
PSS 60	6280	10	0.18	24	26
PSS 61	9910	2.8	0.29	15	7.3
PSS 62	5930	0.93	BDL	6	3.5
PSS 63	2970	0.43	BDL	4.1	1.7
PSS 64	1480	BDL	BDL	1.8	0.49
PSS 65	919	BDL	BDL	1.8	0.98
PSS 66	3590	0.66	BDL	5.7	9.7
PSS 67	7810	1.8	BDL	9.1	3.2
PSS 68	372	BDL	BDL	1.5	0.19
PSS 69	2760	0.51	0.078	3.3	3.6
PSS 70	3390	1.1	0.071	4.8	3.8
PSS 71	2190	0.82	BDL	4	3.4
PSS 72	2340	0.64	0.087	3.6	3.9
PSS 73	1260	0.37	BDL	3	28
PSS 74	2455	0.685	BDL	3.45	1.085
PSS 75	2050	0.86	BDL	3.9	3.7
PSS 76	1080	0.62	BDL	2.7	2.3
PSS 77	6000	2.7	BDL	7.3	4.5
PSS 78	1790	0.85	BDL	3.7	3.7
PSS 79	2290	0.37	BDL	3.8	3.6
PSS 80	319	0.38	BDL	0.69	6.4
PSS 81	2530	0.69	BDL	3.1	1.7
PSS 82	2230	0.89	BDL	4.5	3
PSS 83	5110	0.8	BDL	5.5	3.1
PSS 84	5540	1.2	0.074	6.7	3
PSS 85	10600	2.6	0.067	15	5.7
PSS 86	3920	1.2	BDL	5.2	4.7
PSS 87	4480	1.8	0.066	6.2	3.7
PSS 88	5380	0.13	0.016	0.74	0.38
PSS 89	10200	2.2	0.84	9.7	8.7

Table 2. Trace metal concentrations [mg/kg] (continued).

sample	Aluminum	Arsenic	Cadmium	Chromium	Copper
PSS 90	9400	3.1	0.24	14	14
PSS 91	7600	1	BDL	6	2.5
PSS 92	5330	1.1	BDL	6.7	3.5
PSS 93	4720	0.69	BDL	4.8	25
PSS 94	2230	0.43	BDL	3	2.4
PSS 95	9760	14	1.4	18	54
PSS 96	3410	1.5	BDL	4.5	2.3
PSS 97	3540	1.1	0.069	5.1	4.4
PSS 98	4420	1.1	BDL	5.2	3.6
PSS 99	4500	1.5	0.082	6.9	6.9
PSS 100	6645	1.45	BDL	6.7	4.25
PSS 101	4810	BDL	BDL	0.39	0.27
PSS 102	3490	1.3	BDL	5.5	4
PSS 103	5240	1.2	0.094	7.2	3.7
PSS 104	5810	0.73	BDL	6.1	3.5
PSS 105	2970	0.73	BDL	3.4	1.7
PSS 106	6710	4.7	0.089	8.3	4.8
PSS 107	4890	1.2	BDL	4.3	2.3
PSS 108	4270	0.9	BDL	5.2	4.5
PSS 109	3260	0.97	BDL	3.6	1.8
PSS 110	10700	2.7	0.12	13	7.2
PSS 111	4430	1.2	0.21	6.4	8.9
PSS 112	10400	2.4	0.12	12	6.2
PSS 113	25200	2.8	0.087	21	9.5
PSS 114	8980	1.4	BDL	8	3.5
PSS 115	3050	0.32	BDL	2.9	2.4
PSS 116	5590	0.65	BDL	5.2	2.3
PSS 117	16100	4	0.14	17	9.2
PSS 118	18700	1.9	0.074	23	7.3
PSS 119	14100	1.4	0.089	8.1	4.4
PSS 120	7480	1.1	BDL	5.4	2.3
PSS 121	3890	0.71	BDL	3.2	1.7
PSS 122	6240	0.96	BDL	4.2	2.3
PSS 123	4250	0.73	1.8	60	7.8
PSS 124	31800	1.8	0.071	41	9.8
PSS 125	6200	0.76	BDL	5.4	2.2
PSS 126	8090	1.5	0.072	8.9	32
PSS 127	7240	1.1	BDL	5.2	2.9
PSS 128	14900	0.76	BDL	12	5.3
PSS 129	3600	0.82	BDL	3.1	1.3
RSCTL	80000	2.1	82	210	150
# exceeding	0	33	0	0	0
minimum	319	0.13	0.02	0.39	0.19
maximum	31800	14.00	1.80	60.00	54.00
geomean	5595	1.38	0.14	6.38	4.25

Table 2. Trace metal concentrations [mg/kg] (continued).

sample	Iron	Lead	Mercury	Nickel	Zinc
PSS 01	3120	15.0	0.030	1.2	9.4
PSS 02	3690	12.0	0.013	2.0	19.0
PSS 03	9180	23.0	0.008	4.9	71.0
PSS 04	15300	193	0.36	3.4	45
PSS 04Dup	14900	258	0.4	4.8	69
PSS 05	2500	46	0.1	3.8	84
PSS 06	5400	380	0.035	5.7	150
PSS 06Dup	4800	270	0.043	2.9	130
PSS 07	2500	12	0.019	1.5	21
PSS 08	3500	120	0.037	2.6	91
PSS 09	4100	43	0.016	2.1	91
PSS 10	2500	15.0	0.015	1.8	38.0
PSS 14	4600	18.0	0.012	2.3	60.0
PSS 15	5900	150.0	0.034	2.9	240.0
PSS 16	3300	14.0	0.012	1.7	26.0
PSS 17	10000	8.5	0.005	2.1	22.0
PSS 18	2400	9.9	0.026	1.2	9.5
PSS 19	2800	5.7	0.005	0.9	7.6
PSS 20	6100	7.7	0.011	2.3	13.0
PSS 21	4800	23.0	0.051	1.5	27.0
PSS 22	9300	5.8	0.012	1.4	2.9
PSS 23	4700	3.9	0.015	1.6	12.0
PSS 24	4800	5.4	0.019	1.4	4.8
PSS 25	5800	20.0	0.012	1.5	52.0
PSS 26	8900	16.0	0.007	1.7	14.0
PSS 27	2000	19.0	0.016	1.4	30.0
PSS 28	5500	13.0	0.013	1.4	17.0
PSS 29	1300	7.7	0.011	0.9	5.4
PSS 30	2100	13.0	0.011	1.2	15.0
PSS 31	17000	11.0	0.021	4.7	16.0
PSS 32	7300	34.0	0.049	3.9	81.0
PSS 33	5800	50.0	0.033	4.0	41.0
PSS 34	8700	56.0	0.049	4.5	32.0
PSS 35	2100	8.1	0.012	1.7	6.2
PSS 36	5800	13.0	0.025	5.1	39.0
PSS 37	8100	21.0	0.042	6.4	24.0
PSS 38	18000	15.0	0.034	3.8	16.0
PSS 39	5600	12.0	0.025	4.6	14.0
PSS 40	5400	7.9	0.031	2.3	17.0
PSS 41	2500	6.7	0.012	1.4	9.3
PSS 42	5700	5.8	0.02	2.3	6.1
PSS 43	3000	2.5	BDL	2.1	6
PSS 44	5200	24	0.032	2.4	27
PSS 45	5200	21	0.031	2.3	64

Table 2. Trace metal concentrations [mg/kg] (continued).

sample	Iron	Lead	Mercury	Nickel	Zinc
PSS 46	4450	5.45	BDL[1]	0.955	7.5
PSS 47	11000	50	0.043	4	74
PSS 48	1700	14	0.016	0.84	8.1
PSS 49	1900	BDL	0.021	BDL	BDL
PSS 50	4500	BDL	0.017	BDL	BDL
PSS 51	7100	24	0.025	2.6	8.8
PSS 52	6600	8.4	0.018	2.2	8.8
PSS 53	1400	4.9	0.011	1.2	8
PSS 54	2600	3.8	0.006	1.8	32
PSS 55	4770	17	0.023	3.3	163
PSS 56	8400	19	0.02	4.4	13
PSS 57	12000	11	0.026	4.9	29
PSS 58	5550	5.4	BDL	2.8	131
PSS 59	3330	5.9	0.02	2.5	20
PSS 60	5560	28	0.02	5.7	93
PSS 61	7100	15	0.024	5.2	49
PSS 62	3490	4.8	0.018	1.8	10
PSS 63	1970	9.4	0.016	1.3	3.4
PSS 64	991	2.5	0.005	0.62	3.1
PSS 65	589	8.1	0.008	0.38	1.7
PSS 66	2080	2.5	0.011	0.48	10
PSS 67	4400	3.1	0.012	1.2	10
PSS 68	350	2	0.011	0.22	1.3
PSS 69	1580	2	0.009	1.1	7.3
PSS 70	2190	5.1	0.02	1.2	29
PSS 71	1510	9.1	0.018	1.3	13
PSS 72	1010	5.1	0.025	1.1	18
PSS 73	989	18	0.007	5.6	139
PSS 74	1405	1.8	0.007	1.15	8.05
PSS 75	1730	5	0.017	1.4	22
PSS 76	1140	1.6	BDL	1.1	11
PSS 77	3170	18	0.015	2.2	32
PSS 78	1500	34	0.014	1.2	24
PSS 79	1460	11	0.027	1.4	21
PSS 80	342	2	0.022	0.31	7.8
PSS 81	1710	3.6	0.012	1.1	4.6
PSS 82	1580	2.4	0.025	1.4	10
PSS 83	2590	4.3	0.014	1.6	16
PSS 84	3360	3.7	0.007	1.7	27
PSS 85	4860	18	0.033	3.4	17
PSS 86	2600	11	0.023	1.8	22
PSS 87	3030	23	0.015	2.3	23
PSS 88	3870	2.8	0.013	0.17	7.9
PSS 89	5460	32	0.028	2.6	107

Table 2. Trace metal concentrations [mg/kg] (continued).

sample	Iron	Lead	Mercury	Nickel	Zinc
PSS 90	5330	48	0.038	5.3	106
PSS 91	3770	3.9	0.005	1.8	8.9
PSS 92	3110	9.4	0.018	2.5	8.5
PSS 93	3500	8.5	0.023	1.2	9
PSS 94	1540	7.7	0.013	1.1	15
PSS 95	7160	258	0.089	5.4	289
PSS 96	2250	20	0.032	1.3	17
PSS 97	2470	17	0.019	1.9	34
PSS 98	2970	37	0.013	1.7	32
PSS 99	3000	8.9	0.043	2	29
PSS 100	3930	10.35	0.012	2.45	10.9
PSS 101	2970	0.82	0.008	BDL	0.53
PSS 102	2450	22	0.026	1.8	8.3
PSS 103	3200	15	0.006	2.3	21
PSS 104	3300	8.1	0.021	2.6	109
PSS 105	2090	6.1	0.014	1.3	4.5
PSS 106	3670	5.4	0.01	1.2	14
PSS 107	3020	25	0.014	1.5	7
PSS 108	2680	9.4	0.048	1.9	19
PSS 109	2400	10	0.014	1.4	4.2
PSS 110	7330	13	0.026	3.7	36
PSS 111	4970	16	0.012	1.3	27
PSS 112	7970	46	0.014	3.6	38
PSS 113	12400	18	0.043	6.6	20
PSS 114	5030	4.9	0.008	1.9	6.9
PSS 115	1900	6.7	0.042	1.4	5.4
PSS 116	3270	5.8	0.012	2.5	12
PSS 117	10300	27	0.066	8	48
PSS 118	13700	42	0.056	6.7	13
PSS 119	7460	8	0.034	4.1	7.5
PSS 120	4110	8.8	0.034	2.3	4.7
PSS 121	2560	6.8	0.013	1	4.3
PSS 122	3740	4.9	0.024	2.2	5.4
PSS 123	2690	411	0.018	1.5	11
PSS 124	9110	11	0.031	7.3	18
PSS 125	4860	8	0.025	2.1	5.5
PSS 126	7320	12	0.036	1.7	24
PSS 127	4570	7.6	0.029	1.8	4
PSS 128	4270	22	0.071	3.6	8.4
PSS 129	2290	3.2	0.012	1.1	4.3
RSCTL	53000	400	3	340	26000
# exceeding	0	1	0	0	0
minimum	342	0.82	0.005	0.17	0.53
maximum	18000	411.00	0.38	8.00	289.00
geomean	3585	11.57	0.019	1.95	16.91

Table 3. Average metal concentrations for urban and rural areas [mg/kg].

Metal	Urban	Rural	P value [%]
Aluminum	4069	6071	0.1
Arsenic	1.87	2.03	65
Cadmium	0.27	0.20	49
Chromium	6.99	11.99	0.1
Copper	6.32	6.31	99
Iron	4136	5991	0.3
Lead	31.22	23.48	50
Mercury	0.0283	0.0259	75
Nickel	22.03	3.19	0.01
Zinc	36.64	25.18	8
n[1]	64	47	

1: Sum of samples in urban and rural do not total 126 because some sampling sites were judged to be too close to both land uses to be used for either one.

Table 4. Pearson correlation coefficients between soil properties and trace metal concentrations.

	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
Clay	0.11	-0.14	**0.48**[1]	0.10	-0.01	0.13	**0.57**	-0.06
Silt	0.24	-0.07	**0.46**	0.21	0.08	0.20	**0.62**	0.03
Sand	-0.21	0.09	**-0.49**	-0.18	-0.06	-0.19	**-0.63**	0.00
OM[2]	0.20	-0.17	**0.32**	0.25	0.03	0.14	**0.44**	0.10

1 Values in bold are statistically significant ($p < 0.01$).
2 OM = organic matter content.

The above comparison of the trace metal concentrations with SCTLs shows that, with the exception of As, the concentrations do not exceed the guidelines. However, the SCTLs are regulatory limits that were not designed as indicators for the presence or absence of anthropogenic pollution. To evaluate if the trace metals may originate from anthropogenic activities we applied two indexes that compare observed concentrations to background concentrations, the index of geoaccumulation (Igeo) and the enrichment factor (EF). Many other studies have employed general crustal background concentrations to calculate indexes like these (Covelli and Fontolan, 1997; Ray et al., 2006; Gonzalez et al., 2007). These general values may or may not apply to any particular region due to differences in rocks, climate, and geochemistry, and thus local background values seem much more appropriate. The trace metal concentrations in the present study have a distinct bimodal distribution (Figure 21) and lend themselves to identification of a local background value by statistically separating the two populations (see methods section), one of presumably natural values and one of anthropogenically altered values. The resulting local background concentrations are considerably different from general crustal values (Table 5), illustrating the importance of calculating the local values.

Table 5. Comparison of crustal background values and background values established in the present study [mg/kg].

source	Al	As	Cd	Cr	Cu	Fe	Pb	Hg	Ni	Zn
shale[1]	80000	2.1	0.3	90	45	47200	20	0.4	68	95
sandstone[1]	25000	1	n/a[3]	35	n/a	9800	7	0.03	2	16
crustal avg.[2]	82300	1.8	0.2	100	55	56300	12.5	0.08	75	70
this study	6829	1.6	0.15	6.74	4.69	3248	13.95	0.02	1.62	17.81

1. Source: Turekian and Wedepohl (1961).
2. Source: Taylor (1964).
3. n/a: Not available.

The two indexes yield remarkably similar proportions of polluted sites and levels of pollution given the different calculation methods and naming conventions (Table 6). The indexes show that few sites are strongly polluted. The trace metals with the highest proportion of strongly polluted sites are Pb and Zn, but even these metals reach that pollution level at only 4% to 6% of the sites (Table 6). Maps show that most of these sites are located in the Palafox industrial corridor (Figure 22, Figure 23). Sites at which Pb and Zn reach pollution levels (EF between 2 and 10) are mainly from along the Escambia River and the urban areas of Pensacola, Milton, and the Gulf Breeze peninsula. Cadmium has the lowest pollution levels at the fewest sites, which is consistent with the above made observation that Cd was below the detection limit at many sites. Arsenic, which exceeded the SCTL at the most sites, has fewer polluted sites than most other trace metals, based on the background-based indexes. This indicates that most measured As concentrations are not higher than the background, but that the background is close to the SCTL. This high As background has been observed in other studies in the region (Liebens, 2001). The other trace metals reach pollution levels at roughly 20% to 30% of the sites (Table 6). This indicates that although these trace metals apparently do not exceed safe (SCTL) levels at these sites their concentrations have been modified by anthropogenic inputs. The relative consistency between these two different indexes, except for Cr, lends credence to this observation. The values for the indexes calculated with general background concentrations are very different and in an unsystematic way (Table 7, Table 8). This demonstrates the importance of using appropriate background values and illustrates the need for careful consideration of results from different studies.

Table 6. Proportion [%] of samples at various pollution levels, based on local background concentrations.

Index value	Pollution level	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
		Index of geoaccumulation							
0 - 2	polluted	19.8	7.9	20.6	22.2	18.3	23.0	31.7	25.4
> 2	strongly polluted	1.6	2.4	1.6	1.6	5.6	0.8	0.0	6.3
		Enrichment factor							
2 - 10	polluted	11.1	7.9	8.7	19.8	20.6	19.8	22.2	27.0
> 10	strongly polluted	0.0	1.6	0.8	1.6	4.0	2.4	0.8	4.0

Table 7. Proportion [%] of samples at various pollution levels, based on average background concentrations for shale.

Index value	Pollution level	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
		Index of geoaccumulation							
0 - 2	polluted	8.7	5.6	0.0	0.0	10.3	0.0	0.0	4.0
> 2	strongly polluted	0.8	0.0	0.0	0.0	4.0	0.0	0.0	0.0
		Enrichment factor							
2 - 10	polluted	54.8	31.0	4.8	25.4	54.8	7.9	0.8	44.4
> 10	strongly polluted	38.9	10.3	0.8	2.4	39.7	0.8	0.0	12.7

Table 8. Proportion [%] of samples at various pollution levels, based on average background concentrations for sandstone.

Index value	Pollution level	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
		Index of geoaccumulation							
0 - 2	polluted	36.5		0.8		36.5	7.1	23.8	25.4
> 2	strongly polluted	2.4		0.0		13.5	0.8	0.0	7.1
		Enrichment factor							
2 - 10	polluted	75.4		2.4		52.4	65.9	87.3	12.7
> 10	strongly polluted	17.5		0.8		36.5	4.8	5.6	27.0

Spatial clustering of high concentrations of trace metals, or any other pollutant, can point to the presence of local sources of pollution. Therefore, we further examined the trace metal concentrations in a GIS with hot spot analysis. Hot spot analysis assesses the value at each site within the context of values at neighboring sites and identifies clusters of sites that have significantly higher values than the whole dataset. We performed this hot spot analysis on the PLI, an index that is a measure for the overall magnitude of the trace metal concentrations at a given site. Results show that a clear hot spot exists in the Palafox Industrial Corridor and that elsewhere in the study area the concentrations are lower and of more-or-less comparable magnitude (Figure 24). The spatial concurrence of the hot spot and the industrial corridor does not necessarily represent a causal relationship, but given the well documented pollution history in the industrial corridor (Geraghty and Miller, 1992), and the low values elsewhere in urban areas, it seems fair to assume that this previously undocumented trace metal hot spot is due to the local industry. This observation is also consistent with those for the enrichment factor (see above), which showed a concentration of highly polluted sites in the Palafox Industrial Corridor (Figure 22, Figure 23).

6.3 Effects of Proximity to a Road

Three or four samples were collected at 19 of the initially sampled public places that were near major roads. One of the samples at each site was located as close to the road as safely and practically possible, usually within 2 m from the edge of the road, and 2 or 3 more samples were collected at 20 m intervals depending on the size of the public place. Graphs show that with the exception of Hg the *average* concentration of all analyzed trace metals (As, Cd, Cr, Cu, Ni, Pb, Zn) decreases between the 2 m and the 20 m samples (Figures 25 - 34). Pair wise t-tests of the 2 m and 20 m samples at each site indicate that the decrease is statistically significant (Table 9). The test was not applied to Cd because of the relative large number of analytical results that were below the detection limit (9 out of 19 samples from 20 m from the road). The higher concentrations near the road are obviously related to traffic and derive from the wearing of tires and brake pads, tire weights that fall off, oil drips, and emissions. Arsenic has rarely been associated with traffic activities, in part because studies that examine the influence of transportation on trace metals often focus on more traditional trace metals such as Pb, Zn, Ni and Cu. However, As is present in trace amounts in gasoline, and has been identified in vehicular exhaust (Johansson et al., 2008; Thomaidis et al., 2003), and thus may built up in soils near roads. Some other studies, albeit relatively few (e.g. Luilo et al., 2003), have also observed higher concentrations of As near roads as we did, but others did not come to the same conclusion (e.g. Munch, 1993). Arsenic is emitted by asphalt plants but there is no evidence in the scientific literature that arsenic leaches out of asphalt pavement. In principle, arsenic-containing herbicides may have been used on the road berms that were sampled but clear evidence for the use of herbicides on the shoulders of roads could not be found for our study area. Samples were collected away from swales that often border the roads in the study area and deposition by water draining through the swales is an unlikely source for the As. These observations suggest that traffic is the most likely source for the higher As concentrations near roads in the study area. Mercury is not associated with traffic activities and, accordingly, was not found to decrease with distance from the road (Figure 32). In fact, Hg increased between 2 m and 20 m from the raod.

Table 9. P values [%] for pair wise t-test for trace metal concentrations.

Distance	Al	As	Cd[1]	Cr	Cu	Fe	Pb	Hg	Ni	Zn
2 m - 20 m	69.9	6.6	n/a	2.4	0.4	59.5	1.1	0.8	04.4	0.0
20 m - 40 m	47.3	14.8	n/a	73.1	60.6	43.1	260	83.3	28.0	30.5

1. Too many analytical results were below detection limit to obtain statistically meaningful results.

Between 20 m and 40 m from the road the average concentrations of As, Cr, Cu, Ni and Zn do not further decrease (Figures 25 - 34), and in fact slightly increase. The slight increase is statistically not significant based on pair wise t-tests of the 20 m and 40 m samples at each site (Table 9). This indicates that the impact of road traffic becomes minimal between 20 m and 40 m from the road. This is in line with other studies that have found that the influence of traffic activities on trace metals in soils becomes insignificant at distances of 30 m to 50 m from the road (Fakayode and Olu-Owolabi, 2003), but others have observed limited effects beyond 5 to 10 m from the road (Munch, 1993). Our results are not in contradiction with these latter findings because 5 to 10 m is within the spatial resolution of our sampling scheme. The average concentrations of Cd and Pb, however, did further decrease between 20 m and 40 m (Figure 26, Figure 29). For Cd this observation has to be interpreted in the context of the many analytical results that were below the detection limit, and for Pb the decrease is statistically not significant (Table 9). At the seven sites with a sample at 60 m from the road average Pb concentrations decreased to this last distance. These observations suggest that the effect of traffic is greater for Pb than for any of the other trace metals. A strong influence of traffic on Pb is corroborated by the large decrease in the Pb concentration between the 2 m and the 20 m sample (Figure 29).

Iron and Al occur in high concentrations in most soils and were analyzed in this study for standardization purposes. Changes in the concentrations of these metals with distance from a road were unsystematic (Figure 33, Figure 34) and statistically not significant (Table 9), demonstrating the suitability of these metals for standardization.

The natural composition of soils can change over small distances. The samples at each of the 19 sites sampled for this part of the task were taken within a maximum of 60 m from each other. Consequently, natural soil variations at any given site should be modest. However, to minimize the effect of variations in the natural composition of the soils on our data we standardized the trace metal concentrations with the concentration of Al. Aluminum is a common element in most natural soils and is often employed for standardization. The standardized values for the trace metals (data not shown) show the same trends as those described above for the concentrations, indicating that natural soil variations are indeed small at any given site. The main difference was observed for Zn, for which the standardized values gradually decrease from the 2 m sample to the 60 m sample. This suggests that, in addition to Pb, Zn concentrations may also be substantially influenced by traffic.

To further evaluate the trends of the trace metal concentrations near roads we calculated the enrichment factor (EF) for each metal in each sample. The enrichment factor is a pollution index that compares the standardized concentration of a metal to the standardized background concentration of the metal as described in the methods section. A sample is generally considered to be polluted when the EF exceeds a value of two (Wang et al., 2006). Lead and Zn have the highest proportions of samples from near the roads (2 m samples) that reach pollution levels (Table 10). Nickel, another metal that has been linked to traffic sources by other studies, reaches pollution levels in 56 % of the 2 m samples. A comparison of the EF for the samples from near the roads with those for the 126 samples analyzed for the main phase of this task shows that proportionally many more 2 m samples are polluted (Table 6, Table 10). These findings corroborate the above finding that the concentrations of the trace metals, with the exception of Hg, are elevated near roads, and that Pb and Zn are most strongly affected. Even though the raw concentrations, on average, are higher for the 2 m samples than for the 126 samples, As is still the only element that exceeds the FL DEP RSCTL (Table 10). This shows that, in spite of their elevated nature, most trace metal concentrations along roads in the study area should not be considered to be of direct environmental concern.

Table 10. Average concentrations and pollution levels for samples collected near roads and comparison with samples from main phase of Task A-1.

Samples	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
				Geomean concentration [mg/kg]				
2 m	1.91	0.18	10.20	6.98	31.10	0.01	3.51	51.95
20 m	1.43	0.13	6.81	4.18	11.54	0.02	2.28	22.70
40 m	1.88	0.14	7.27	3.96	8.83	0.02	2.49	20.45
Set of 126	1.38	0.14	6.38	4.25	11.57	0.02	1.95	16.91
				Proportion [%] with EF[1] > 2				
2 m	11	11	22	28	67	6	56	78
20 m	0	0	0	6	11	22	22	22
40 m	17	0	6	6	0	17	56	28
Set of 126	3	8	9	20	21	20	22	27
				Proportion [%] above RSCTL[2]				
RSCTL	2.1	82	210	150	400	3	340	26000
2 m	50	0	0	0	0	0	0	0
20 m	28	0	0	0	0	0	0	0
40 m	50	0	0	0	0	0	0	0
Set of 126	26	0	0	0	0	0	0	0

1. Enrichment factor
2. RCSTL = residential soil cleanup target level.

6.4 Effects of Proximity to CCA Treated Wood

Wood treated with chromated copper arsenate (CCA) has been used for many years in outdoors structures because it resists decomposition much better than untreated wood, especially in the warm humid climate of Florida. The Cr, Cu and As can leach out of the wood and migrate into surrounding soils (Chirenje et al., 2003b). Because the Cr, Cu and As can have negative effects on human and ecosystem health, and because their concentrations in soils are regulated by state and federal agencies, we included an assessment of Cr, Cu and As concentrations near treated wood structures in public places as a secondary objective of our project. To our knowledge such an assessment has never been carried out in the region. To locate treated wood structures we carried out an extensive field survey based on maps of public places provided by county agencies. We discovered that CCA treated wood structures remain in only five public places in the two-county study area. The soil samples at these locations were collected about

2.5cm from the wood and without touching it. All soils consisted of white quartz-rich play sand. A statistical analysis is obviously not appropriate given the very small dataset, but a visual analysis of the analytical results shows a clear influence of the treated wood on some metal concentrations (Table 11).

Sample PSS101 has very low concentrations for all the trace metals (Table 11). It is unclear why that is so. Another sample was taken at the same public park for the main phase of this task. That sample was collected at an undisturbed location away from the wooden structures, and on a different date. The metal concentrations in this original sample were among the lowest in the dataset, suggesting that for an unknown reason metal concentrations in the park are very low in general. The other four samples from near treated wood have elevated concentrations for As, Cr, and Cu (Table 11). The As concentrations in the four samples exceed the highest concentration measured in the original dataset of 126 samples, and are all above the RSCTL by about an order of magnitude. The four measured trace metals that are not explicitly used in the CCA treating of wood (Pb, Hg, Ni, Zn) have concentrations that are below the geomean for the original dataset of 126 samples. These low concentrations demonstrate that these four soil samples are not generally polluted, and indicate that the elevated concentrations for As, Cr, and Cu most likely originate from the treated wood. The below average concentrations for Pb, Hg, Ni, and Zn can be explained by the sandy and quartz rich nature of the soils, which don't have the chemical binding capacity to hold the metals if delivered to the soil. This lack of chemical binding capacity suggests that the high concentrations of As, Cr, and Cu are due to very high input rates and that leaching of these three metals may be high. Even though SCTL are not intended to determine the possibility of illness, Cr and Cu concentrations near the wooden structures do not seem to pose a health risk given that the concentrations are below the RSCTL and that the concentrations can be expected to decrease rapidly with distance from the treated wood (Chirenje et al., 2003b). Arsenic concentrations are well above the FL DEP RSCTL (2.1 mg/kg) close to the wood, and also exceed the commercial/industrial SCTL of 12 mg/kg, and may justify further scrutiny.

6.5 Speciation of Trace Metals

Even though most regulatory guidelines for trace metals are based on total concentrations, mobility of the trace metals in the environment and bioavailability greatly depend on the speciation of the metals (Ramos et al., 1999; Singh et al., 1999; Watmough et al., 2005). To address this issue, an additional sample was collected at 22 public places that had detectable concentrations for all trace metals in the main phase of this task. The metals in these additional samples were extracted with a sequential extraction method that separately extracted various phases of the metals. The five forms extracted in the present study were water extractable phases of the metals, exchangeable phases, oxide-bound phases, organic matter-bound phases, and the residual phase.

Table 11. Trace metal concentrations [mg/kg] for soil samples collected near CCA treated wood, and descriptive statistics for main dataset.

Sample	Arsenic	Cadmium	Chromium	Copper	Lead	Mercury	Nickel	Zinc
Soils near CCA treated wood								
PSS 45	25	BDL	12	16	9.1	0.014	1.8	12
PSS 75	21	BDL	12	24	1.4	BDL	0.27	9.9
PSS 77	15	BDL	15	8.9	0.84	BDL	BDL	0.89
PSS 79	79	BDL	24	32	2.2	BDL	0.48	13
PSS 101	BDL[1]	BDL	0.35	BDL	0.16	BDL	BDL	1.1
Main dataset of 126 samples								
minimum	0.13	0.02	0.39	0.19	0.82	0.005	0.17	0.53
maximum	14	1.8	60	54	411	0.38	8	289
geomean	1.38	0.14	6.38	4.25	11.57	0.019	1.95	16.91
RSCTL	2.1	82	210	150	400	3	340	26000

1. BDL: Below detection limit.

The water extractable fraction is present in the soil solution, the exchangeable fraction is electrostatically bound to soil colloids. These two fractions are the most mobile and bioavailable forms in a soil environment and can derive from the parent material or from anthropogenic pollution. The exchangeable proportion is not necessarily directly linked to bioavailability (Forstner, 1993), in part due to the complex influence of often highly variable soil properties, but a strong relationship is often assumed to exist between the two (Singh et al., 1999). In the present study the proportions of the various metals in these two forms are generally low, except for As and exchangeable Zn (Table 12). Oxide bound forms of the metals are usually adsorbed to Fe and/or Mn oxides and are sensitive to changes in redox potential and pH. The proportions of the various metals in this form are also low, with the exception of Pb and Zn (Table 12). Organic matter influences trace metal concentrations because of its capacity to chelate and adsorb metals. Any change in the soil that affects the organic matter content, such as changes in the oxidizing conditions of the soils, has the potential to lead to a release of the metals. In the study area high proportions (about 41%) of Pb and Cu are organically bound, the other metals have more modest proportions in this form (Table 12). The residual phase is considered to be immobile under common natural conditions (Ramos et al., 1999), and is not affected by anthropogenic inputs. Most of the trace metals are in this form in the study area. Lead, which plotted separately from the other metals in the factor loadings plot (Figure 20), has the lowest proportion of all metals in the residual phase indicating that it is not chiefly of natural origin. Results also show that the proportions of the five phases are highly variable among the metals (Table 12). This variability is largely a reflection of the geochemical characteristics of the metals and the chemical properties of the soils.

Table 12. Average relative proportions [%] of various metal phases.

Metal[1]	Water Extractable	Exchangeable	Oxide-bound	OM-bound	Residual
As	9.85	6.30	5.07	8.03	70.76
Cr	2.02	1.56	0.14	26.95	69.32
Cu	0.13	2.15	1.94	40.93	54.85
Pb	0.39	3.89	34.80	41.10	19.82
Ni	BDL	1.36	BDL	4.85	94.06
Zn	2.28	21.75	20.76	14.68	40.53
Al	3.91	1.54	4.81	14.26	75.47
Fe	4.46	0.07	5.34	9.83	80.30

1. Cd was omitted due to the large number of results below the detection limit (BDL).

As observed above, As is elevated in many of the soil samples. The sequential extraction results show that a major portion of the As in the soils is present as a residual phase (Figure 35, Table 12). In dust in a road and subway tunnel As has also been found to be predominantly in the residual phase (Sysalova and Szakova, 2006). The large residual portion implies that even though total As is often elevated in the present study, and exceeds the RSCTL in more than 26% of the samples of the main dataset, much of it is present in a form that is not readily available to other parts of the environment. However, As has a larger proportion in the water extractable phase than any of the other metals, indicating that it is one of the most available trace metals in the study area. Cadmium presents the opposite pattern. Cadmium is usually present in low, often non-detectable, concentrations. Most of the detectable Cd is, however, in exchangeable forms (Figure 36) that are adsorbed to the surface of soil particles and can be easily replaced by other cations and released into the rest of the environment. Because the absolute concentrations of these exchangeable forms of Cd are low they do not seem to pose an immediate threat to humans or other elements of the environment. Having the majority of the Cd species in an exchangeable form is unusual (Birch et al., 1999) and may be spurious because of the very low number of samples with detectable levels of Cd in the various phases. Chromium and Cu are mostly present in organic matter-bound and residual forms (Figure 37, Figure 38, Table 12). For Cr the stable residual phase predominates, for Cu the organic matter-bound forms dominate. This indicates that changes in Eh and pH could lead to some mobilization of Cu. Large proportions of Cu in residual and OM-bound forms have also been observed in aquatic sediments (Singh et al., 1999; Jha et al., 1990; Pardo et al., 1990; Huang et al., 2007). Lead and Zn, which were present at relatively high concentrations but without exceeding the RSCTL in the original dataset, are present in significant amounts in all but the water extractable forms (Figure 39, Figure 40, Table 12). An even spread of Zn among the different fractions has been observed in some other soils (Lestan et al., 2003) but high proportions of Zn were found to be in the residual fraction in reclaimed marine muds (Huang et al., 2007) and in sediments (Hong and Forstner, 1983). Compared to the other metals Zn has high proportions of exchangeable forms. A dominance of unstable exchangeable forms of Zn has been reported for soils and sediments (Birch et al, 1999; Wasay et al., 1998). Lead is dominated in many of the samples by relatively stable oxide and organic matter-bound forms, which is not unusual (Tessier et al., 1980; Pardo et al., 1990; Chlopecka et al., 1996), but these forms can be released into the environment by changes in pH, redox potential, and decomposition of organic matter (Birch et al., 1999). Nickel is almost exclusively present in residual forms (Figure 41). The high percentage is somewhat artificial because of the BDL values for water extractable and oxide bound Ni, but is in agreement with the results of the factor analysis that showed that Ni derives predominantly from the parent material of the soils. Aluminum and Fe have high proportions in the residual phase. This is consistent with their presence in many rock forming minerals and corroborates the above made contention that they are associated with the parent materials of the soils. Given the speciation of As, Pb and Zn, and their relatively high concentrations, these three trace metals seem to have the greatest potential for impacting other parts of the environment in the study area.

To evaluate the influence of soil characteristics on the bioavailable fractions of these three trace metals we ran a backward stepwise regression and hierarchical clustering on the concentrations of these fractions and particle size data, pH, organic matter content, Al content, and total trace metal content. Results for Pb show that for the exchangeable fraction and the bioavailable fraction (exchangeable plus water extractable) pH and total Pb are the best explanatory variables (Table 13). The cluster tree for the hierarchical clustering visually illustrates the close association between the exchangeable and bioavailable fractions, and pH and total Pb content (Figure 42). It also shows that the residual fraction is closely related to the various available fractions and that the organic matter and oxide bound fractions of Pb are more closely associated with sand content than clay content. The various available Zn fractions are also best explained by the total metal concentration but not by pH (Table 13). The cluster tree for Zn (Figure 43) shows that all Zn fractions are strongly interdependent and confirms the regression result that total Zn is strongly related to the various available fractions. The cluster tree also shows that, although pH was not retained by the regression analysis, it is more closely associated with the Zn fractions than the other soil characteristics. The As data were not amenable to a stepwise regression analysis (Table 13) but the cluster tree for As (Figure 44) indicates that the various As fractions are more closely related to total As content than any soil characteristic. The soil characteristics with most influenceon the available As fractioons are pH and sand content. These observations indicate that, in the absence of a sequential extraction, total metal content is the single best predictor of the bioavailability of these metals. This is an interesting observation because total metal determination is a relatively straightforward standard procedure that has advantages over the more complicated sequential extraction. The observations also demonstrate that pH is the soil characteristic with most influence on the bioavailability of these three metals, and thus that any disturbance of the soil that can lead to a change in pH has the potential to affect the bioavailability of these metals.

6.6. Radioactivity of Surface Soils

A secondary objective of this task was to assess the radioactivity of the surface soils in the public places of the study area. For this assessment we conducted a field-based pilot project using a hand-held Geiger counter to measure the total radioactivity at the 126 public places sampled during the main phase of this task. The Geiger counter had a Geiger-Mueller tube with a thin mica window and detected alpha, beta, gamma, and X-rays. The total radioactivity was determined in the field by placing the Geiger counter on the surface of the soil after removing grass, weeds and any other loose debris.

Table 13. Stepwise regression results for bioavailable fractions and soil characteristics.

Metal	Fraction	Dependent variables retained[1] (p value [%])	R^2
Lead	Water extractable	too many sites BDL	
	Exchangeable	pH (8.4), total Pb (3.2)	0.763
	Bioavailable	pH (6.6), total Pb (3.0)	0.777
Zinc	Water extractable	clay content (1.6), organic matter content (4.1), total Zn (0.0)	0.792
	Exchangeable	total Zn (0.1)	0.450
	Bioavailable	total Zn (0.0)	0.469
Arsenic		too many sites with large influence to run reliable stepwise regression	

1. Backward stepwise regression was run with tolerance of 0.001, probability to enter and be removed of 0.15, and no variables were forced in.

Most regulatory guidelines are based on the dose-rate of specific radiation types (α, β, γ). Measuring these various specific radiation types was beyond the scope of this pilot project but a comparison of the total radioactivity for our study area with that for other areas elsewhere in the world shows that the radioactivity of the study area is at common levels (Table 14) (Sarida et al., 2005; Al-Jundi et al., 2003; Malanca et al., 1996). The highest gross activity measured was 56 CPM, the highest dosage measured was 19 μR/hr. These values are of the same magnitude as background levels found elsewhere (Baranwal et al., 2006; Erees et al., 2006; USEPA, 2006; Ramli, 1997).

Table 14. Descriptive statistics for radioactivity of surface soils.

	Field measurements		Calculations	
	Dose rate [mR/hr]	Counts [cpm]	Disintegrations [dpm]	Annual dose rate [mSv/yr]
Mean	0.011	35	43.75	0.9636
Minimum	0.005	16	20	0.438
Maximum	0.019	56	70	1.6644
Standard deviation	0.008	9		

7. Conclusions

This project was the first to survey the trace metal pollution of surface soils in the two-county area. It focused on surface soils in public places, where many people have most contact with soil materials. The project was inspired by the multitude of potential sources of pollution in the area and findings by other PERCH tasks that some elements of the environment have elevated levels of pollution. Results of the project show that dioxin/furan TEQ, PAH TEQ, and trace metal concentrations are highest in the Palafox Industrial Corridor. This pollution is spatially limited, suggesting that the sources are local and point to the impact of the local (former) industry on the environment. Dioxin/furan TEQs do not exceed the EPA screening level but do exceed the FL DEP RSCTL at about half of the sampled locations in the industrial corridor, and are significantly higher there than in other parts of the study area. These observations indicate that at some of the sampled locations the dioxin/furan content of the surface soils may be of environmental health concern. The PAH TEQs also exceed the FL DEP RSCTL at some sites in the Palafox Industrial Corridor, indicating that further study of PAHs may also be warranted. The TEQs are not beyond what has been observed at some other moderately polluted locations elsewhere.

Arsenic exceeds the RSCTL throughout the study area in both urban and rural areas indicating that it may originate from a regional, rather than local, source. Lead and Zn have somewhat elevated concentrations but remain below the RSCTL. These two trace metals have higher concentrations in urban than rural areas, which can be explained by their known association with traffic activities. Chromium and nickel are higher in rural than urban areas because they derive mainly from the parent material of the soils, which is naturally richer in trace metals in the northern rural parts of the study area. Evaluation of soil pollution indexes that take into account background concentrations and/or standardization parameters shows that most trace metals are "polluted" at 20% to 30% of the sites, implying that these sites have been significantly impacted by anthropogenic inputs. Lead and Zn have the most, but still modest number, of "strongly polluted" sites. Most of these sites are in the Palafox Industrial Corridor.

Because traffic has often been identified as a source of trace metal pollution in soils we evaluated trace metal levels near major roads as raw concentrations, standardized values, and index values. Results show that all trace metals except for Hg are elevated close to a road, illustrating the influence of traffic on trace metal concentrations. This influence disappears at distances of more than 20 m from the road. At greater distances only Pb and Zn seem to be affected by vehicular traffic. Few studies have examined the influence of proximity to a road on As concentrations but this study shows that at distances of less than 20 m from a road As is elevated. In spite of the elevated trace metal concentrations near roads, As remains the only metal to exceed its RSCTL near roads. The presence of CCA-treated wood structures is also a potential source of local soil pollution. In the study area, we identified few structures of CCA treated wood, probably because of the voluntary phase out of its production for use in play structures. At the five structures that were identified soils are obviously affected by the Cr, Cu and As, as evidenced by concentrations that are substantially higher than at non-CCA locations. The high concentrations can be expected to decrease rapidly with distance from the structures, based on reports in the literature. Given the high porosity and quartz rich nature of the soils at the structures some leaching into the groundwater is also to be expected. Arsenic is the only metal to exceed its RSCTL at these structures, roughly by an order of magnitude. In principle this should be reason for further study but the possibility of negative impacts on people may be limited because of the very limited spatial extent of the pollution. Nevertheless, it seems best to avoid contact with soils in very close proximity to these CCA treated structures until further assessment is carried out.

Even though most regulatory guidelines are based on total trace metal contents, speciation of trace metals allows for a better evaluation of the potential for transfer of a trace metal to other parts of the environment. The two most loosely bound fractions of the metals, often considered to be the bioavailable fractions, have relatively low proportions in the study area. Arsenic, which exceeds it RSCTL at some sites, and Zn, which also has relatively high concentrations, have the largest bioavailable fractions (16.15% and 24.03% respectively). This implies that because of the magnitude of their concentrations and their availability these two trace metals have the greatest potential to negatively affect other parts of the environment. Evaluating the radioactivity was a secondary objective of this task and results of our pilot study indicate that the radioactivity of the soils in the study area is near background levels and does not exceed levels reported in the literature for unpolluted locations.

In summary, most trace metals in the soils we examined have a clear anthropogenic component but rarely exceed regulatory guidelines. Arsenic seems to deserve most attention in follow-up studies, but as shown by this and other studies, may be elevated because of naturally high background concentrations. Dioxin/furan and PAH TEQs exceed the FL DEP RSCTL in the Palafox Industrial Corridor and may also warrant further consideration.

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APPENDIX 1: FIGURES

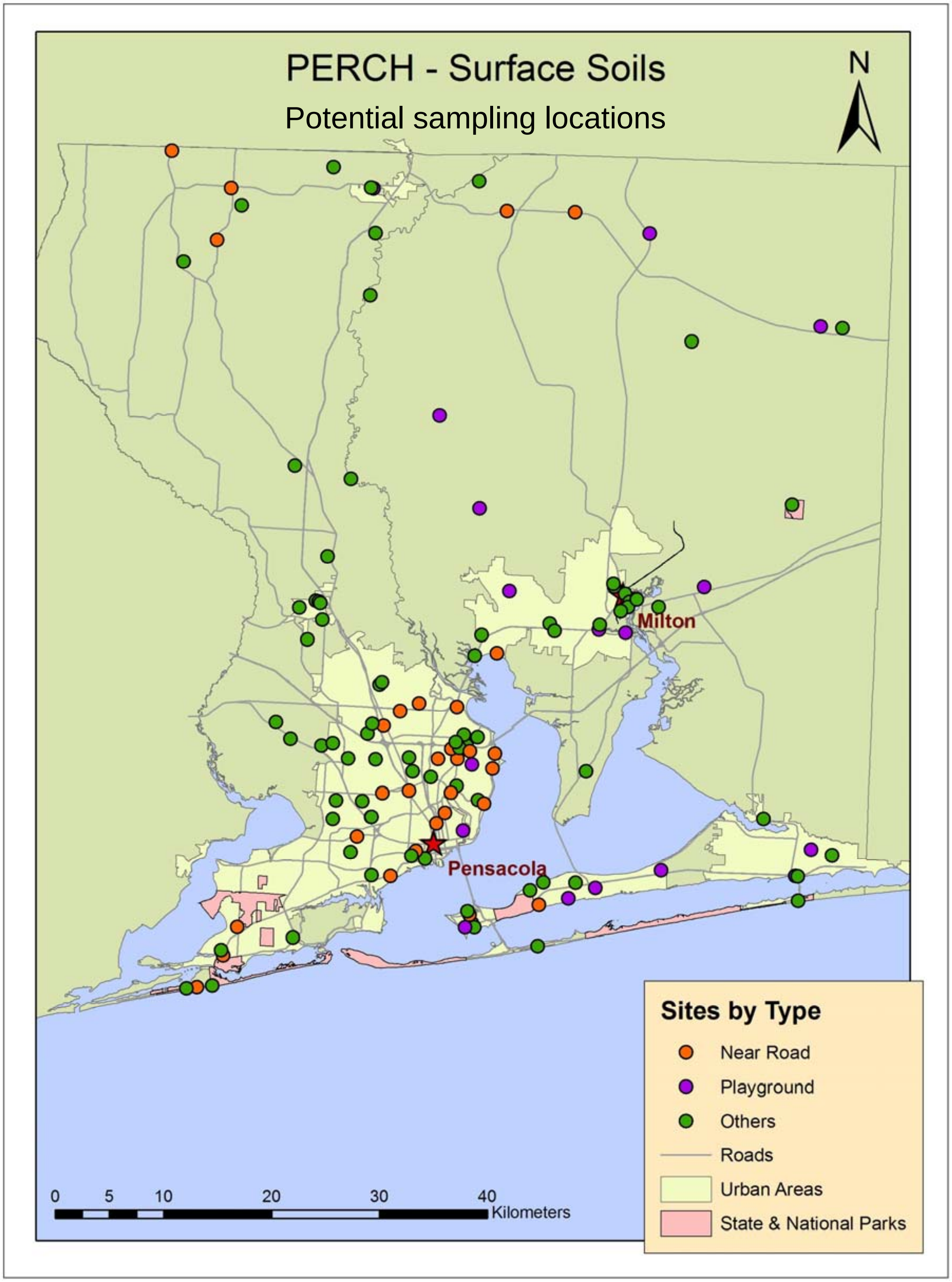

Figure 1. Location of potential sampling sites.

Figure 2. Example of public park where soil sample was collected.

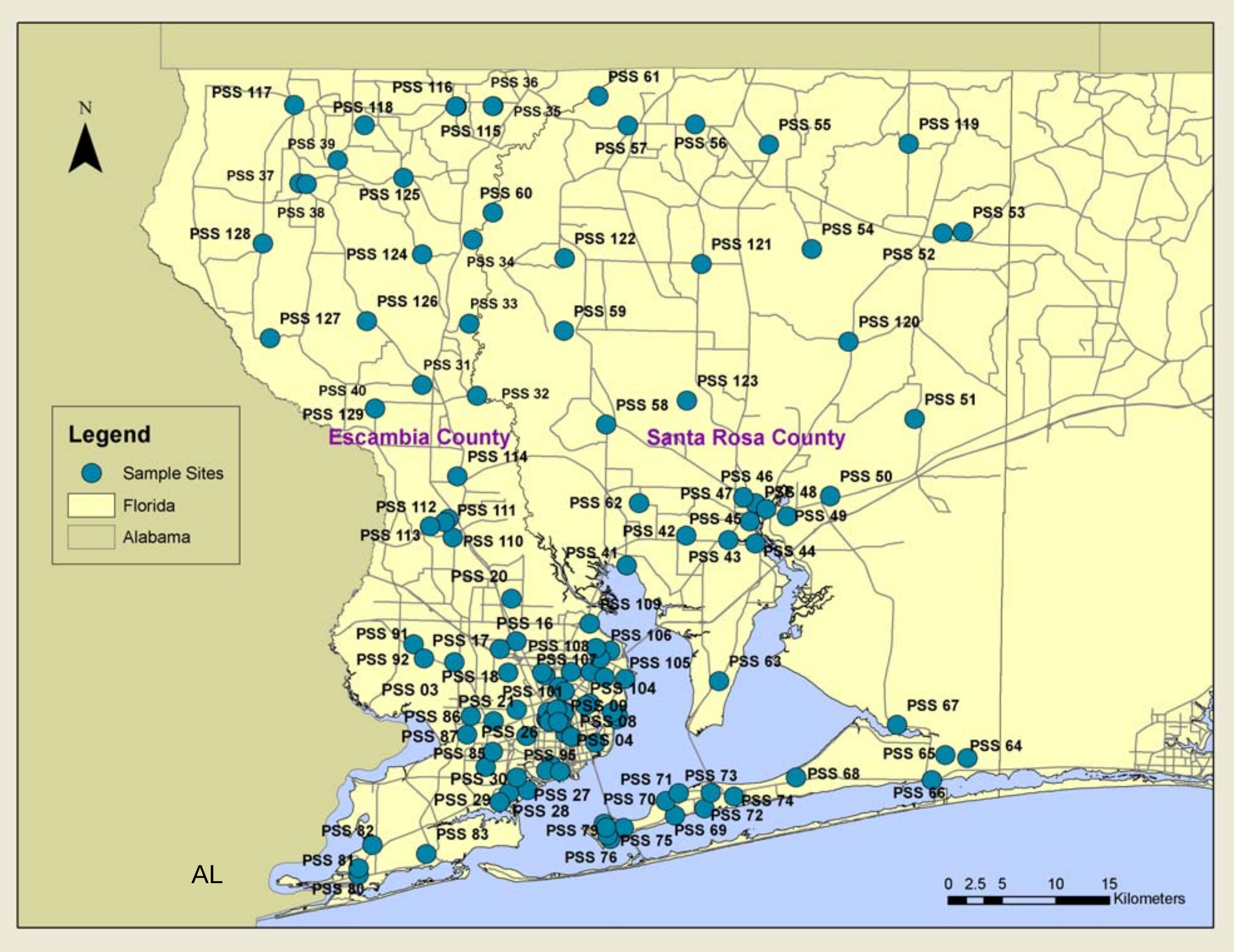

Figure 3. Sample IDs for all samples.

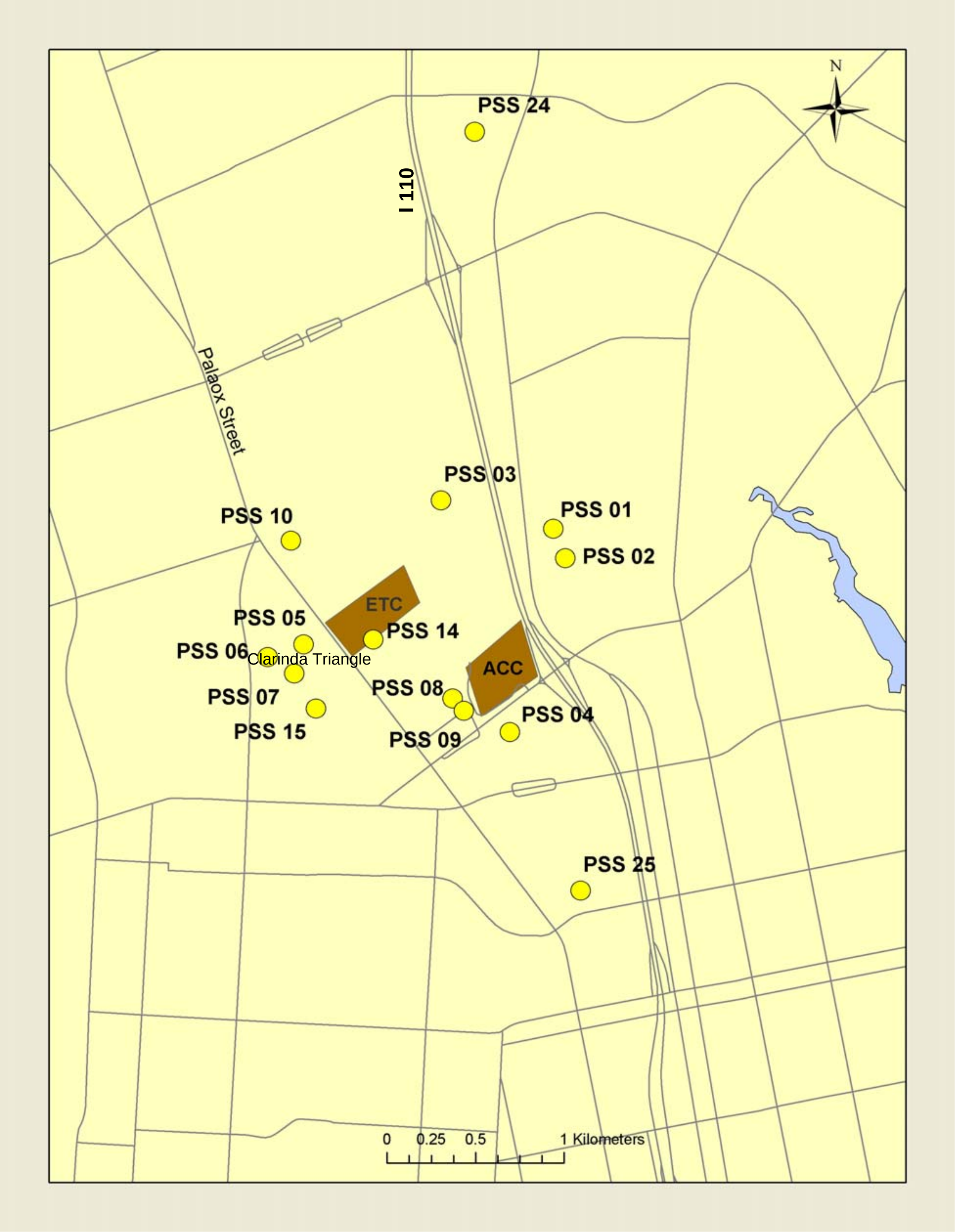

Figure 4. Sample IDs in Palafox industrial corridor. ETC marks location of Escambia Treating Company site, ACC marks location of Agrico Chemical Company site.

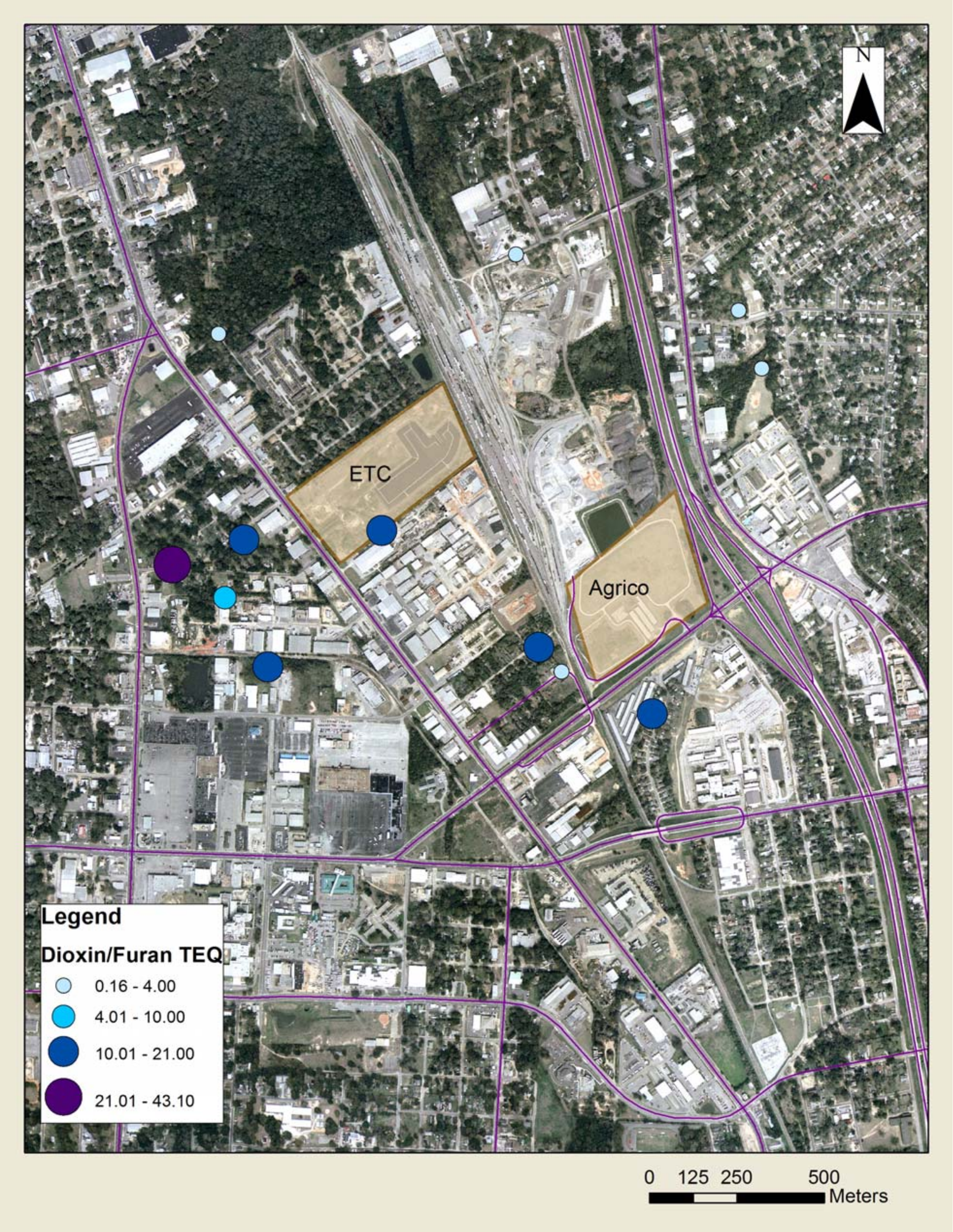

Figure 5. Dioxin/furan TEQs [ng/kg] in Palafox industrial corridor.

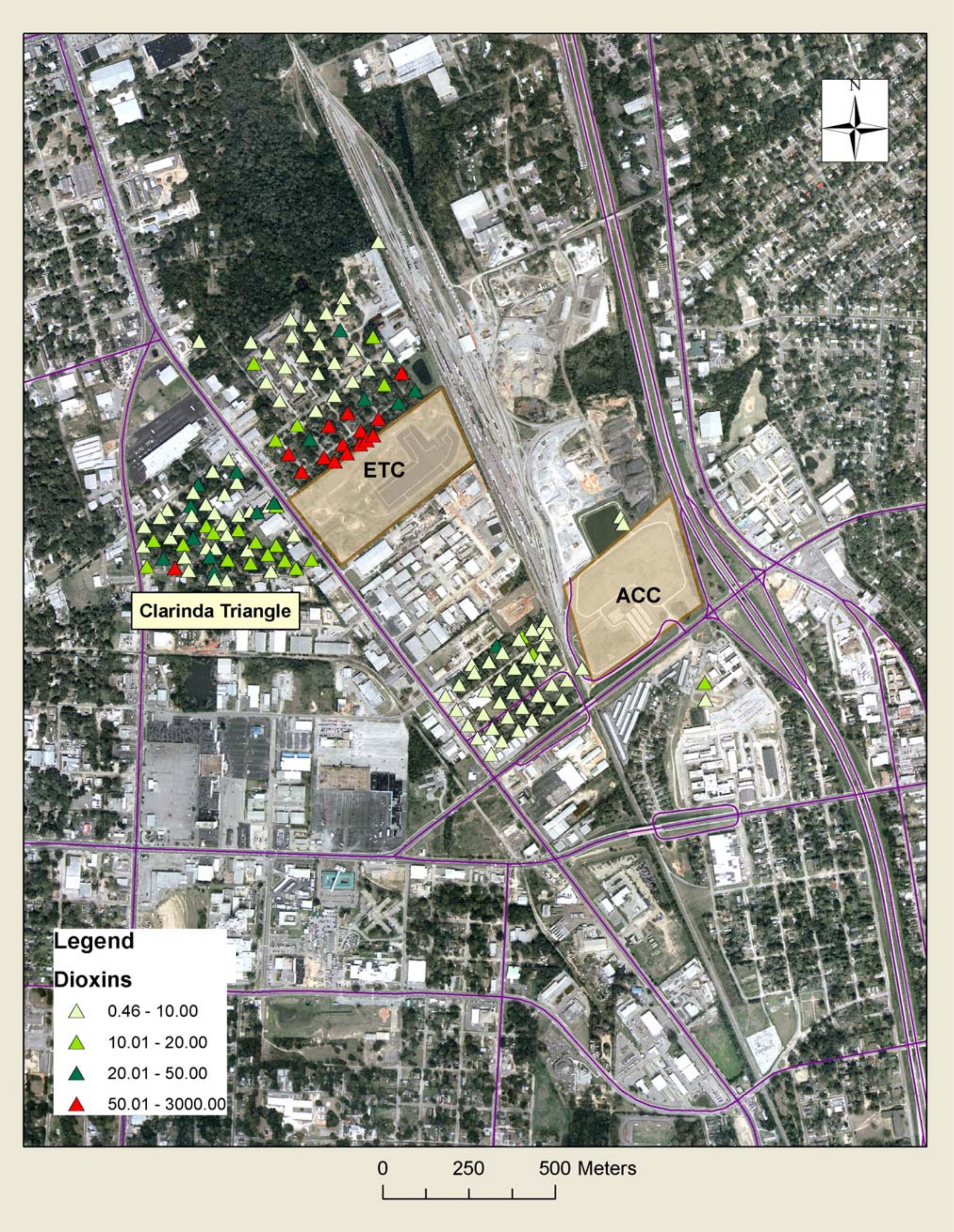

Figure 6. Dioxin/furan TEQs [ng/kg] in Palafox industrial corridor from previous studies.

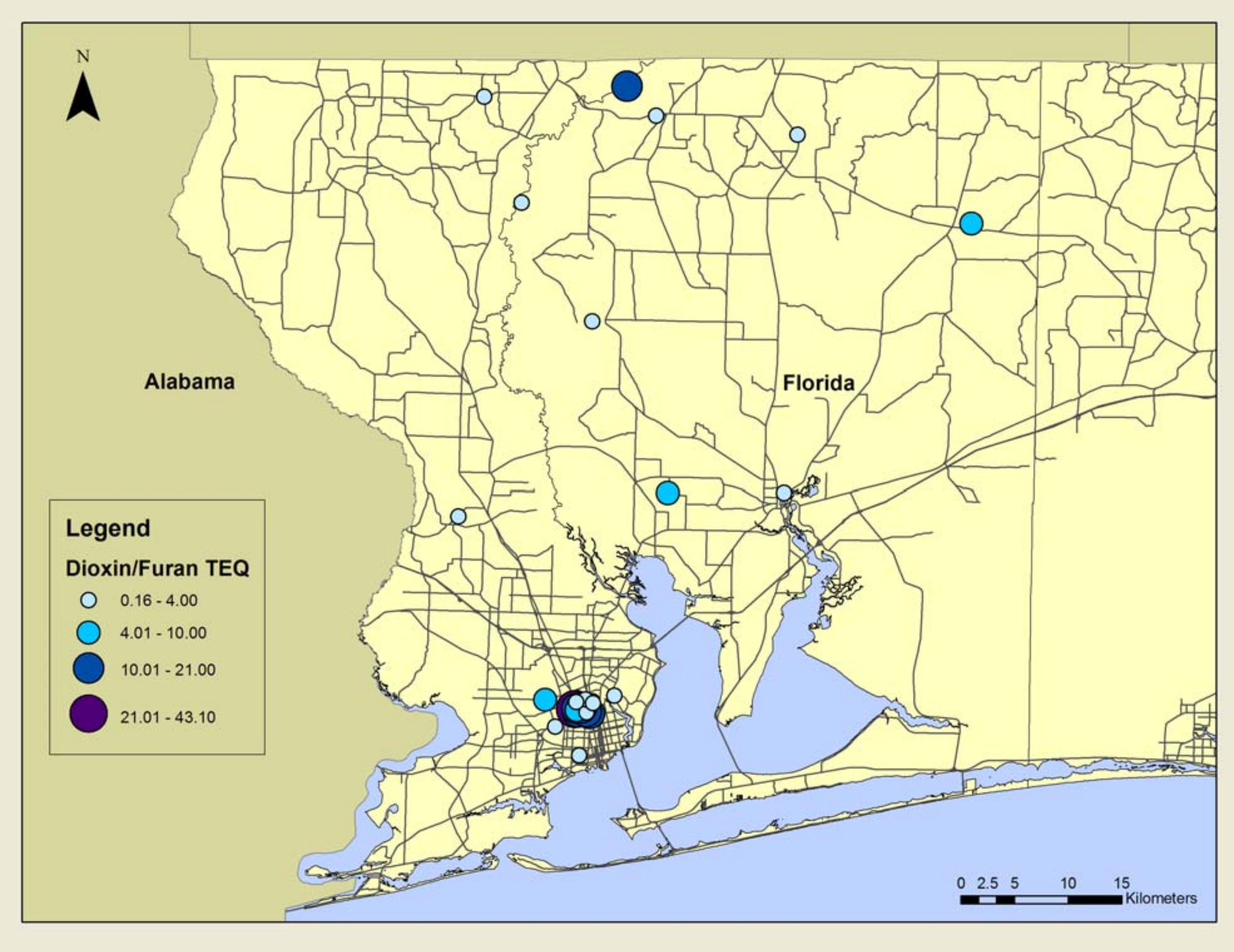

Figure 7. Dioxin/furan TEQs [ng/kg] in study area.

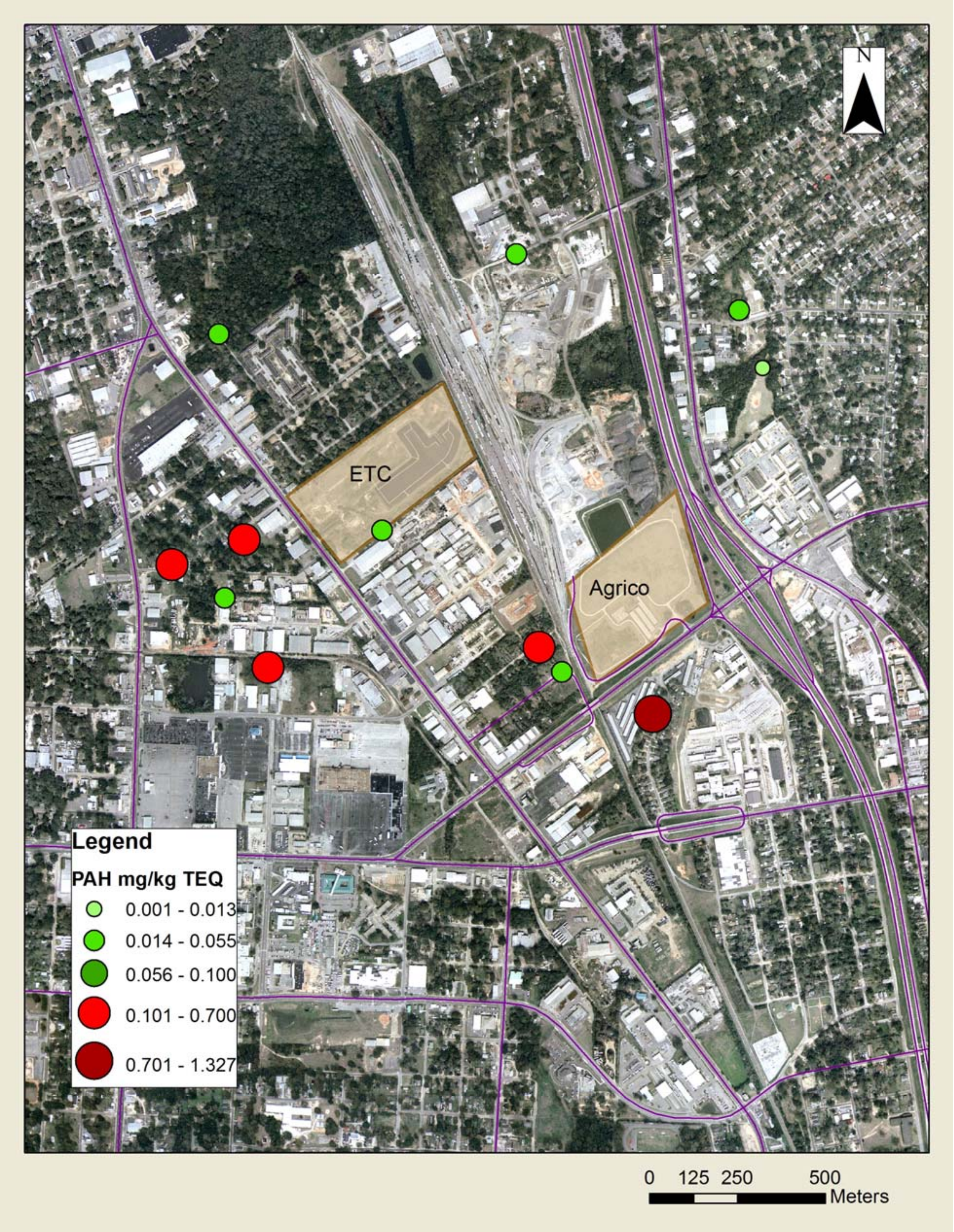

Figure 8. Benzo(a)pyrene equivalents [mg/kg] in Palafox industrial corridor.

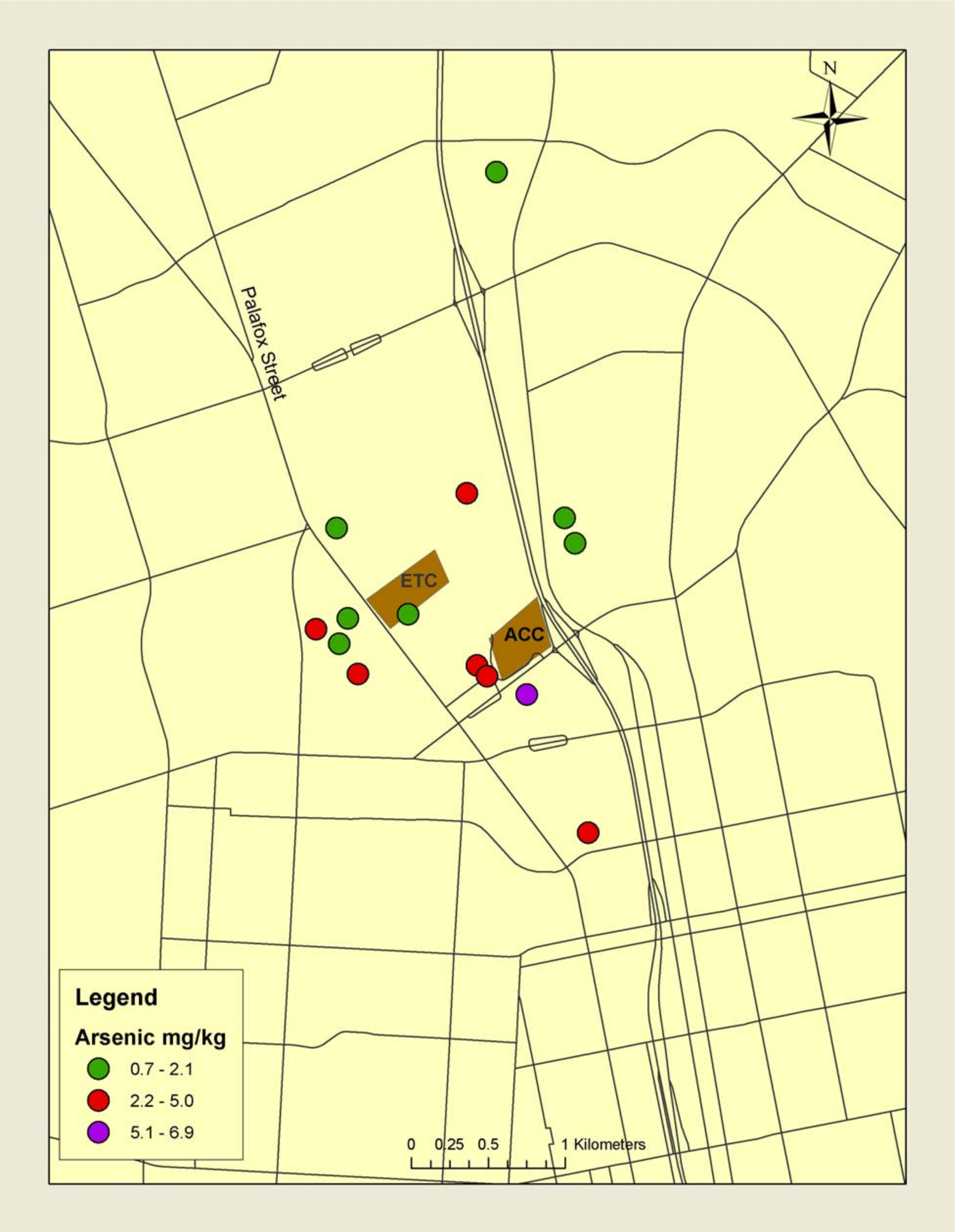

Figure 9. Arsenic concentrations [mg/kg] in Palafox industrial corridor. Residential SCTL is 2.1 mg/kg.

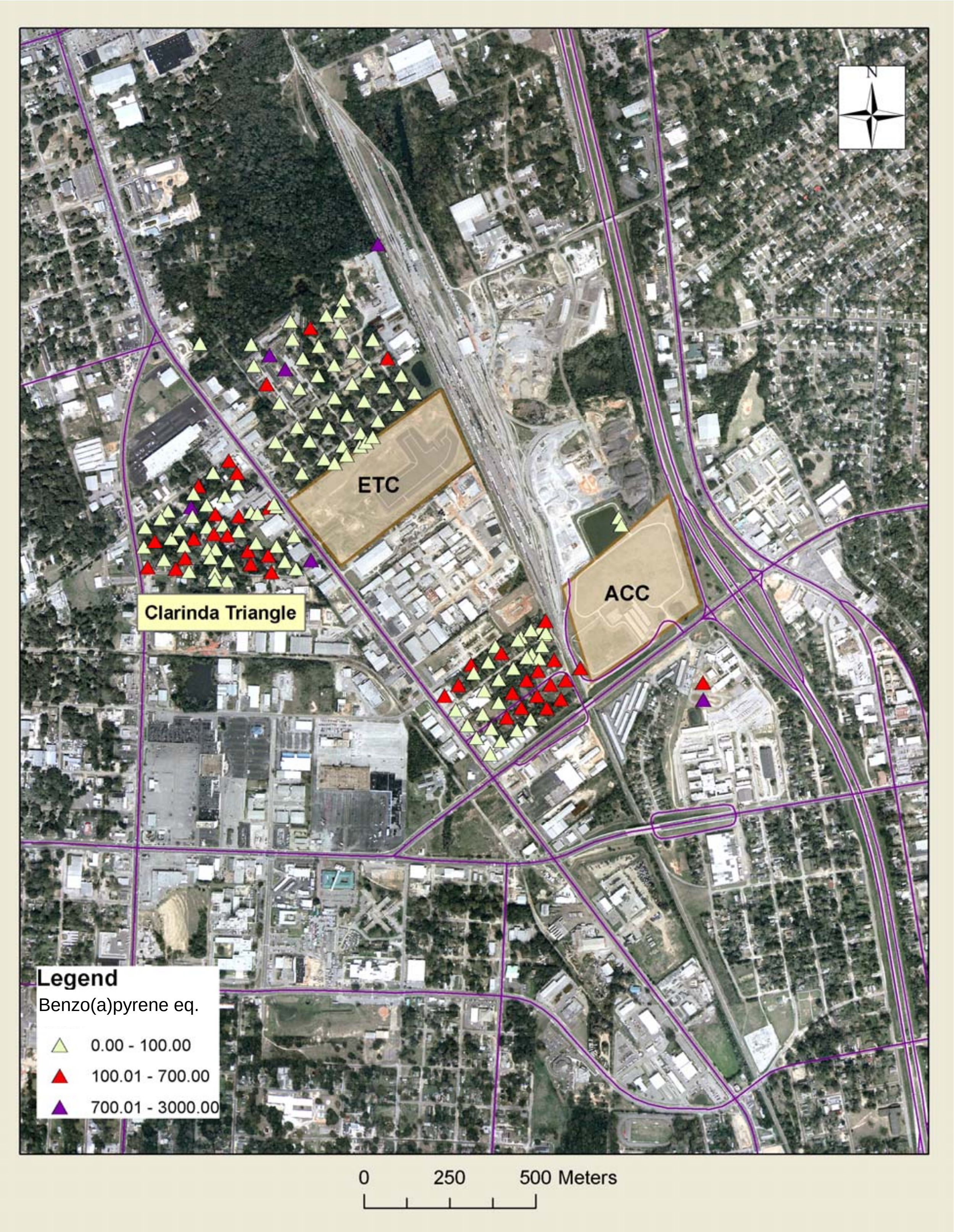

Figure 10. Benzo(a)pyrene equivalents [µg/kg] in Palafox industrial corridor from previous studies.

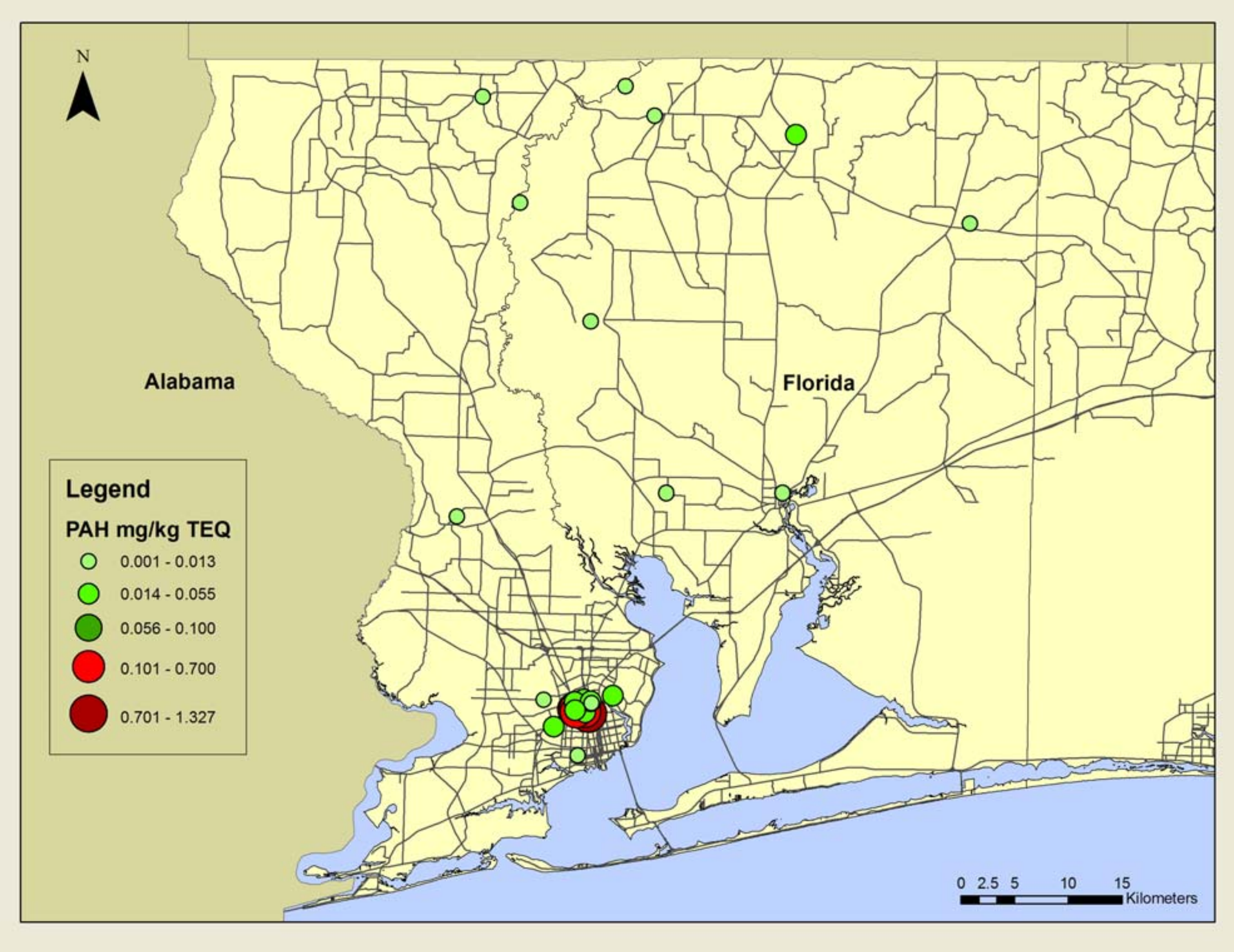

Figure 11. Benzo(a)pyrene equivalents [mg/kg] in study area.

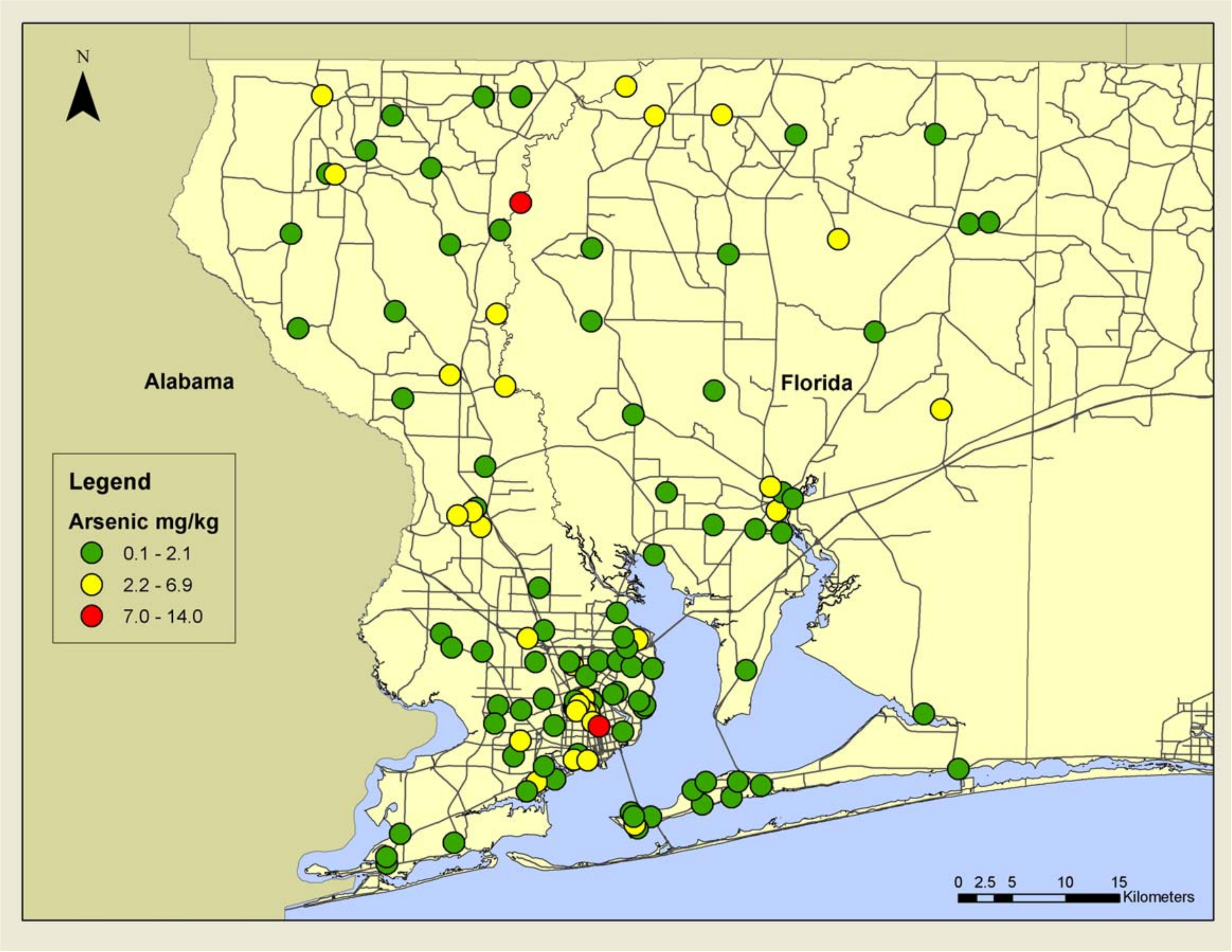

Figure 12. Arsenic concentrations [mg/kg] in surface soils. Residential SCTL is 2.1 mg/kg.

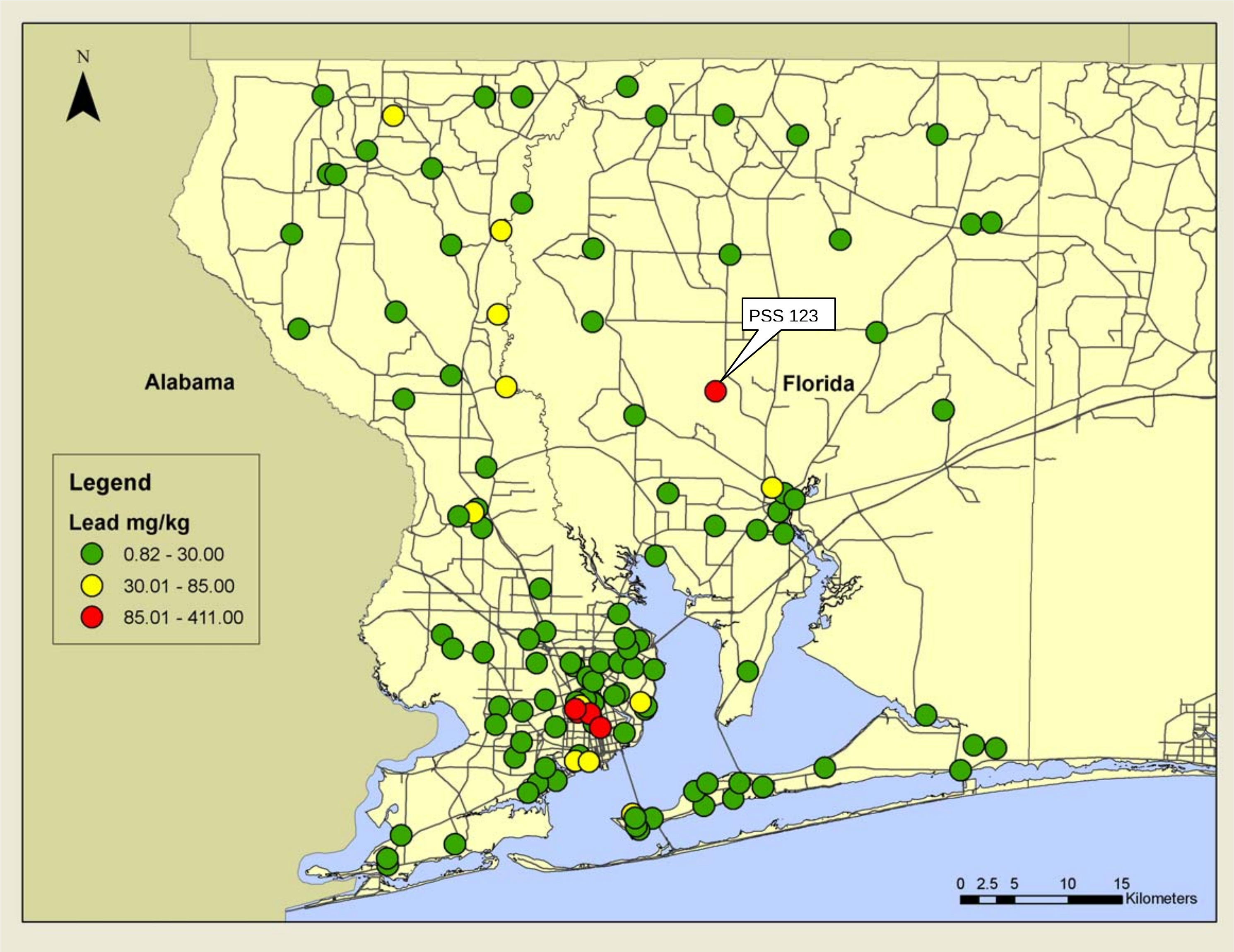

Figure 13. Lead concentrations [mg/kg] in surface soils.

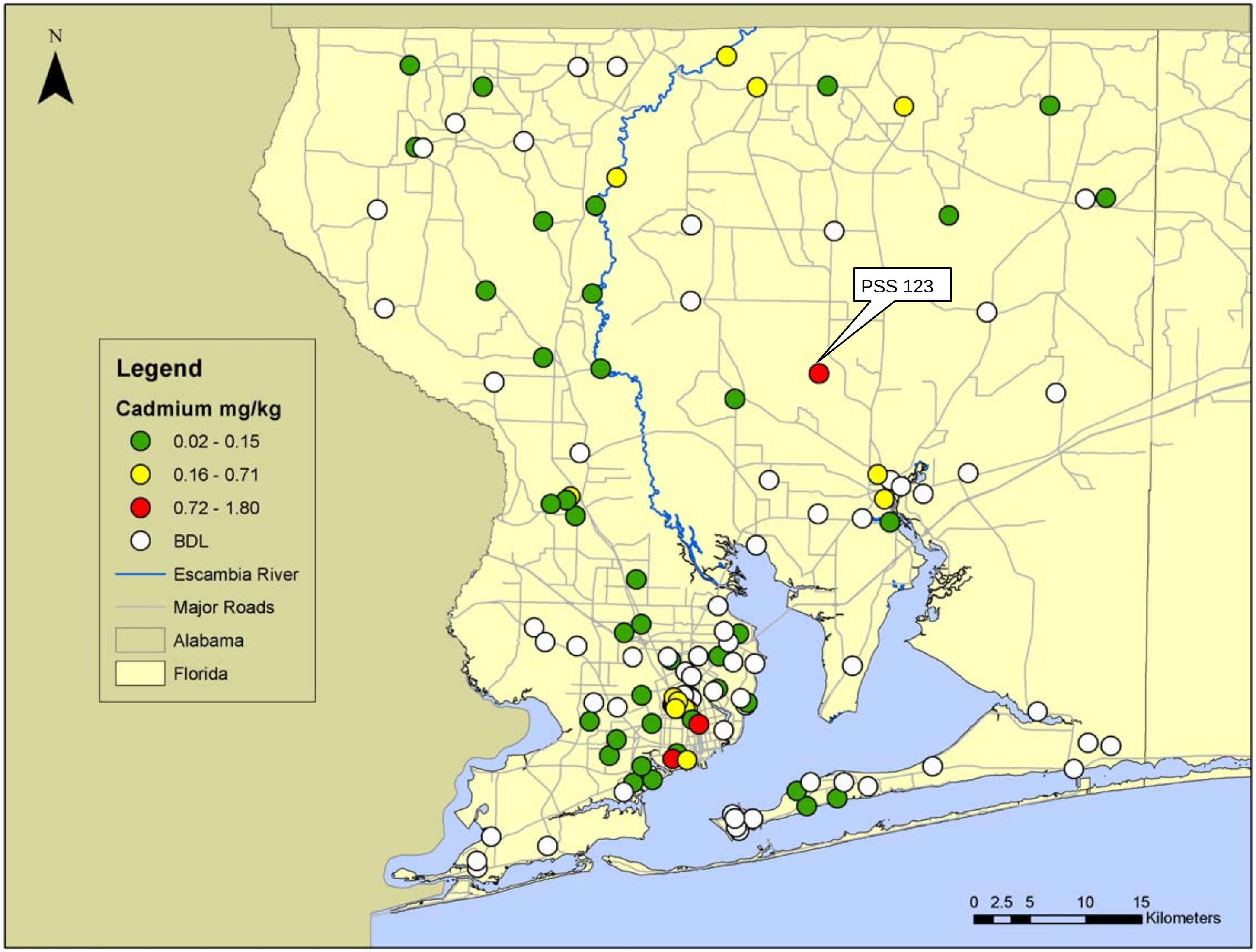

Figure 14. Cadmium concentrations [mg/kg] in surface soils.

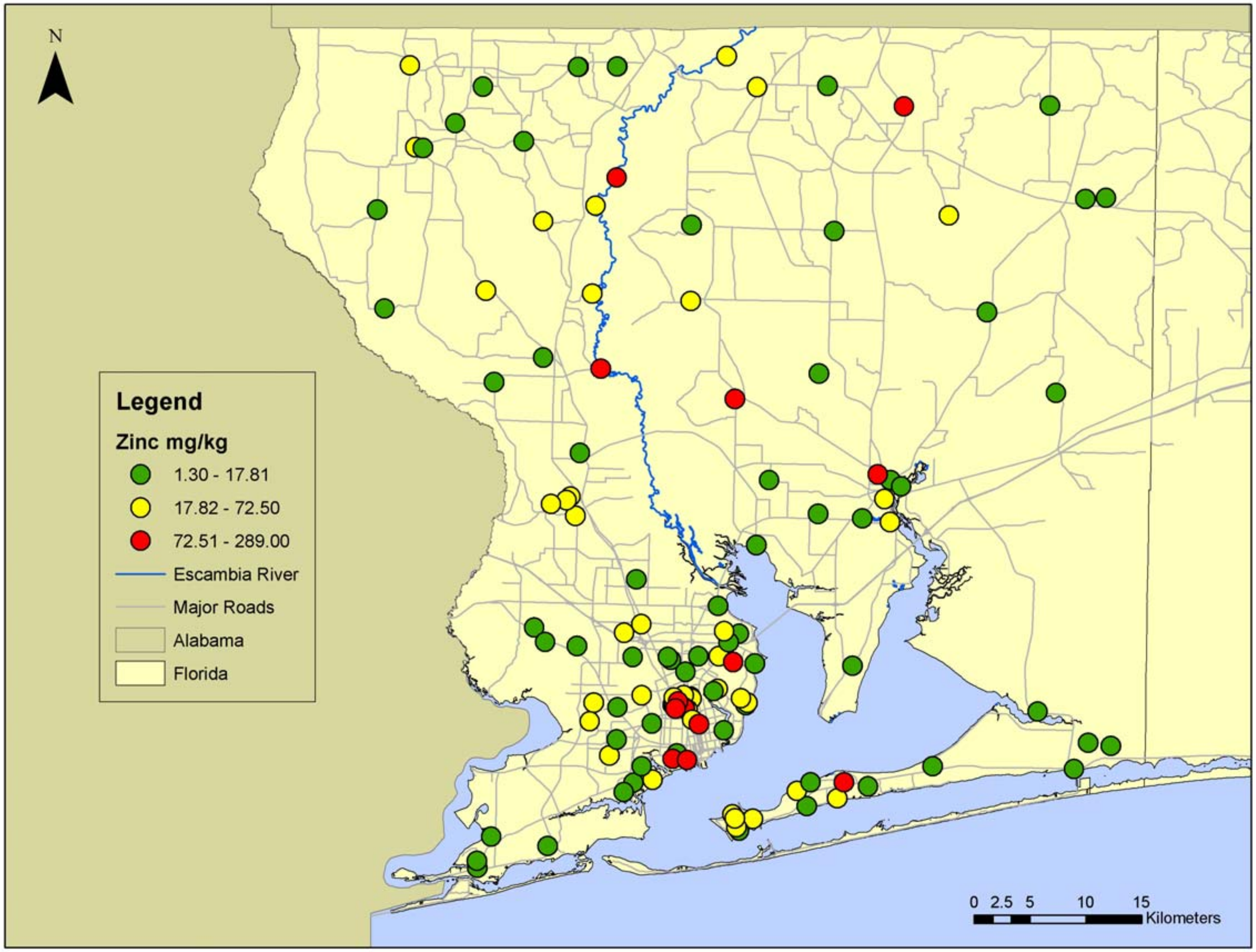

Figure 15. Zinc concentrations [mg/kg] in surface soils.

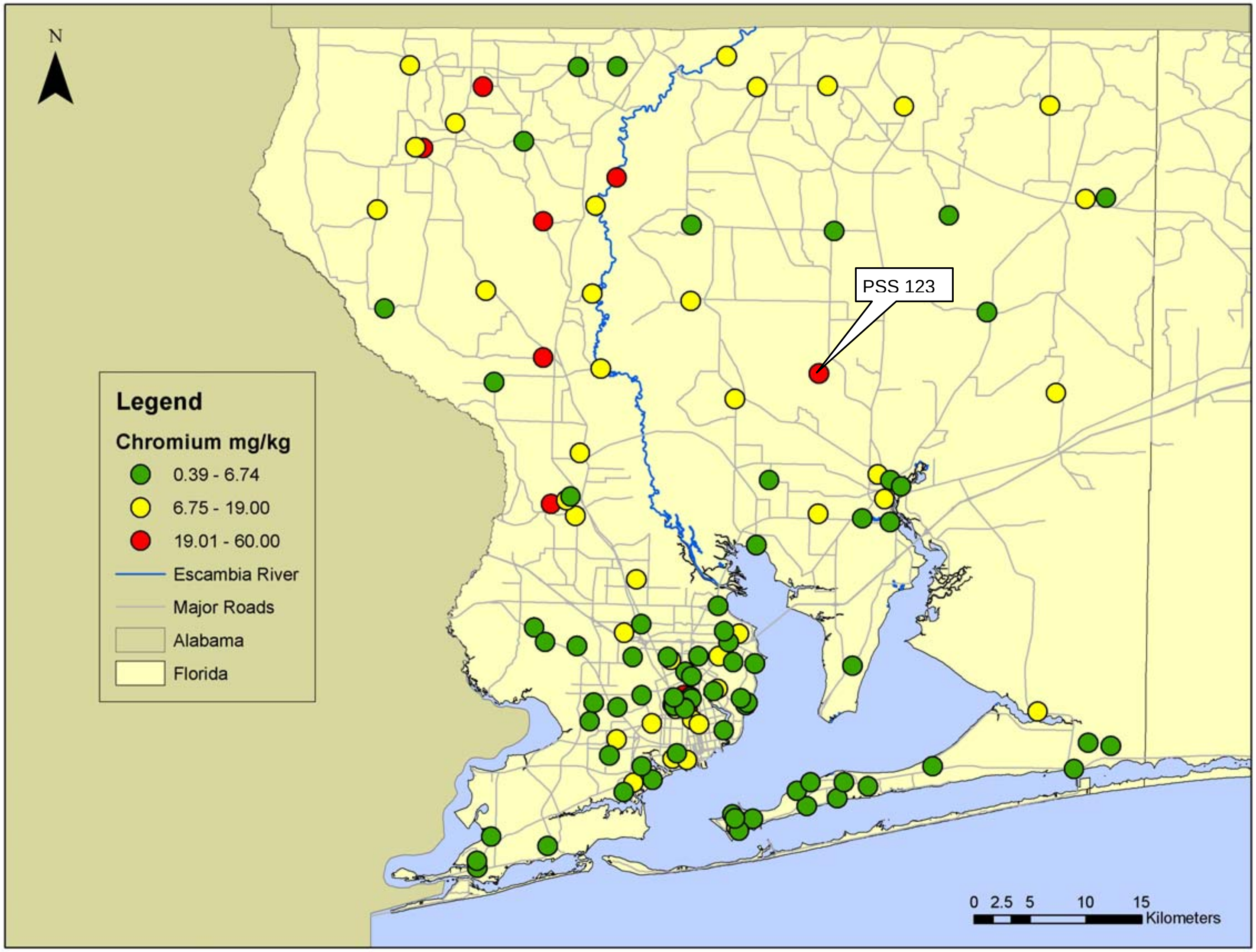

Figure 16. Chromium concentrations [mg/kg] in surface soils.

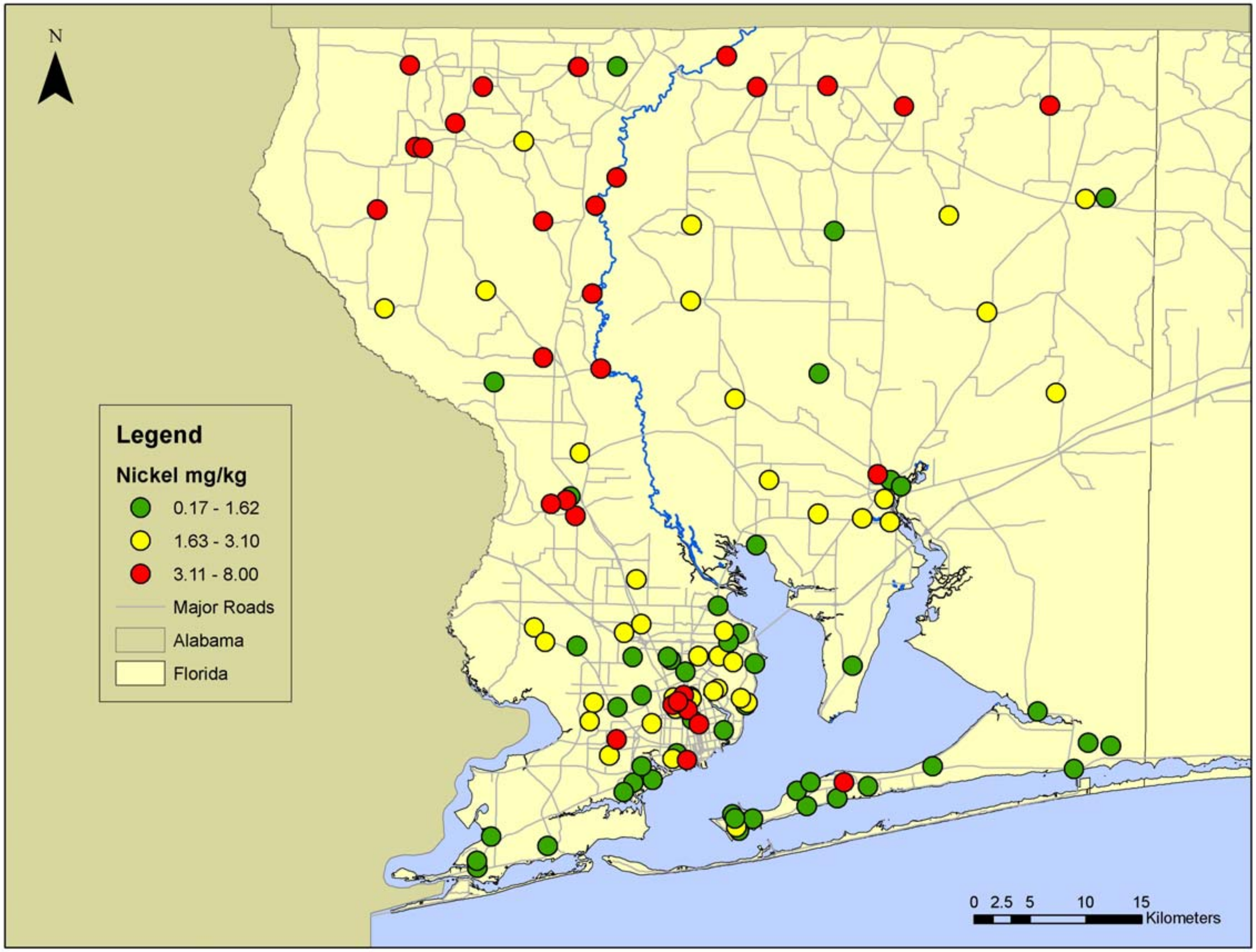

Figure 17. Nickel concentrations [mg/kg] in surface soils.

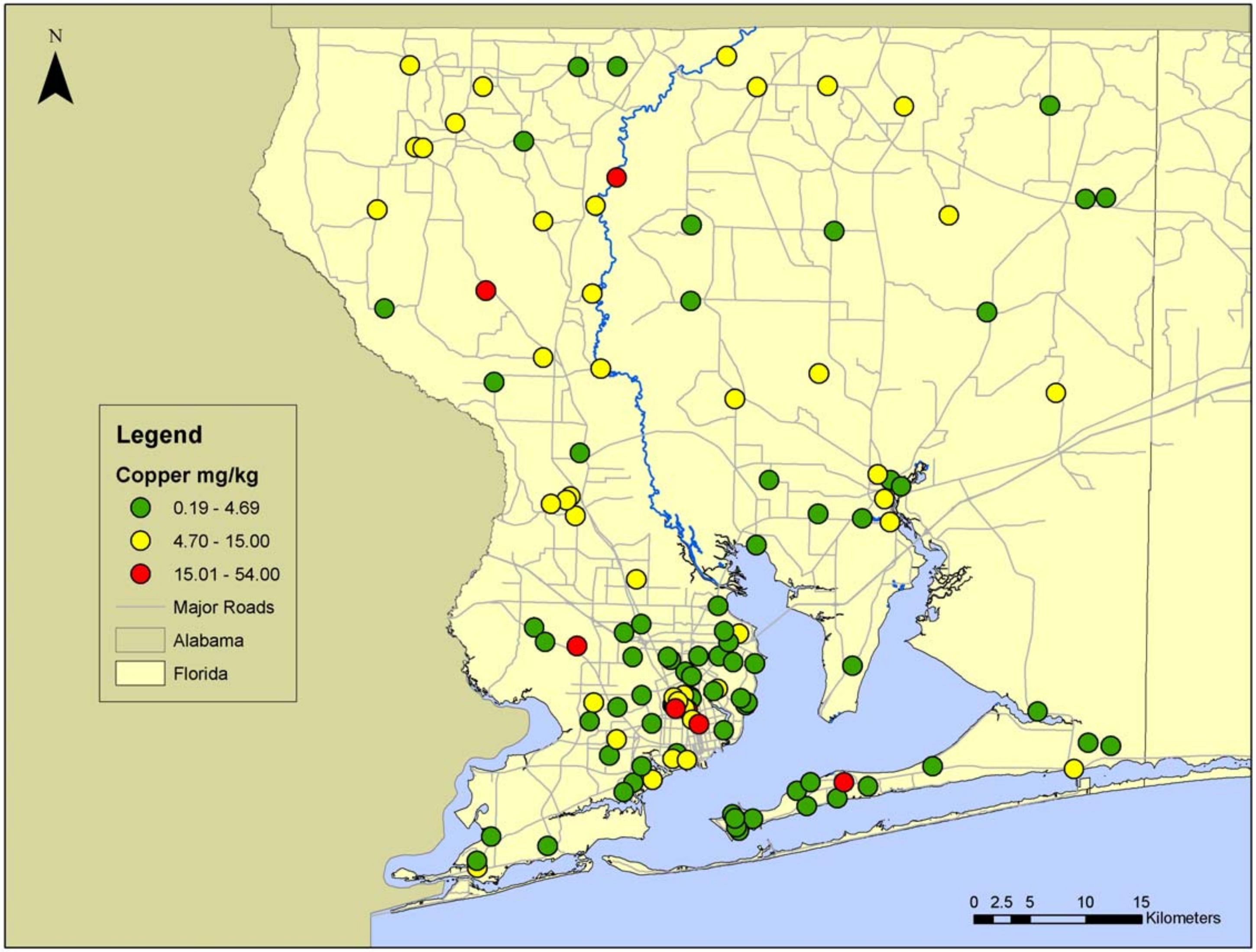

Figure 18. Copper concentrations [mg/kg] in surface soils.

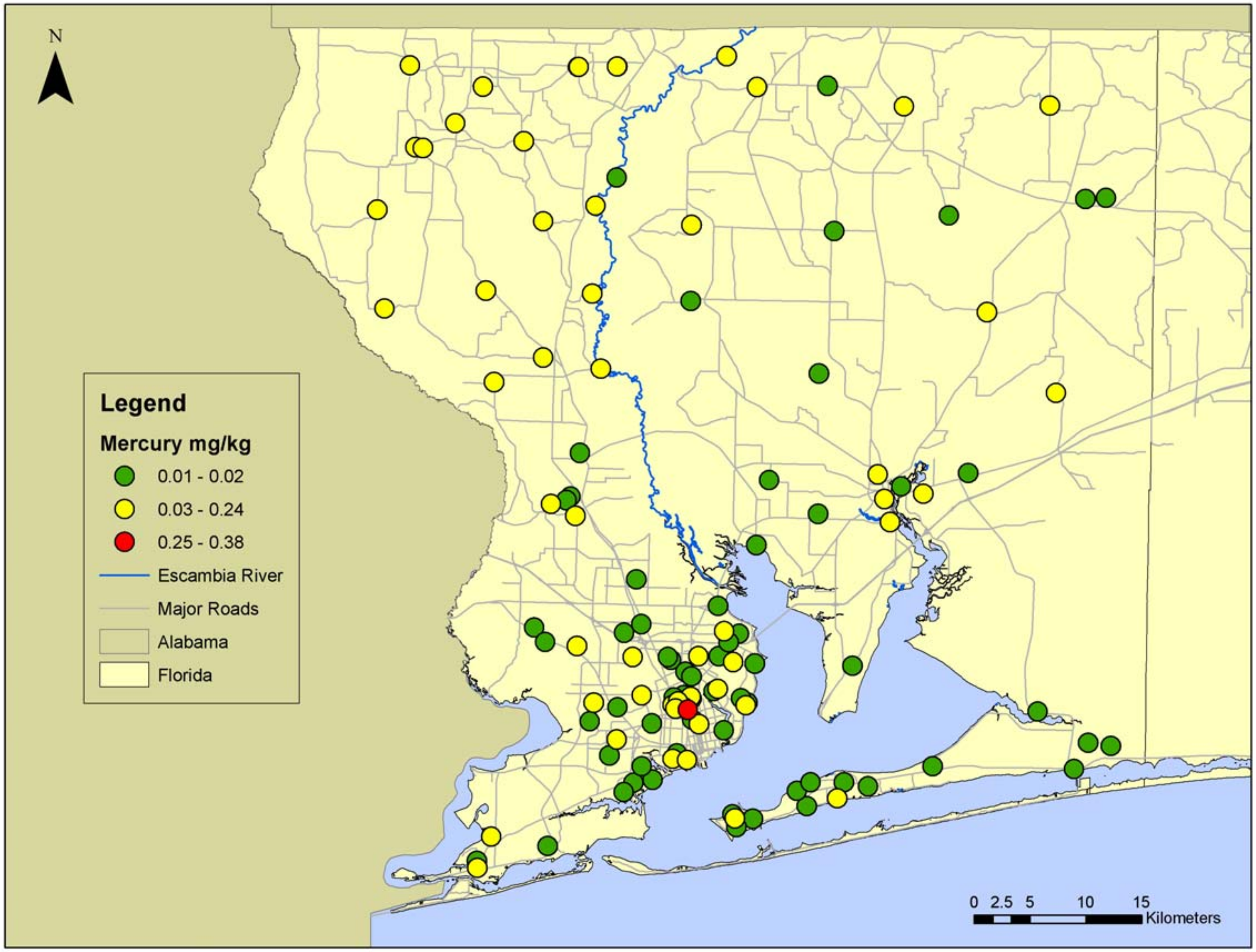

Figure 19. Mercury concentrations [mg/kg] in surface soils.

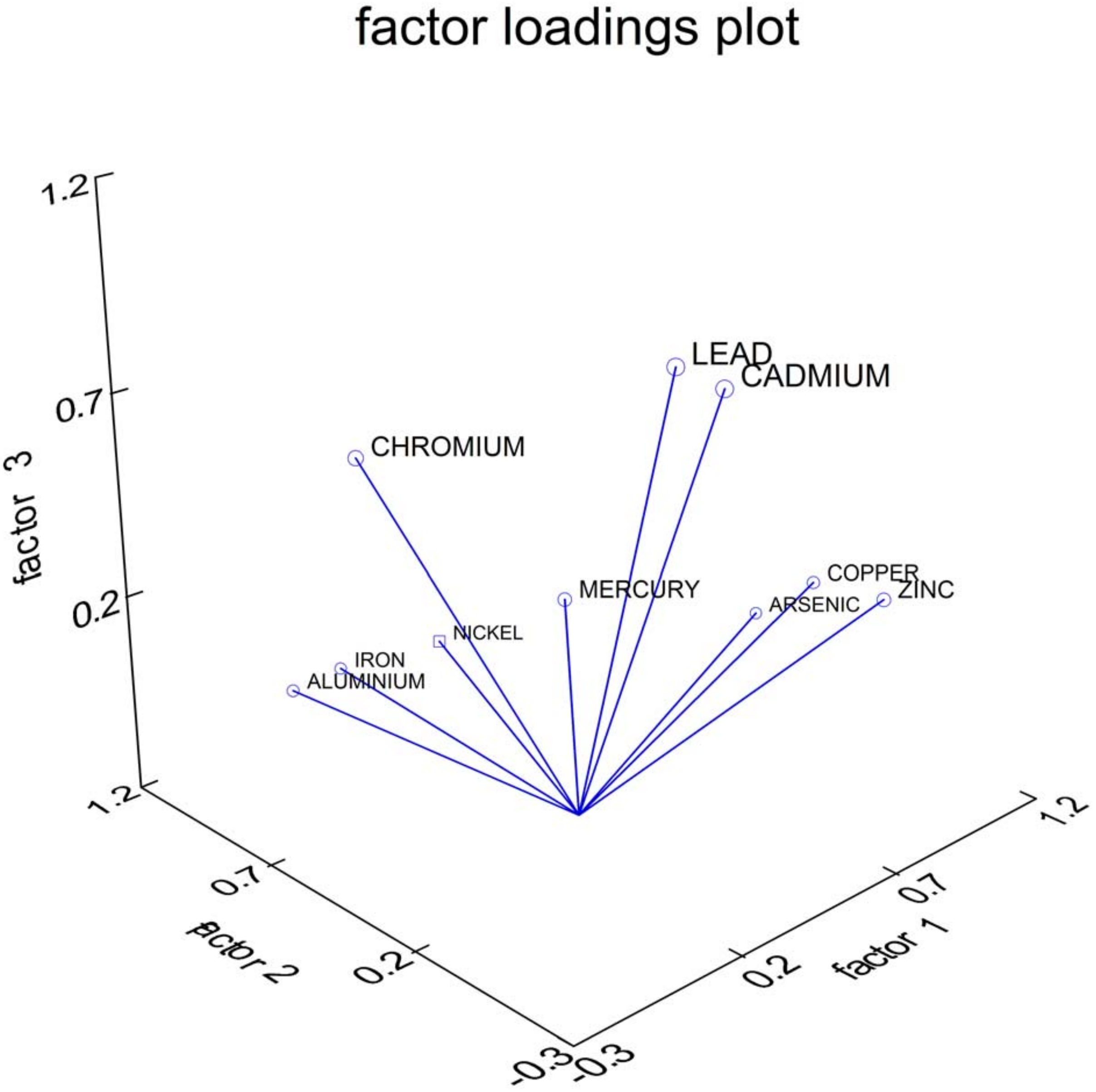

Figure 20. Factor loading plot for all metals. Metals plotting in the same part of the graph are assumed to be of common origin.

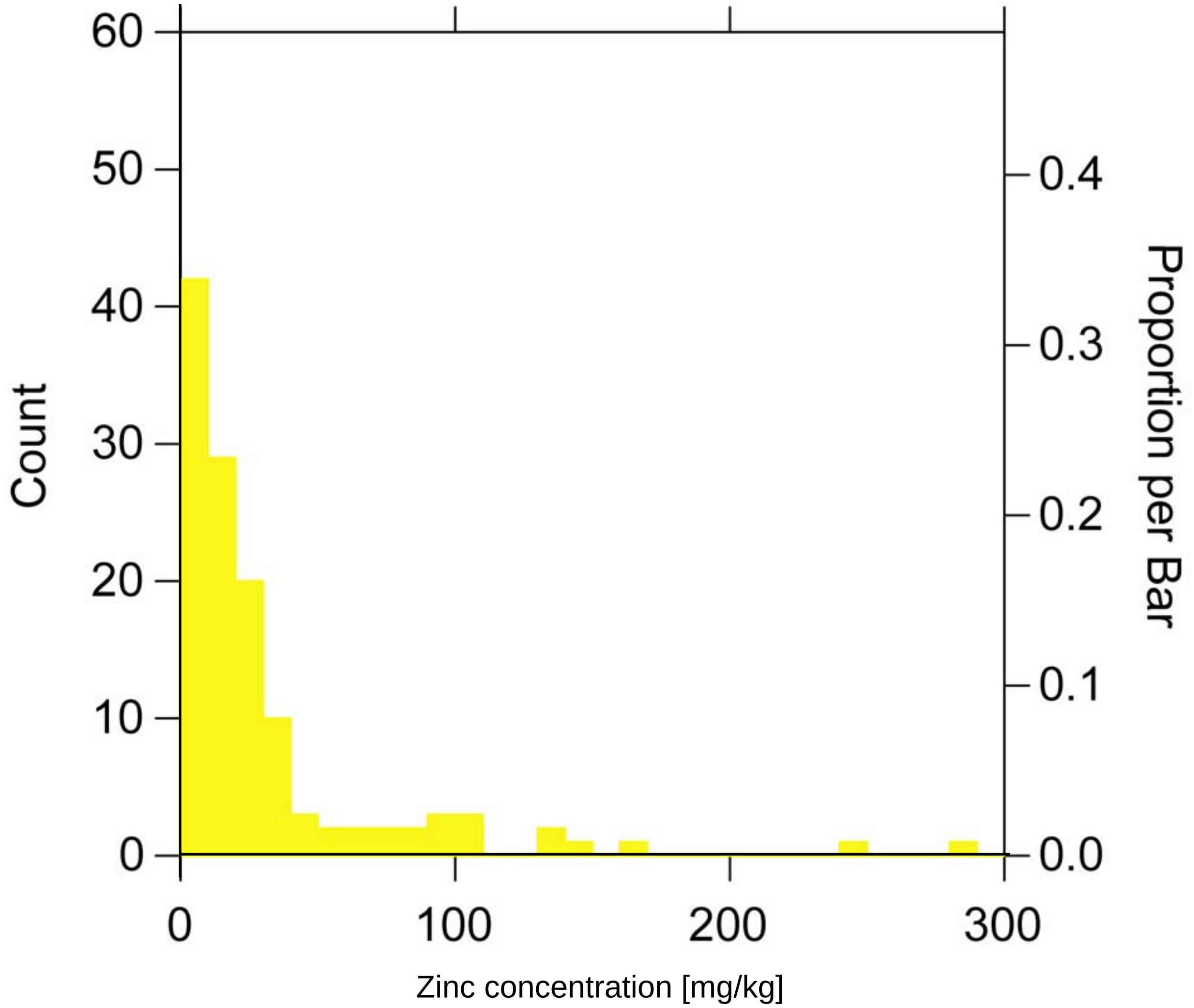

Figure 21. Histogram for Zn concentration. Histogram shows one population between 0 mg/kg and approximately 70 mg/kg, and a smaller and presumably polluted population above approximately 70 mg/kg.

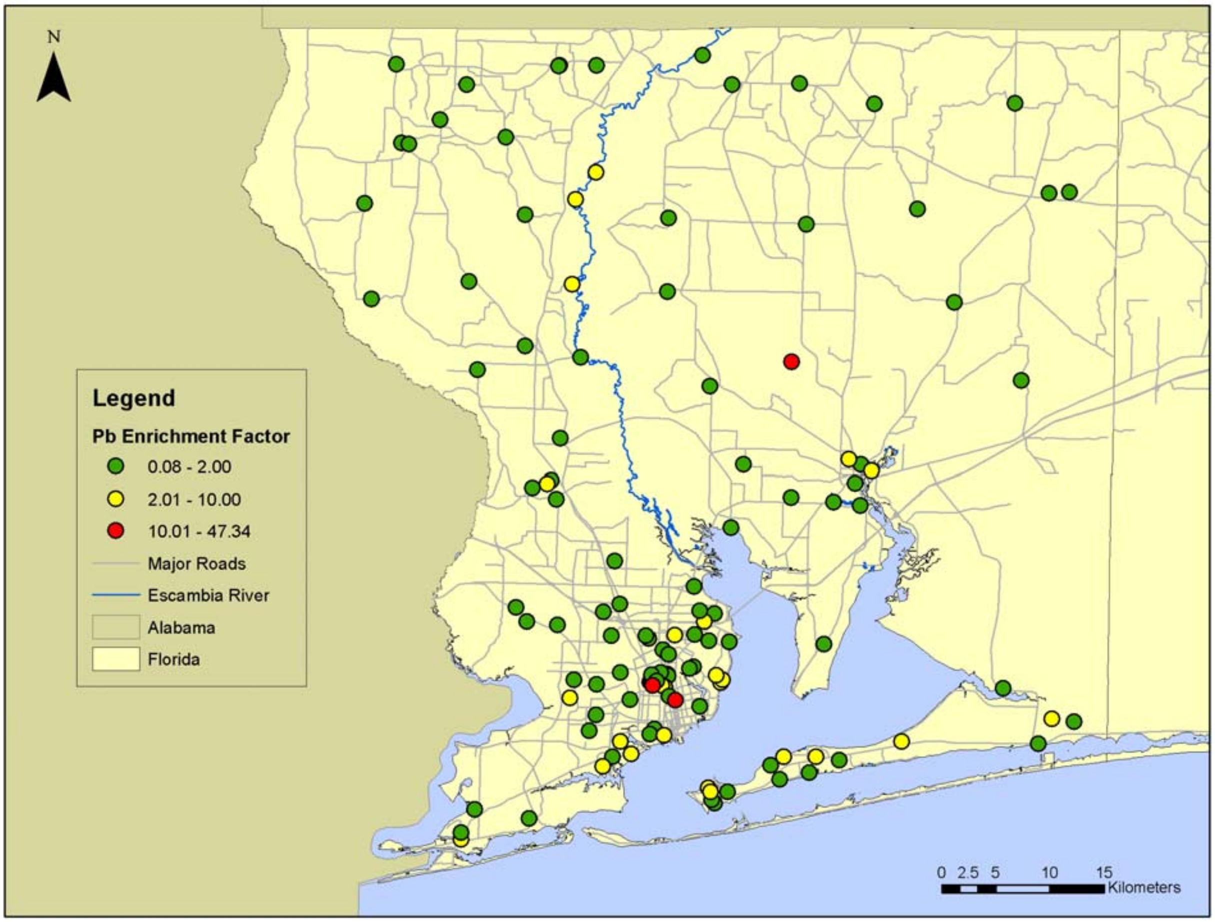

Figure 22. Enrichment factor for Pb. Two sites with EF > 10 in the Palafox industrial corridor are masked by other symbols.

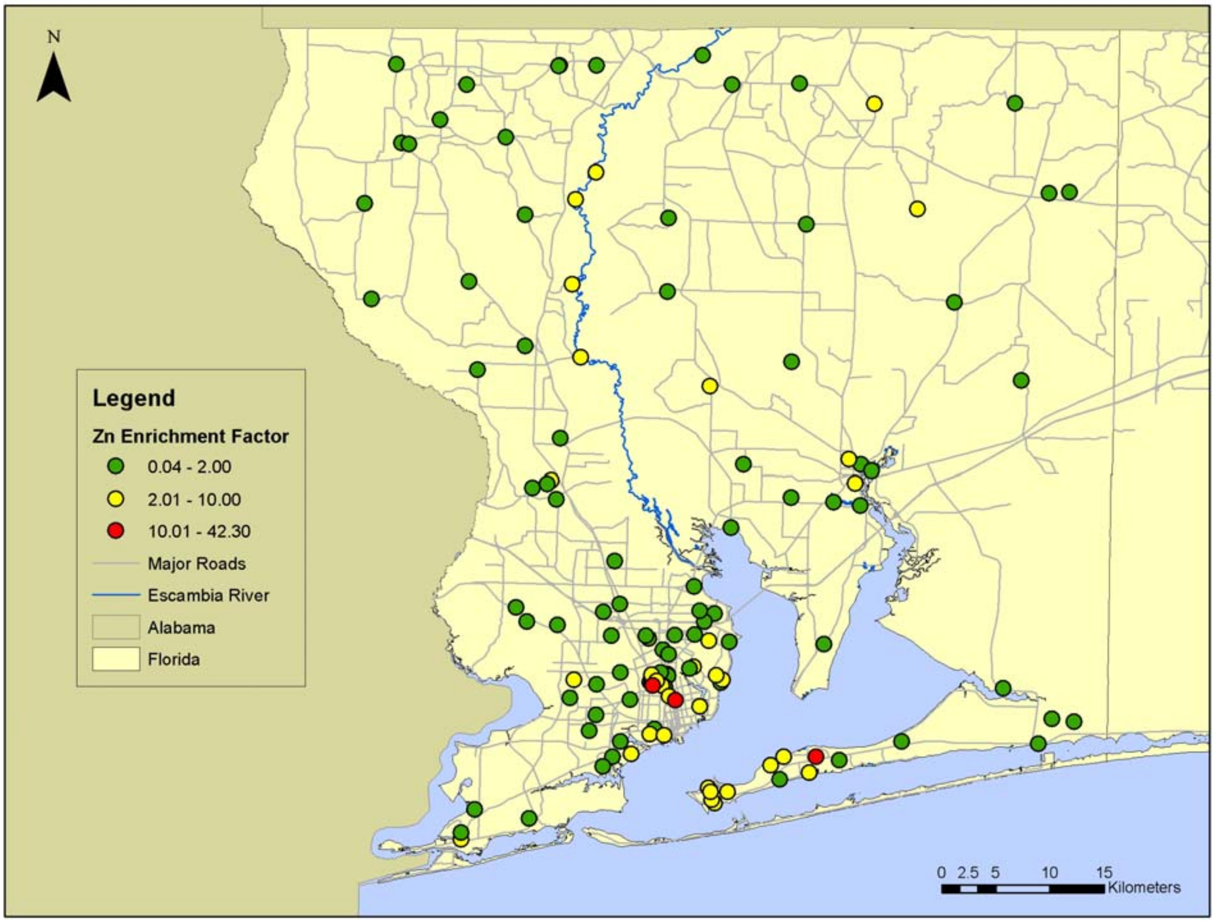

Figure 23. Enrichment factor for Zn. Two sites with EF > 10 in the Palafox industrial corridor are masked by other symbols.

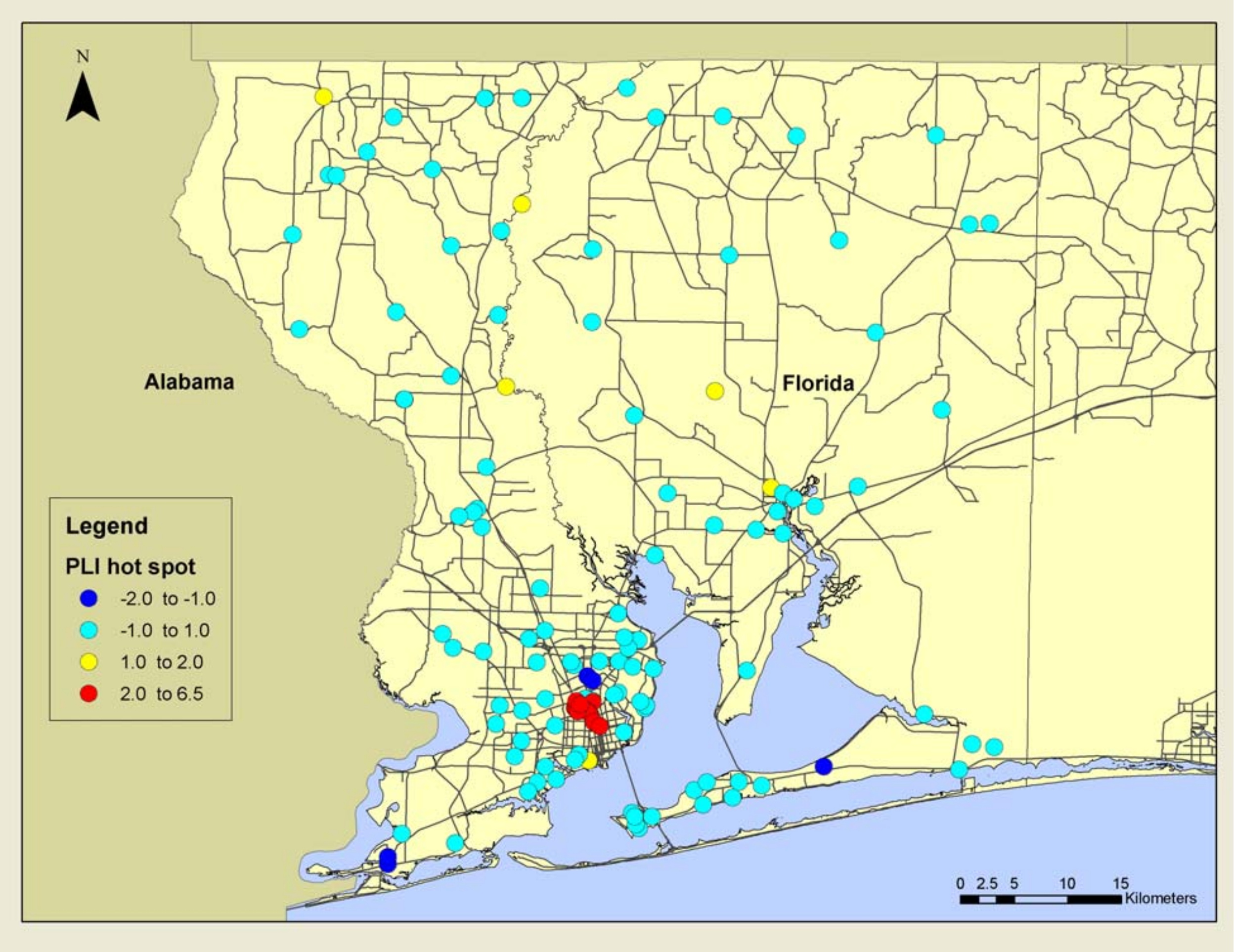

Figure 24. Z values from hot spot analysis for PLI index for trace metals. Red color marks cluster of points with PLI values higher in magnitude than can be expected from random chance.

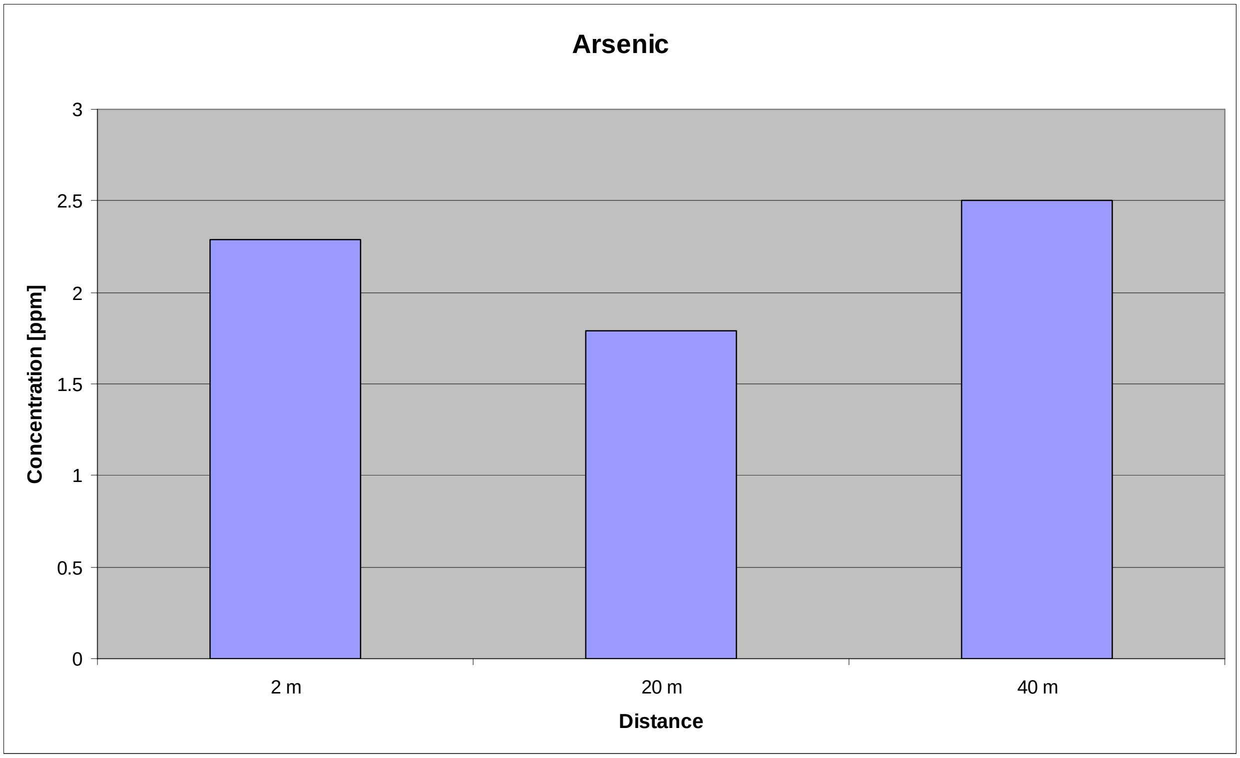

Figure 25. Changes in average As concentration with distance from road.

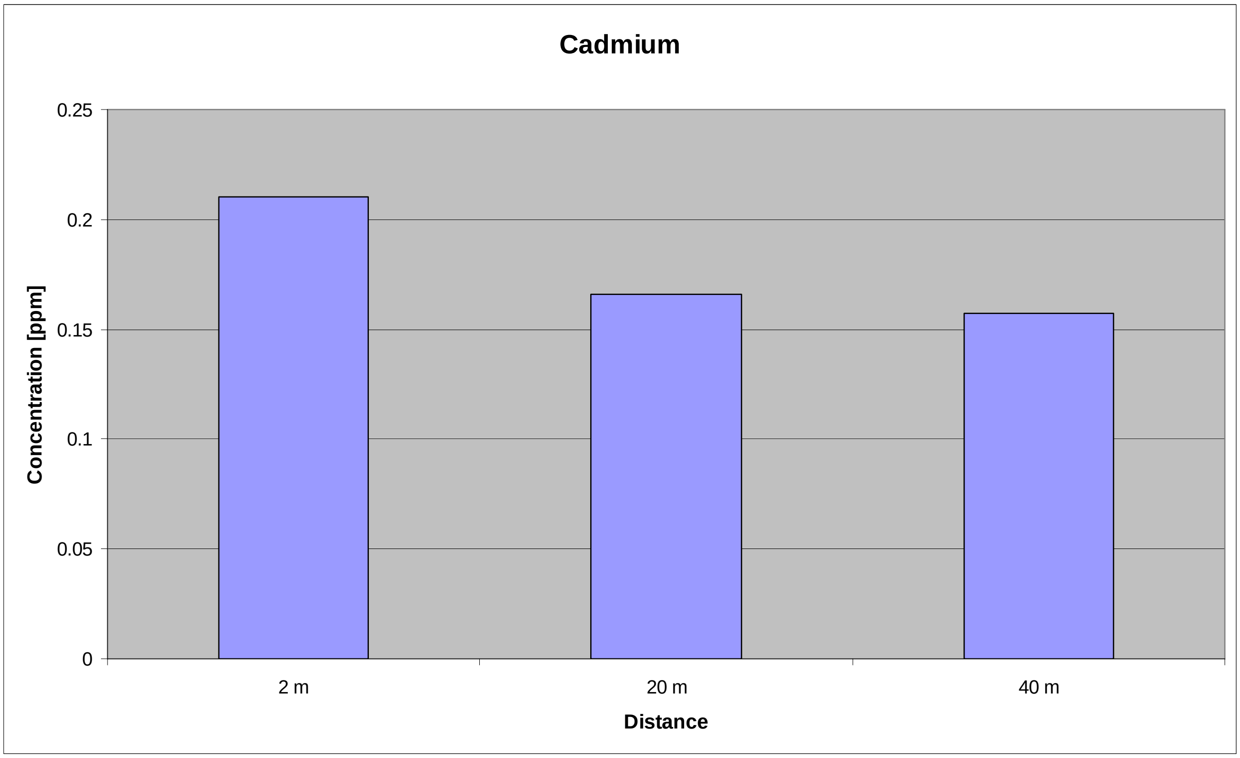

Figure 26. Changes in average Cd concentration with distance from road.

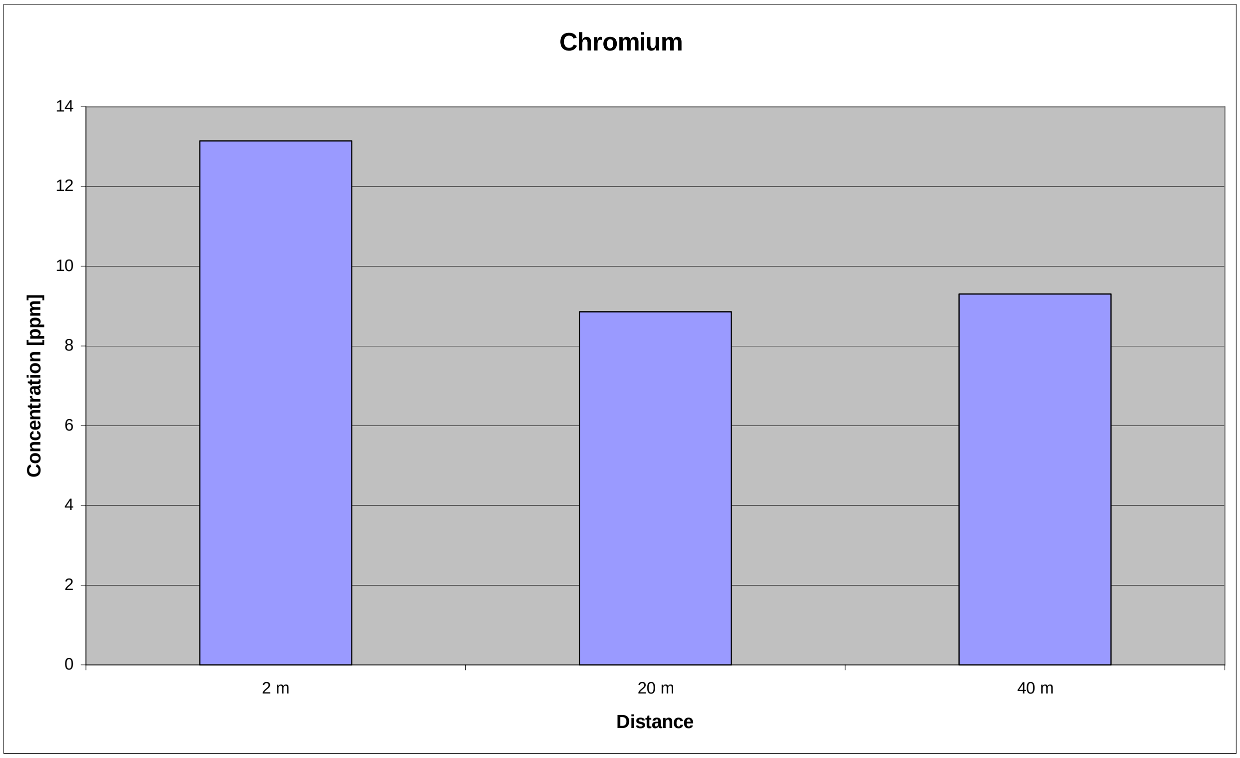

Figure 27. Changes in average Cr concentration with distance from road.

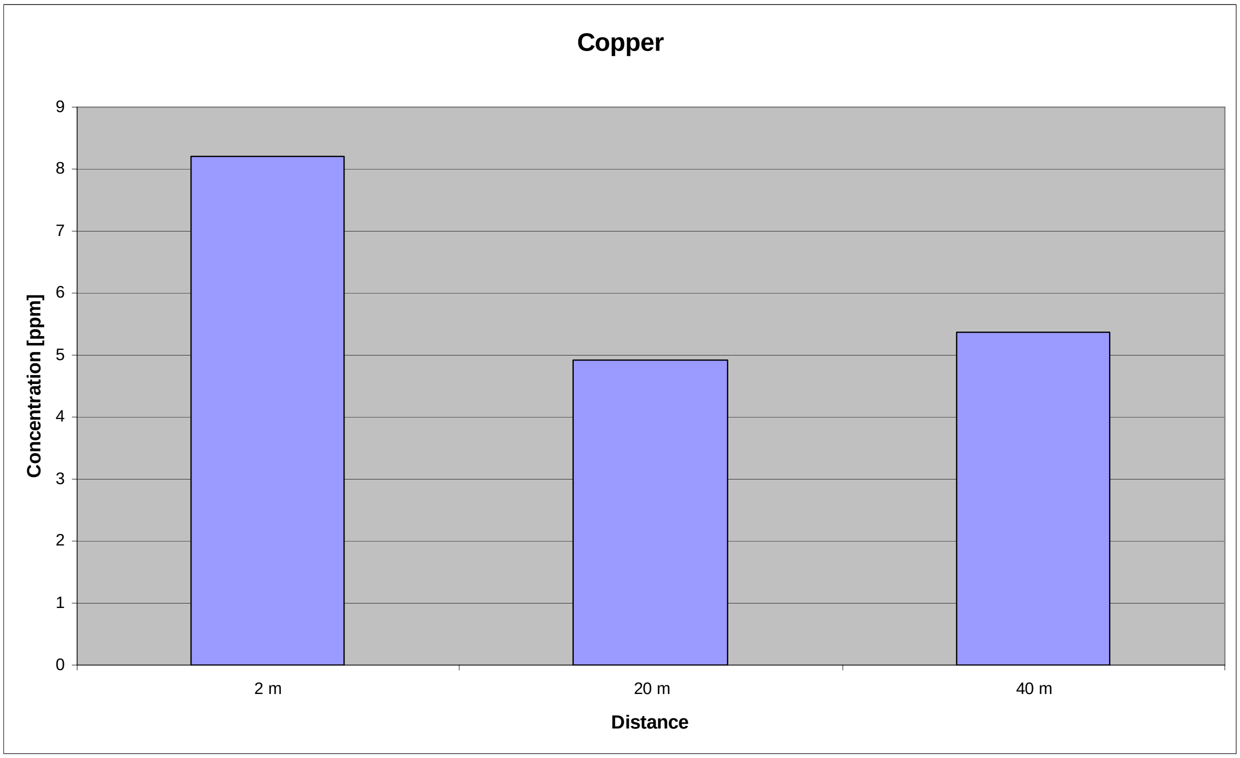

Figure 28. Changes in average Cu concentration with distance from road.

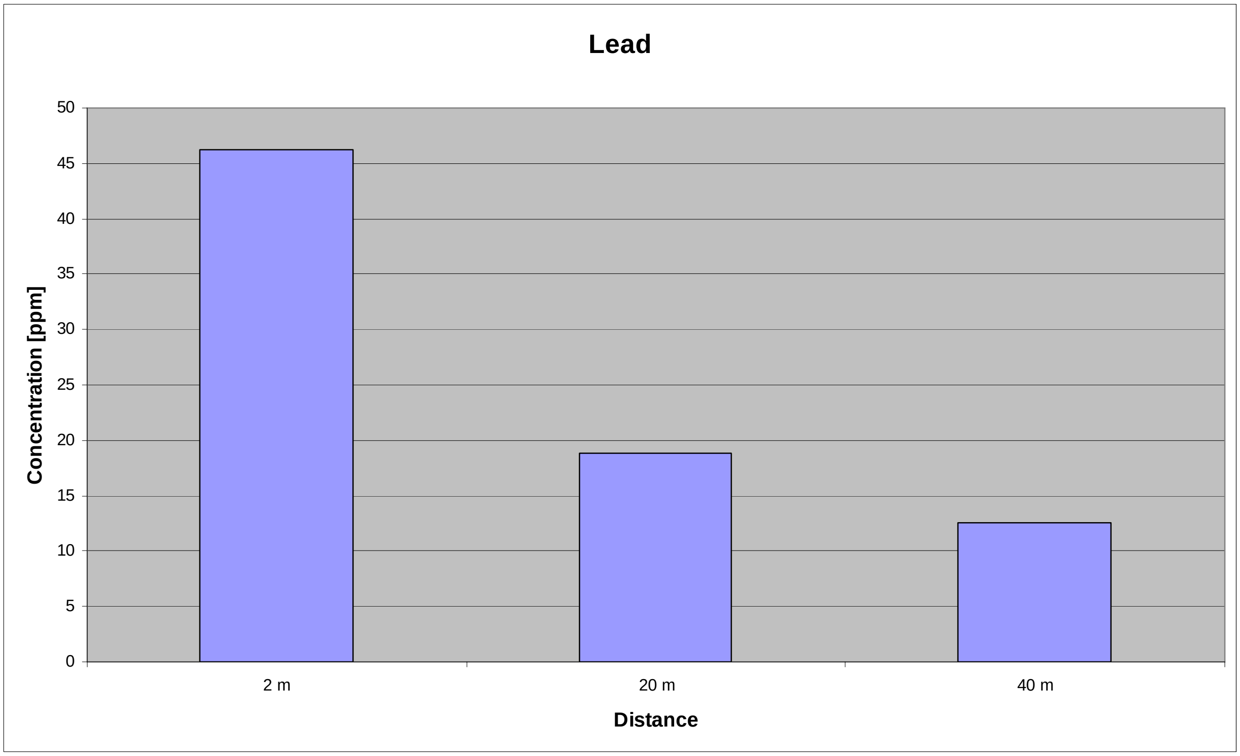

Figure 29. Changes in average Pb concentration with distance from road.

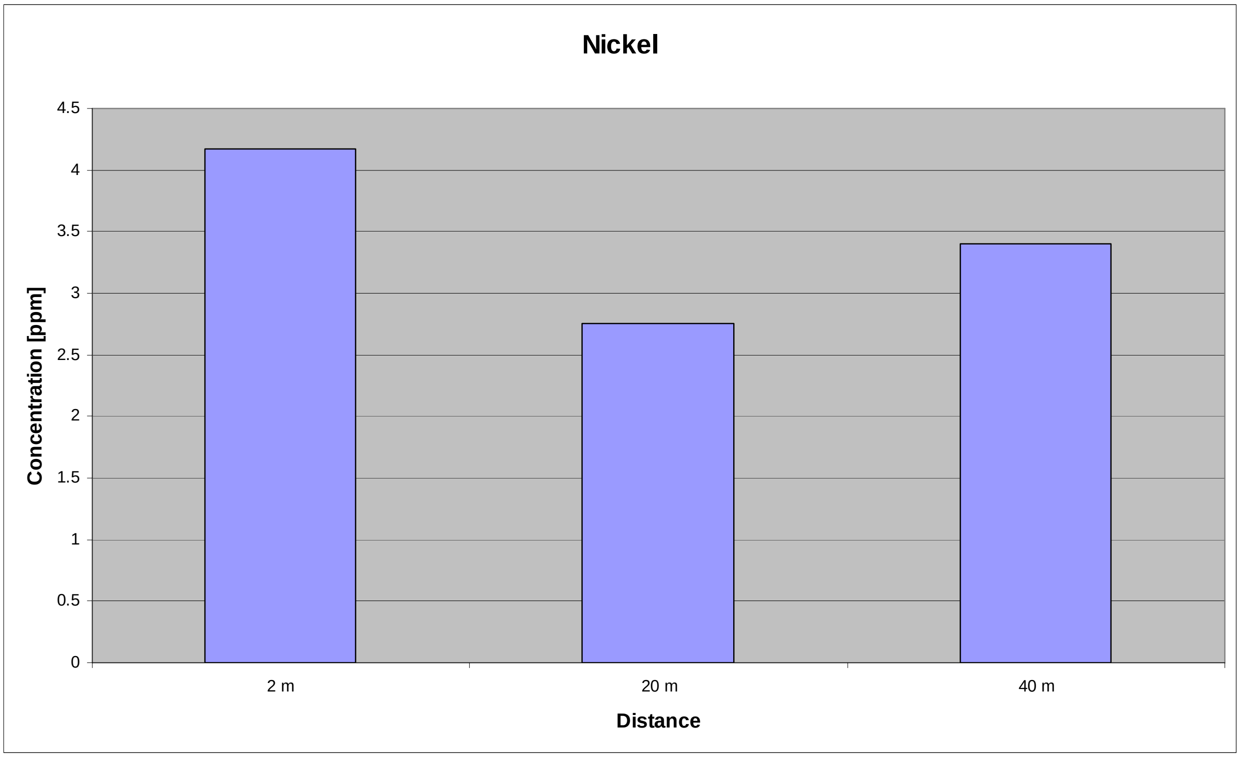

Figure 30. Changes in average Ni concentration with distance from road.

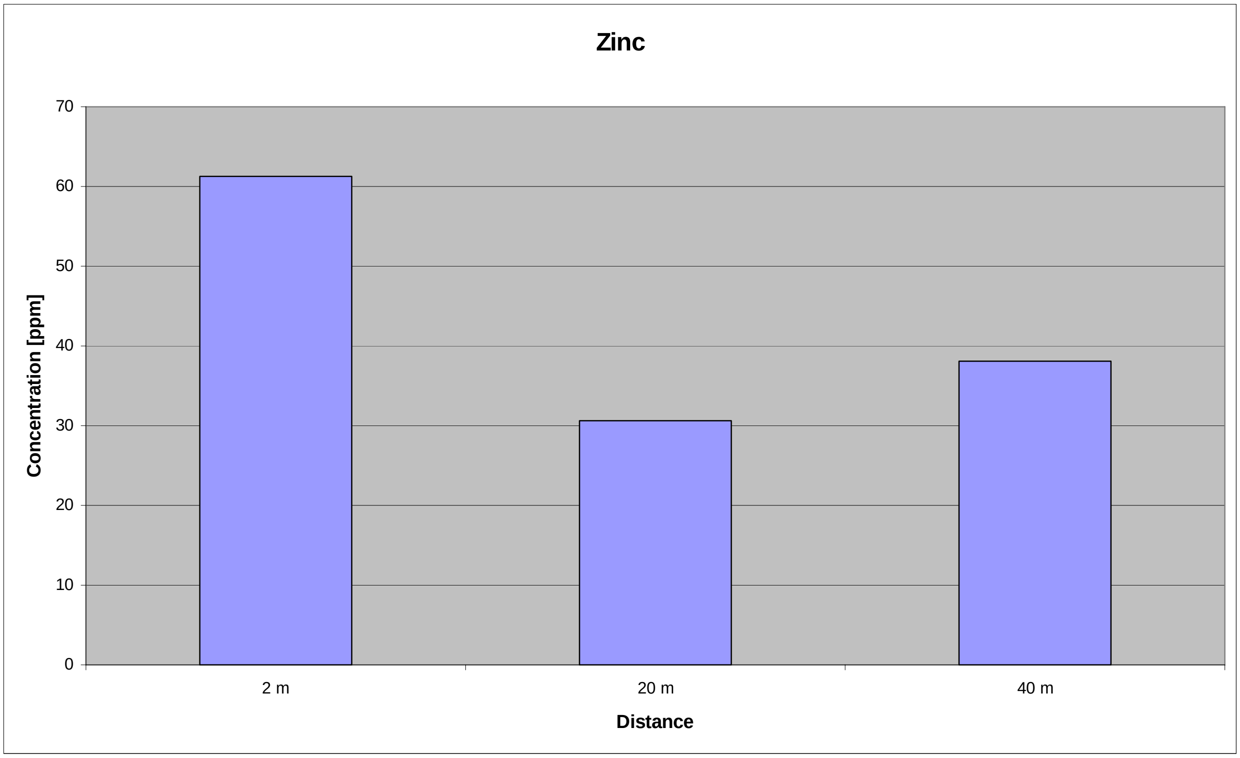

Figure 31. Changes in average Zn concentration with distance from road.

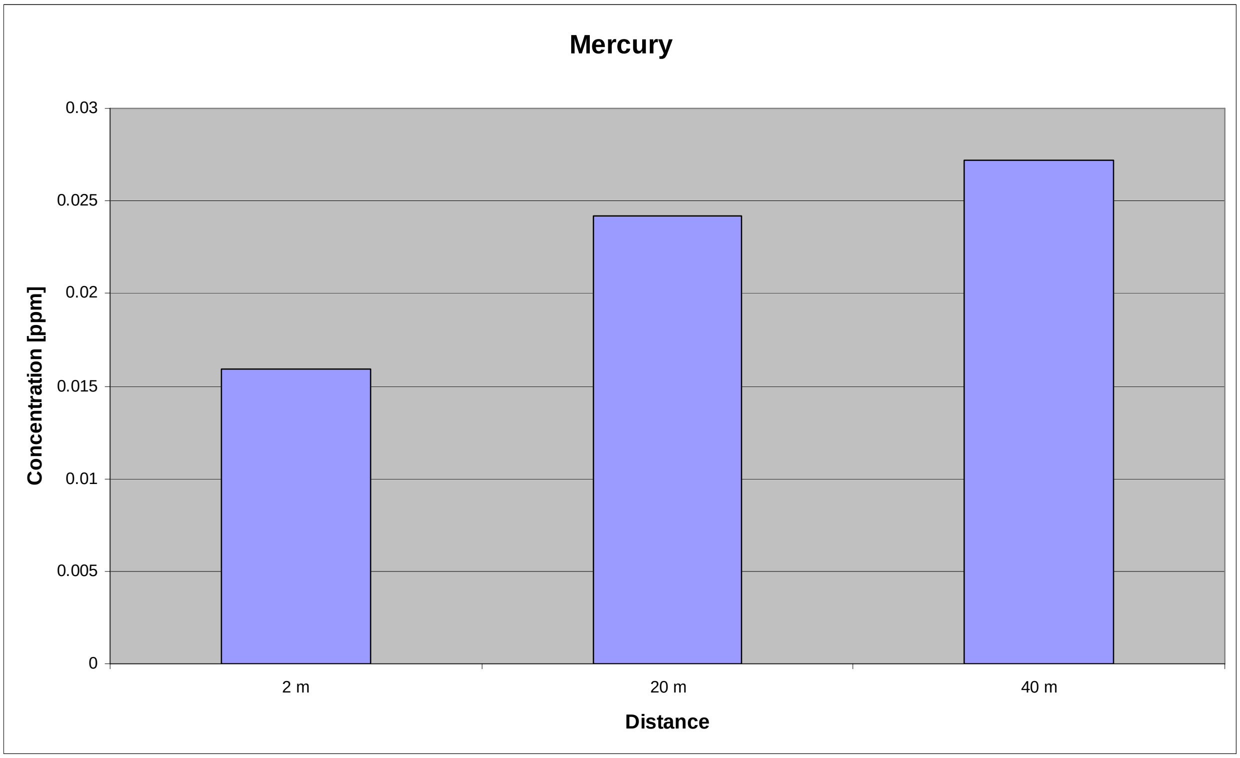

Figure 32. Changes in average Hg concentration with distance from road.

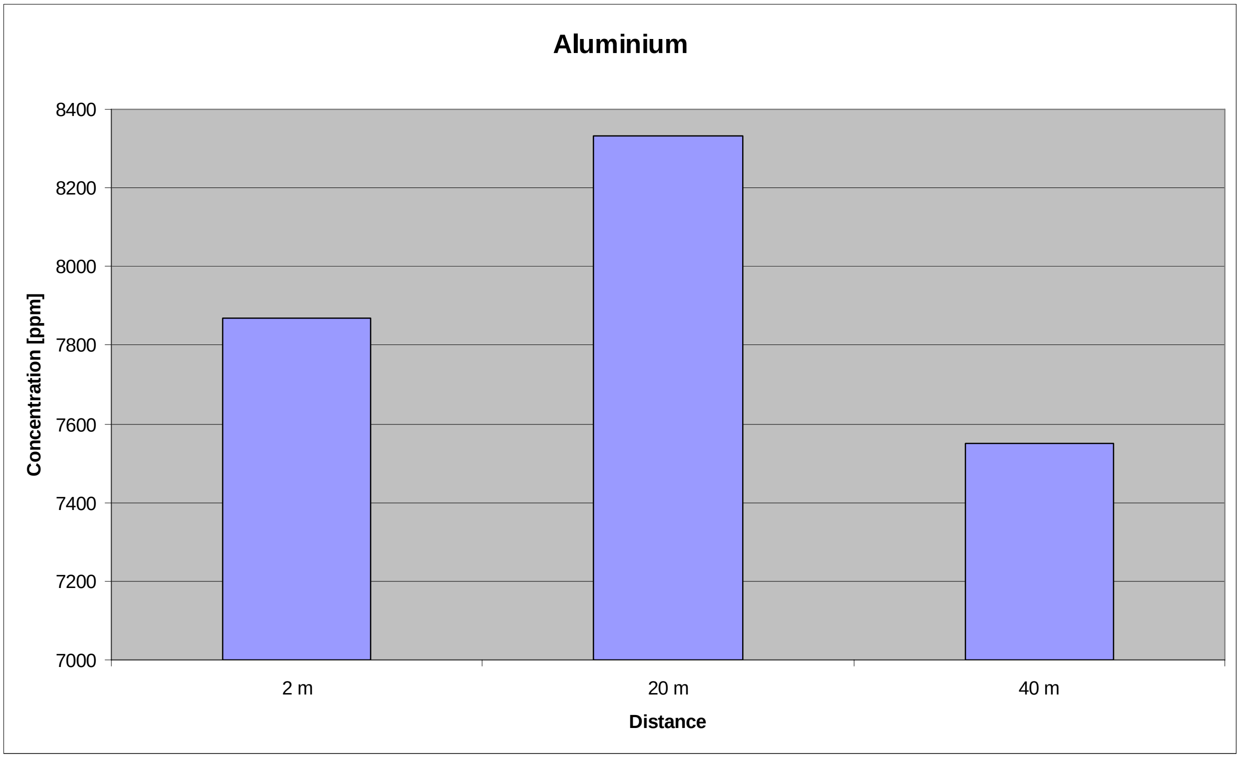

Figure 33. Changes in average Al concentration with distance from road.

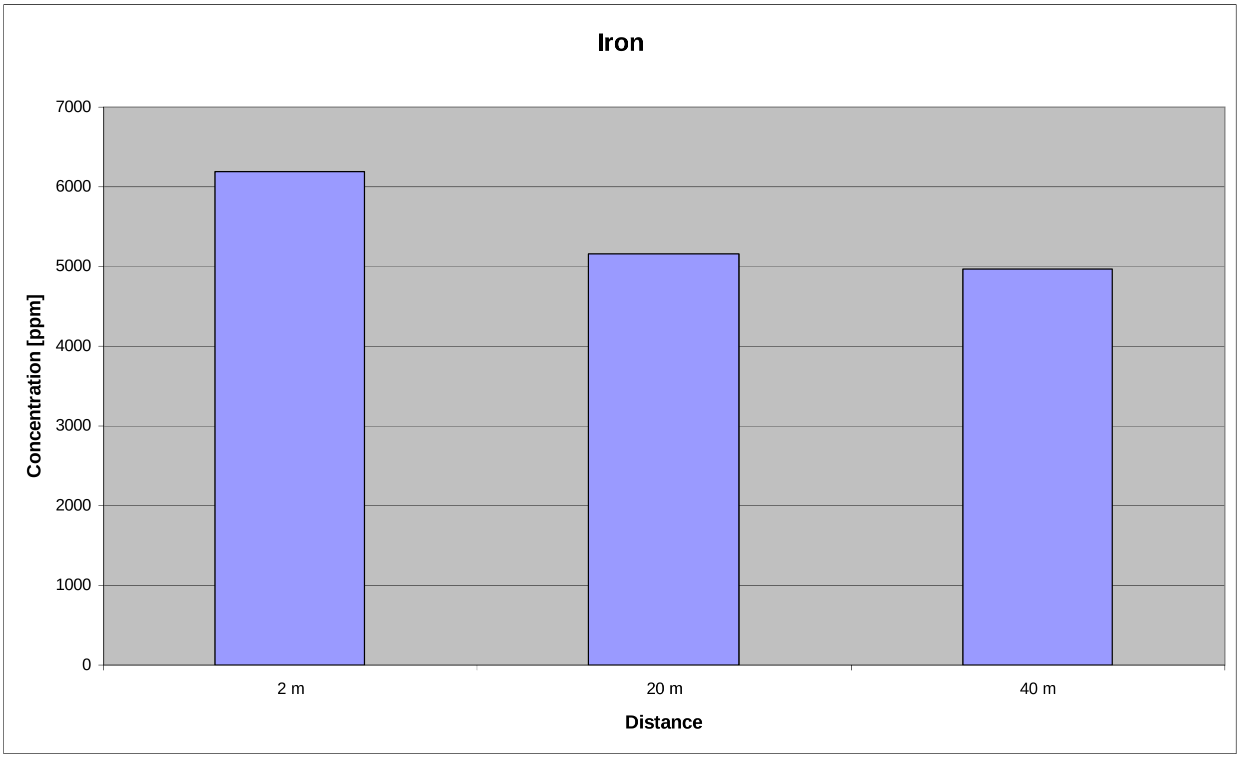

Figure 34. Changes in average Fe concentration with distance from road.

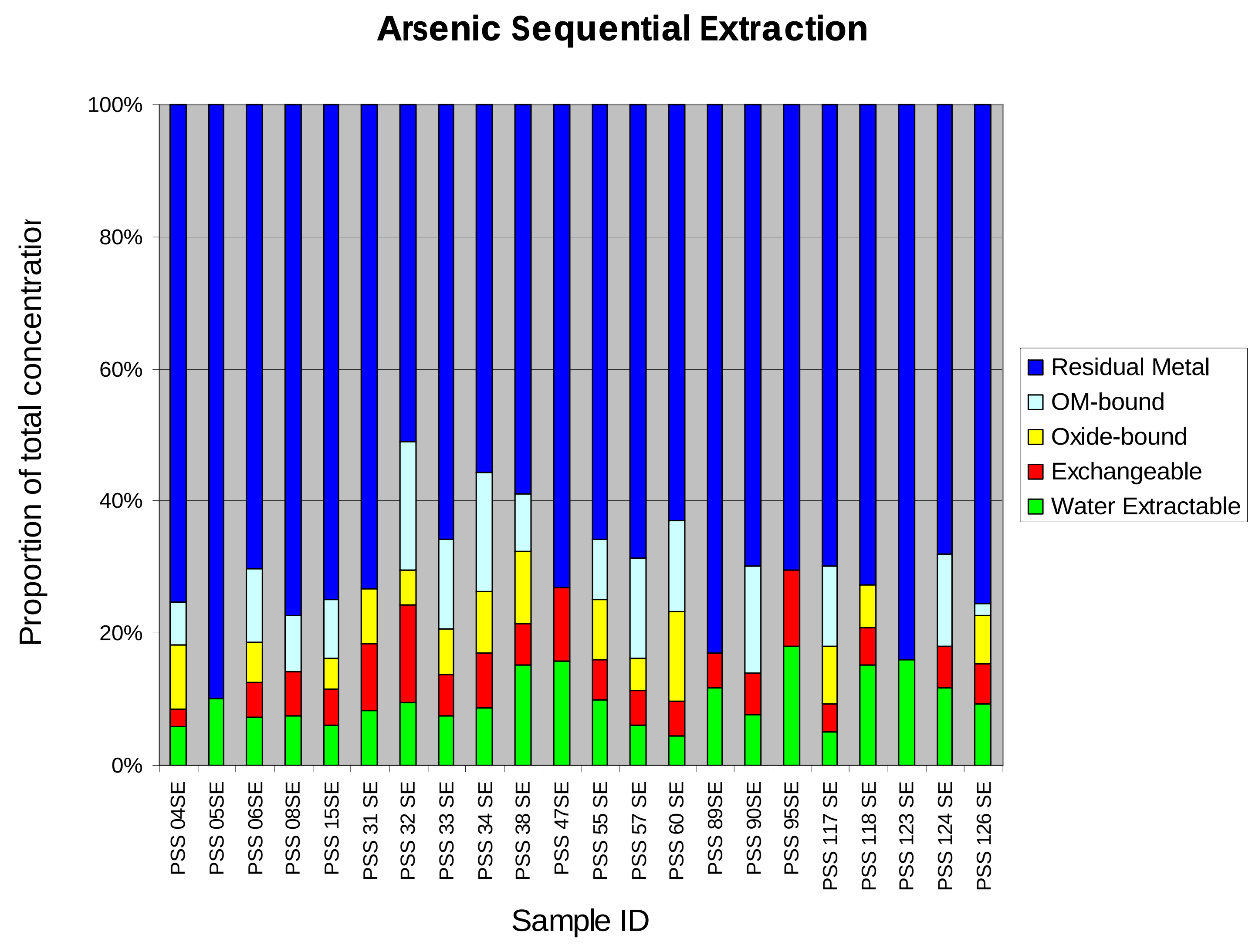

Figure 35. Arsenic speciation in surface soils.

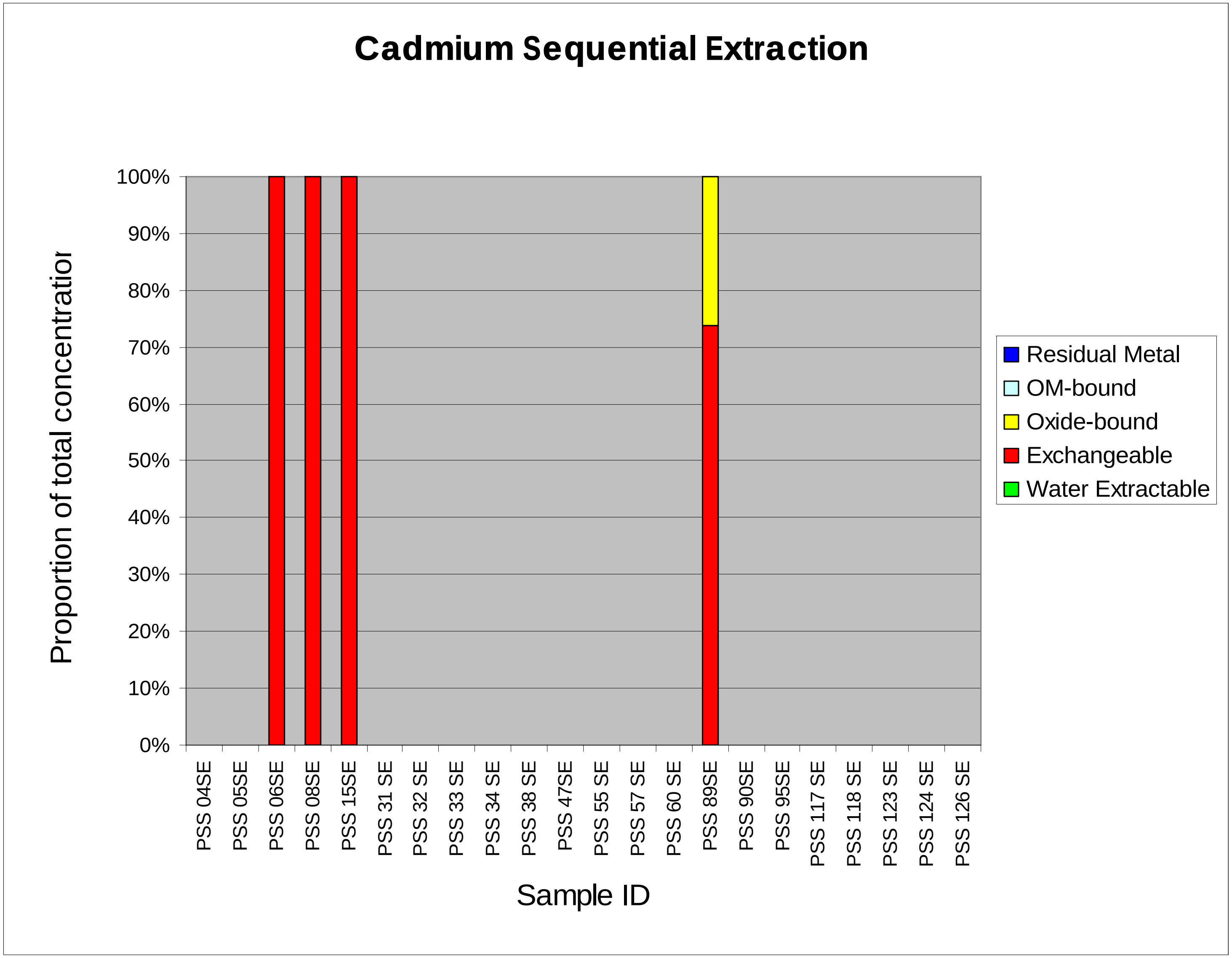

Figure 36. Cadmium speciation in surface soils.

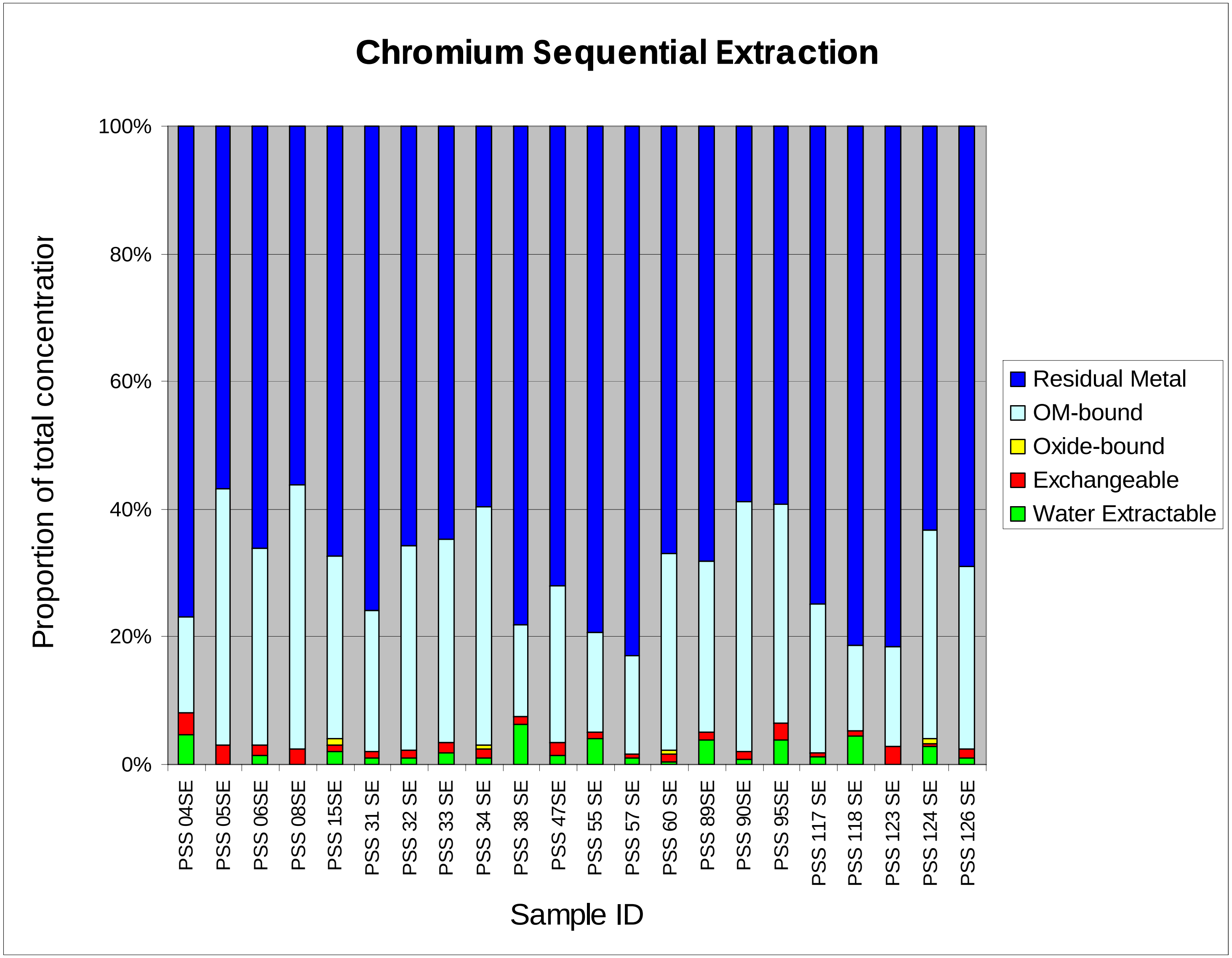

Figure 37. Chromium speciation in surface soils.

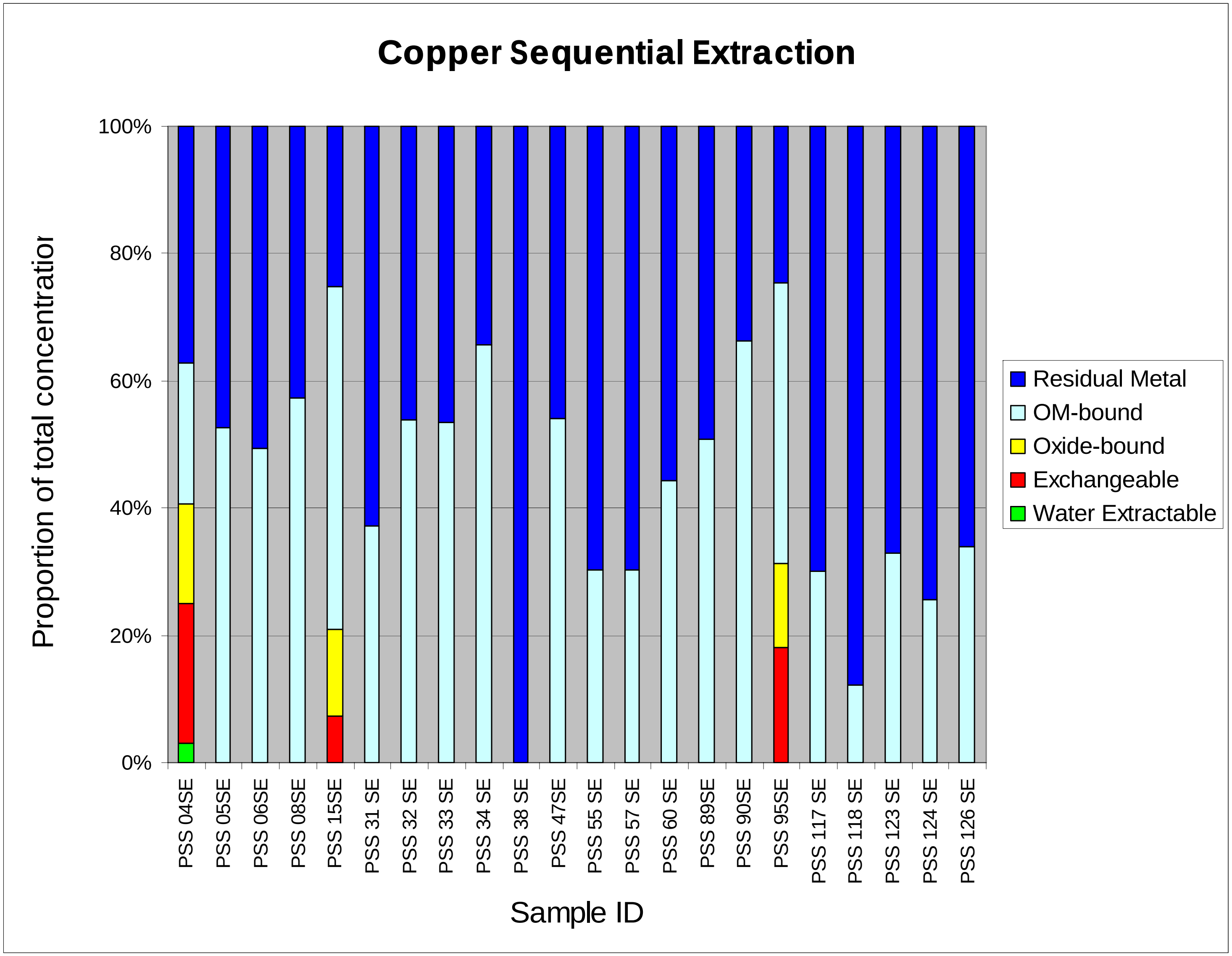

Figure 38. Copper speciation in surface soils.

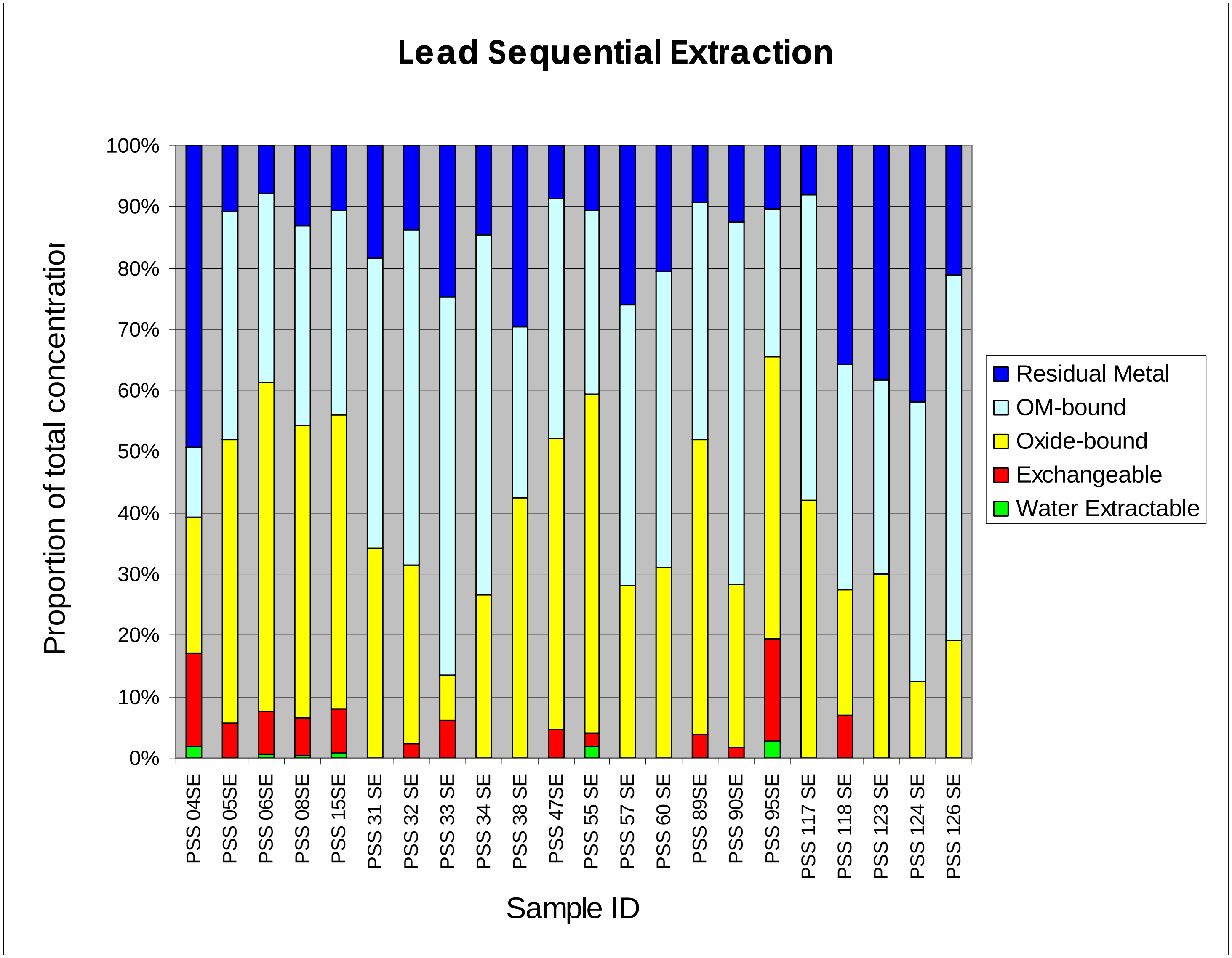

Figure 39. Lead speciation in surface soils.

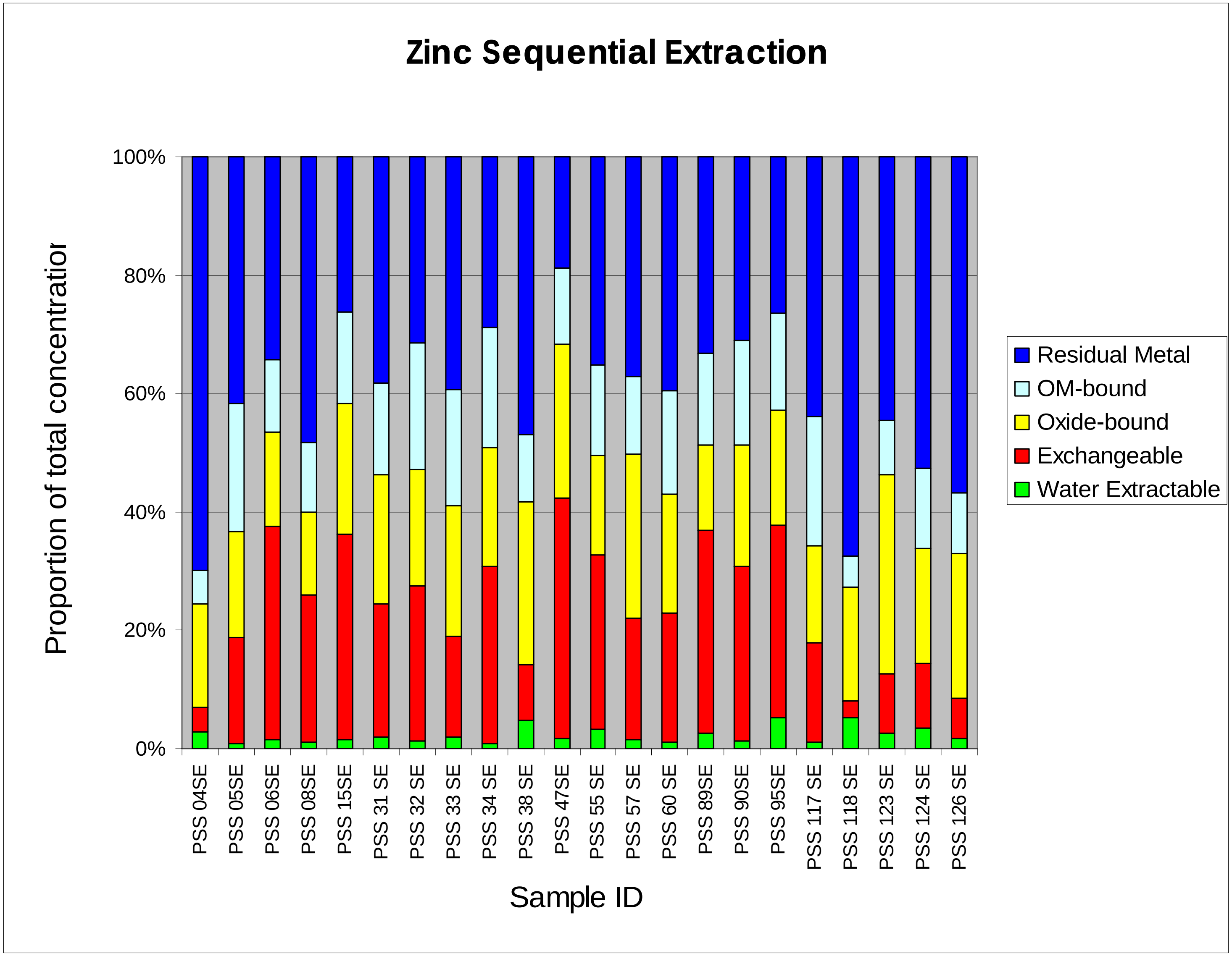

Figure 40. Zinc speciation in surface soils.

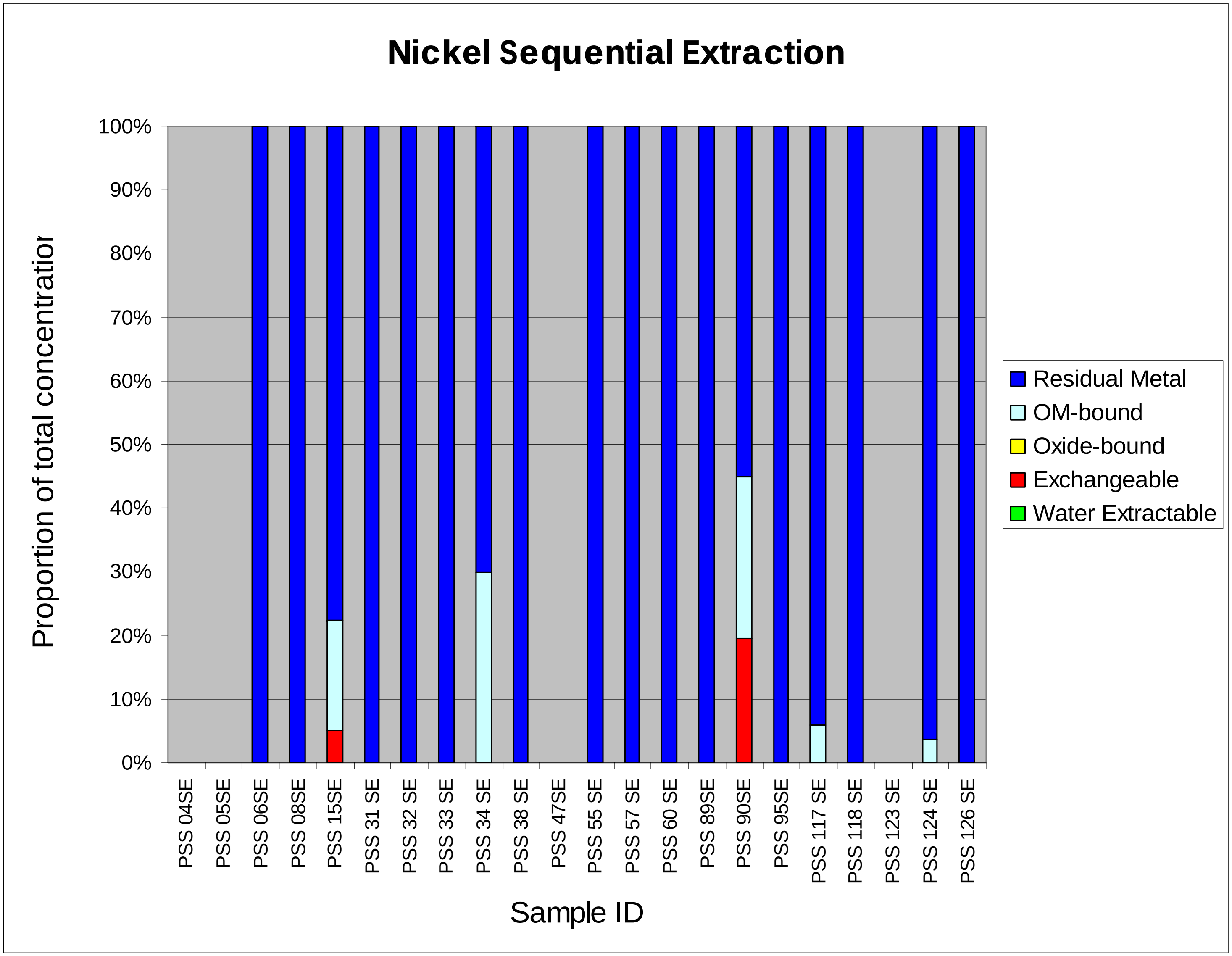

Figure 41. Nickel speciation in surface soils.

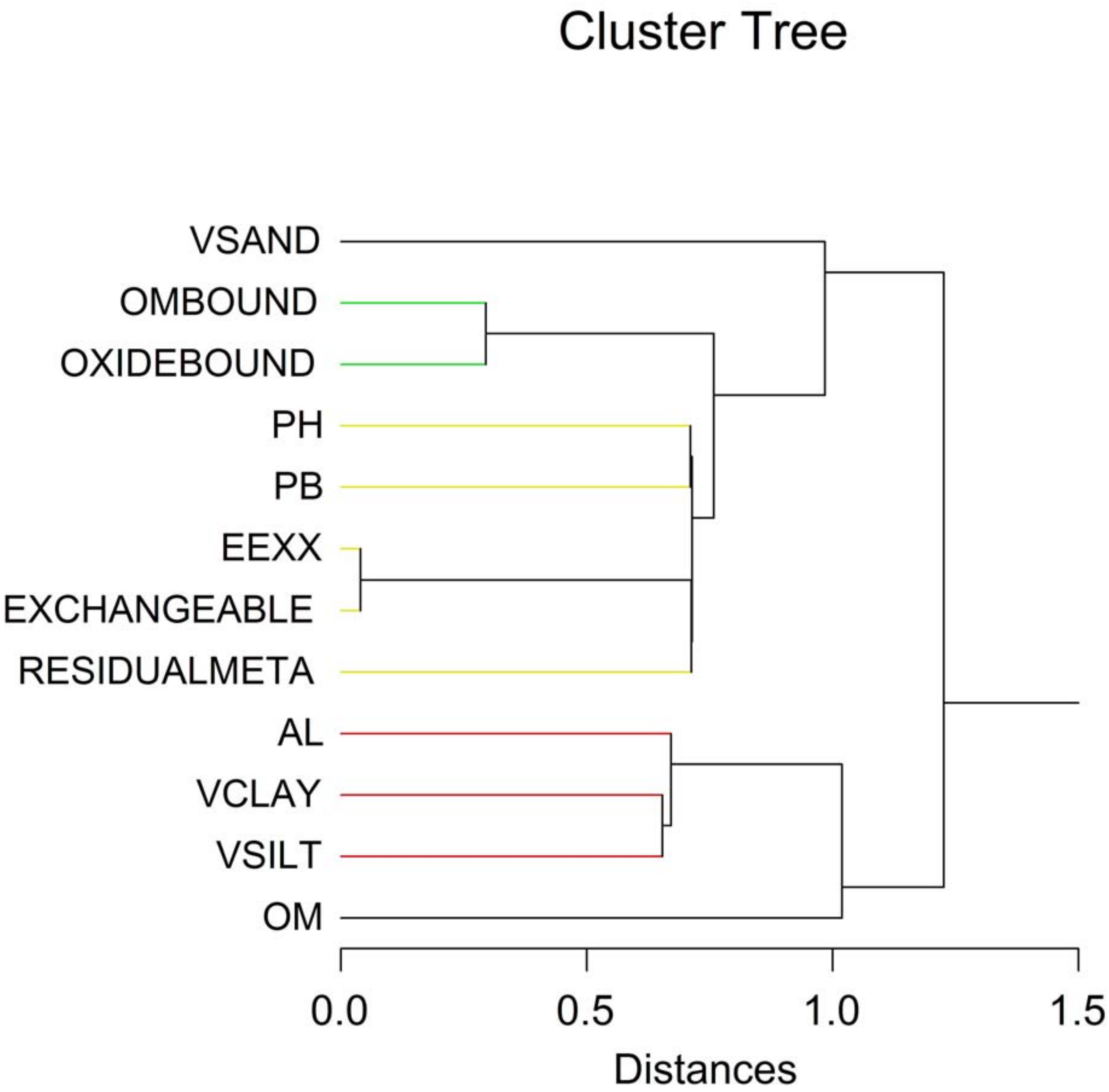

Figure 42. Cluster tree for hierarchical clustering of Pb fractions and soil characteristics. EEXX indicates bioavailable fraction. Data were statistically standardized for cluster analysis.

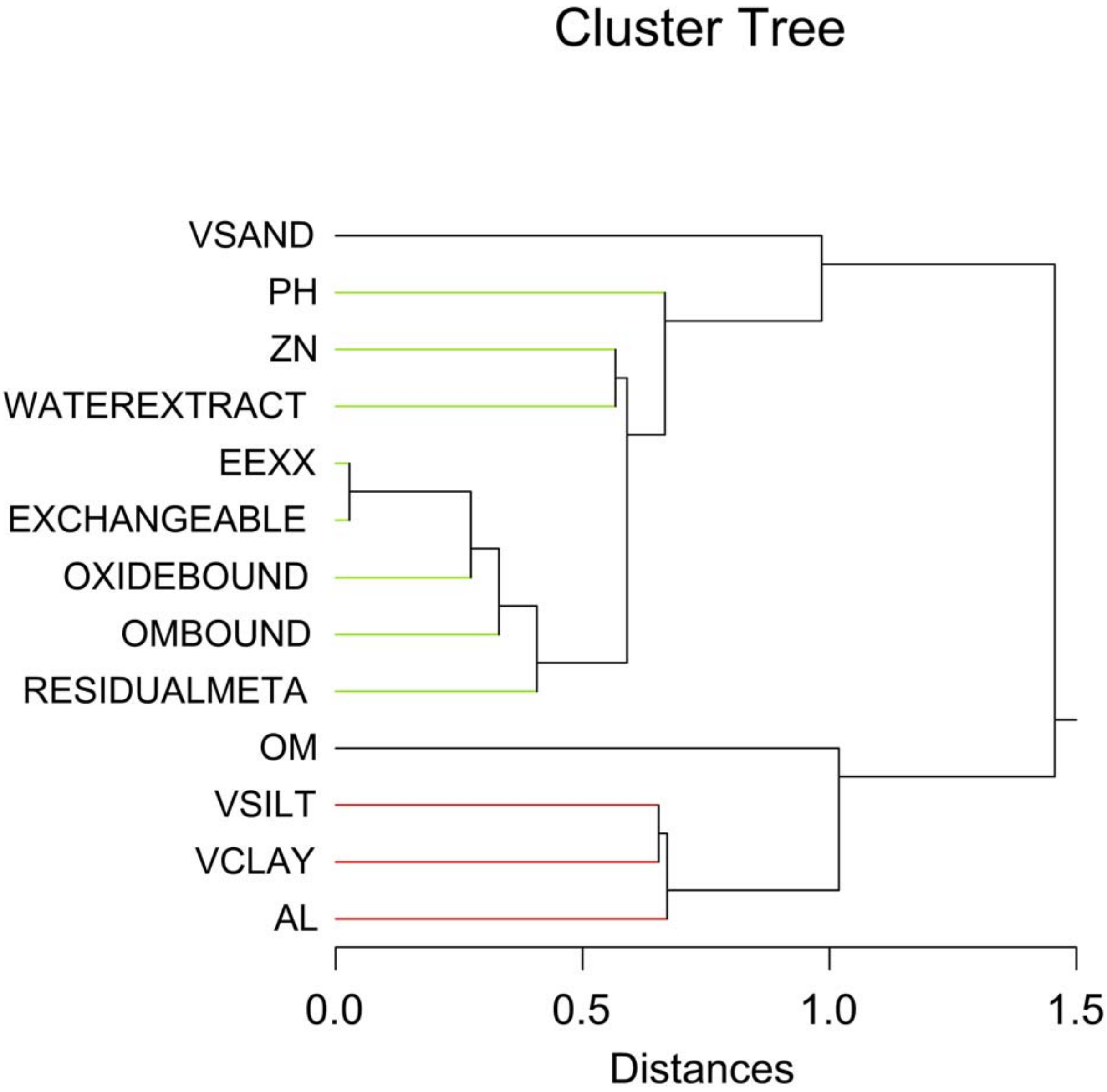

Figure 43. Cluster tree for hierarchical clustering of Zn fractions and soil characteristics. EEXX indicates bioavailable fraction. Data were statistically standardized for cluster analysis.

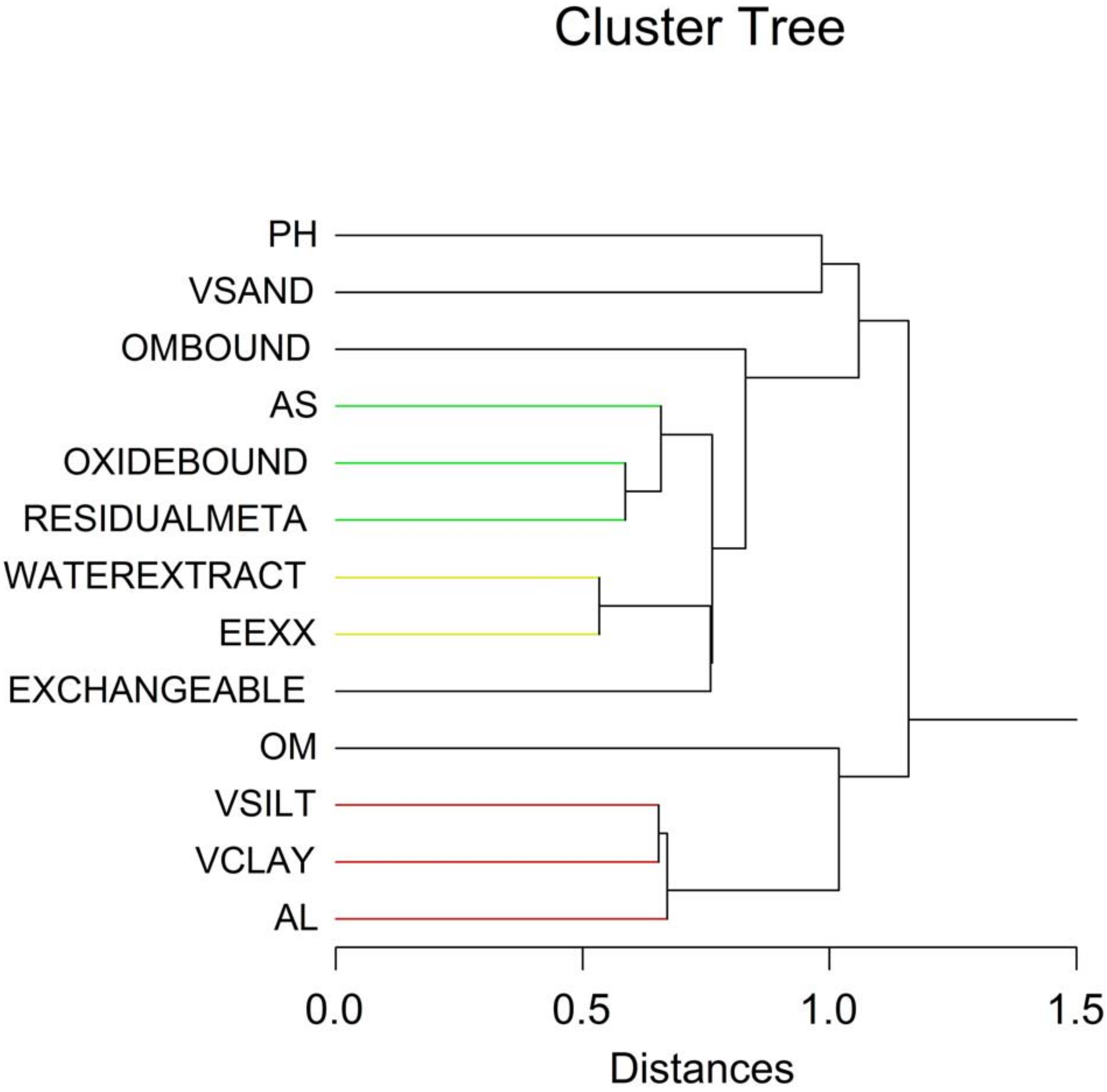

Figure 44. Cluster tree for hierarchical clustering of As fractions and soil characteristics. EEXX indicates bioavailable fraction. Data were statistically standardized for cluster analysis.

APPENDIX 2. ADDITIONAL TABLES

Table 15. Trace metal concentrations [mg/kg] for sequential extraction.

	Water Extractable	Exchangeable	Oxide-bound	OM-bound	Residual
Aluminum					
PSS 04	378	107	162	478	3450
PSS 05	55	46	140	495	1940
PSS 06	147	66	288	991	5050
PSS 08	41	60	144	414	1960
PSS 15	295	42	367	924	7040
PSS 31	217	189	408	1550	10600
PSS 32	154	232	810	1550	6050
PSS 33	143	74	264	589	2820
PSS 34	52	59	444	871	2280
PSS 38	956	139	299	778	7040
PSS 47	142	41	158	687	3280
PSS 55	811	113	431	1320	11300
PSS 57	303	42	399	2680	13700
PSS 60	59	79	410	906	4330
PSS 89	595	55	185	1240	7380
PSS 90	126	49	319	2000	8000
PSS 95	349	84	102	359	1940
PSS 117	329	172	779	2320	11700
PSS 118	1730	245	358	1230	18800
PSS 123	97	87	150	817	3610
PSS 124	1530	315	1180	3520	28200
PSS 126	269	764	1770	2820	11000
Arsenic					
PSS 04	0.66	0.3	1.1	0.72	8.5
PSS 05	0.19	BDL	BDL	BDL	1.7
PSS 06	0.23	0.16	0.19	0.35	2.2
PSS 08	0.23	0.21	BDL	0.26	2.4
PSS 15	0.29	0.26	0.23	0.42	3.6
PSS 31	0.16	0.19	0.16	BDL	1.4
PSS 32	0.3	0.46	0.17	0.61	1.6
PSS 33	0.25	0.21	0.23	0.45	2.2
PSS 34	0.34	0.33	0.37	0.71	2.2
PSS 38	0.36	0.15	0.26	0.21	1.4
PSS 47	0.26	0.18	BDL	BDL	1.2
PSS 55	0.39	0.24	0.36	0.36	2.6
PSS 57	0.25	0.21	0.2	0.62	2.8
PSS 60	0.23	0.26	0.69	0.71	3.2
PSS 89	0.34	0.15	BDL	BDL	2.4
PSS 90	0.25	0.21	BDL	0.53	2.3
PSS 95	0.28	0.18	BDL	BDL	1.1
PSS 117	0.2	0.17	0.35	0.49	2.8
PSS 118	0.5	0.19	0.21	BDL	2.4
PSS 123	0.21	BDL	BDL	BDL	1.1
PSS 124	0.31	0.17	BDL	0.37	1.8
PSS 126	0.27	0.18	0.21	0.05	2.2

Table 15. Trace metal concentrations [mg/kg] for sequential extraction (cont'd).

	Water Extractable	Exchangeable	Oxide-bound	OM-bound	Residual
			Cadmium		
PSS 04	BDL	BDL	BDL	BDL	BDL
PSS 05	BDL	BDL	BDL	BDL	BDL
PSS 06	BDL	0.3	BDL	BDL	BDL
PSS 08	BDL	0.22	BDL	BDL	BDL
PSS 15	BDL	0.19	BDL	BDL	BDL
PSS 31	BDL	BDL	BDL	BDL	BDL
PSS 32	BDL	BDL	BDL	BDL	BDL
PSS 33	BDL	BDL	BDL	BDL	BDL
PSS 34	BDL	BDL	BDL	BDL	BDL
PSS 38	BDL	BDL	BDL	BDL	BDL
PSS 47	BDL	BDL	BDL	BDL	BDL
PSS 55	BDL	BDL	BDL	BDL	BDL
PSS 57	BDL	BDL	BDL	BDL	BDL
PSS 60	BDL	BDL	BDL	BDL	BDL
PSS 89	BDL	0.45	0.16	BDL	BDL
PSS 90	BDL	BDL	BDL	BDL	BDL
PSS 95	BDL	BDL	BDL	BDL	BDL
PSS 117	BDL	BDL	BDL	BDL	BDL
PSS 118	BDL	BDL	BDL	BDL	BDL
PSS 123	BDL	BDL	BDL	BDL	BDL
PSS 124	BDL	BDL	BDL	BDL	BDL
PSS 126	BDL	BDL	BDL	BDL	BDL
			Chromium		
PSS 04	0.19	0.15	BDL	0.62	3.2
PSS 05	BDL	0.13	BDL	1.7	2.4
PSS 06	0.094	0.12	BDL	2.1	4.5
PSS 08	BDL	0.13	BDL	2.2	3
PSS 15	0.22	0.12	0.1	3.1	7.3
PSS 31	0.12	0.13	BDL	2.6	9
PSS 32	0.12	0.13	BDL	3.5	7.2
PSS 33	0.16	0.14	BDL	2.8	5.7
PSS 34	0.089	0.12	0.067	3.3	5.3
PSS 38	0.62	0.12	BDL	1.4	7.6
PSS 47	0.09	0.12	BDL	1.5	4.4
PSS 55	0.48	0.12	BDL	1.8	9.2
PSS 57	0.16	0.089	BDL	2.2	12
PSS 60	0.071	0.16	0.1	4.5	9.8
PSS 89	0.39	0.12	BDL	2.7	6.9
PSS 90	0.079	0.11	BDL	3.8	5.7
PSS 95	0.2	0.14	BDL	1.8	3.1
PSS 117	0.14	0.087	BDL	2.8	9
PSS 118	1.1	0.18	BDL	3.3	20
PSS 123	BDL	0.11	BDL	0.61	3.2
PSS 124	1.4	0.23	0.36	16	31
PSS 126	0.14	0.18	BDL	3.7	8.9

Table 15. Trace metal concentrations [mg/kg] for sequential extraction (cont'd).

	Water Extractable	Exchangeable	Oxide-bound	OM-bound	Residual
			Copper		
PSS 04	0.7	5.2	3.7	5.2	8.8
PSS 05	BDL	BDL	BDL	2	1.8
PSS 06	BDL	BDL	BDL	4.1	4.2
PSS 08	BDL	BDL	BDL	7.4	5.5
PSS 15	BDL	2.7	5.1	20	9.4
PSS 31	BDL	BDL	BDL	1.6	2.7
PSS 32	BDL	BDL	BDL	2.8	2.4
PSS 33	BDL	BDL	BDL	2.3	2
PSS 34	BDL	BDL	BDL	6.1	3.2
PSS 38	BDL	BDL	BDL	BDL	2.2
PSS 47	BDL	BDL	BDL	1.3	1.1
PSS 55	BDL	BDL	BDL	1.6	3.7
PSS 57	BDL	BDL	BDL	1.6	3.7
PSS 60	BDL	BDL	BDL	2.7	3.4
PSS 89	BDL	BDL	BDL	3.2	3.1
PSS 90	BDL	BDL	BDL	6.9	3.5
PSS 95	BDL	1.1	0.81	2.7	1.5
PSS 117	BDL	BDL	BDL	1.9	4.4
PSS 118	BDL	BDL	BDL	0.82	5.9
PSS 123	BDL	BDL	BDL	0.64	1.3
PSS 124	BDL	BDL	BDL	2.8	8.1
PSS 126	BDL	BDL	BDL	1.7	3.3
			Iron		
PSS 04	186	2	158	133	3210
PSS 05	33	4.9	178	502	5000
PSS 06	62	1.7	218	336	4060
PSS 08	28	3.9	181	297	3540
PSS 15	124	11	559	688	6320
PSS 31	108	1.6	239	682	10300
PSS 32	40	2.6	516	1200	3620
PSS 33	61	4.1	556	830	3250
PSS 34	29	2.5	200	554	3400
PSS 38	430	1.2	209	306	6340
PSS 47	74	6.7	163	291	3600
PSS 55	379	BDL	249	188	7280
PSS 57	136	1.6	208	320	9300
PSS 60	25	11	736	1100	4680
PSS 89	235	1.5	108	253	5080
PSS 90	54	11	1060	1490	4260
PSS 95	149	2.2	97	129	2110
PSS 117	133	1.3	477	1010	8240
PSS 118	846	1.7	83	268	369
PSS 123	40	1.8	107	241	2350
PSS 124	252	1.2	145	347	9150
PSS 126	99	2.5	587	1820	8360

Table 15. Trace metal concentrations [mg/kg] for sequential extraction (cont'd).

	Water Extractable	Exchangeable	Oxide-bound	OM-bound	Residual
			Lead		
PSS 04	1.6	13	19	9.8	42
PSS 05	BDL	2.5	20	16	4.7
PSS 06	1.2	13	102	58	15
PSS 08	0.83	11	87	59	24
PSS 15	1.6	12	81	56	18
PSS 31	BDL	BDL	2.8	3.9	1.5
PSS 32	BDL	0.74	9.1	17	4.3
PSS 33	BDL	0.65	0.78	6.5	2.6
PSS 34	BDL	BDL	6.8	15	3.7
PSS 38	BDL	BDL	2.3	1.5	1.6
PSS 47	BDL	0.9	9.3	7.6	1.7
PSS 55	0.49	0.55	14	7.6	2.7
PSS 57	BDL	BDL	2.7	4.4	2.5
PSS 60	BDL	BDL	5.3	8.3	3.5
PSS 89	BDL	1.2	15	12	2.9
PSS 90	BDL	0.82	13	29	6.1
PSS 95	0.98	5.8	16	8.4	3.6
PSS 117	BDL	BDL	11	13	2.1
PSS 118	BDL	0.68	2	3.6	3.5
PSS 123	BDL	BDL	0.86	0.91	1.1
PSS 124	BDL	BDL	1.4	5.1	4.7
PSS 126	BDL	BDL	3.1	9.6	3.4
			Nickel		
PSS 04	BDL	BDL	BDL	BDL	BDL
PSS 05	BDL	BDL	BDL	BDL	BDL
PSS 06	BDL	BDL	BDL	BDL	0.73
PSS 08	BDL	BDL	BDL	BDL	0.26
PSS 15	BDL	0.24	BDL	0.83	3.7
PSS 31	BDL	BDL	BDL	BDL	1.8
PSS 32	BDL	BDL	BDL	BDL	0.52
PSS 33	BDL	BDL	BDL	BDL	0.35
PSS 34	BDL	BDL	BDL	0.23	0.54
PSS 38	BDL	BDL	BDL	BDL	1.1
PSS 47	BDL	BDL	BDL	BDL	BDL
PSS 55	BDL	BDL	BDL	BDL	1.5
PSS 57	BDL	BDL	BDL	BDL	2.6
PSS 60	BDL	BDL	BDL	BDL	0.94
PSS 89	BDL	BDL	BDL	BDL	0.59
PSS 90	BDL	0.29	BDL	0.38	0.82
PSS 95	BDL	BDL	BDL	BDL	1.1
PSS 117	BDL	BDL	BDL	0.24	3.8
PSS 118	BDL	BDL	BDL	BDL	5.1
PSS 123	BDL	BDL	BDL	BDL	BDL
PSS 124	BDL	BDL	BDL	0.24	6.2
PSS 126	BDL	BDL	BDL	BDL	1.9

Table 15. Trace metal concentrations [mg/kg] for sequential extraction (cont'd).

	Water Extractable	Exchangeable	Oxide-bound	OM-bound	Residual
			Zinc		
PSS 04	0.63	0.96	4	1.3	16
PSS 05	0.79	15	15	18	35
PSS 06	1.7	41	18	14	39
PSS 08	0.67	15	8.3	7.1	29
PSS 15	3.6	78	50	35	59
PSS 31	0.46	5.4	5.3	3.7	9.2
PSS 32	0.48	9.2	6.9	7.5	11
PSS 33	0.44	3.6	4.7	4.2	8.4
PSS 34	0.82	28	19	19	27
PSS 38	0.71	1.4	4.1	1.7	7
PSS 47	0.63	14	9	4.4	6.5
PSS 55	2.3	21	12	11	25
PSS 57	0.46	6.1	8.2	3.9	11
PSS 60	0.34	7.2	6.6	5.7	13
PSS 89	2.4	31	13	14	30
PSS 90	0.9	20	14	12	21
PSS 95	2.6	16	9.5	8	13
PSS 117	0.65	10	9.6	13	26
PSS 118	1	0.55	3.7	1	13
PSS 123	0.29	1.1	3.7	1	4.9
PSS 124	0.93	2.9	5.2	3.6	14
PSS 126	0.31	1.1	4.1	1.7	9.5

Table 16. Trace metal concentrations [mg/kg] as a function of proximity to a road.

sample	dist. to rd.	Al	As	Cd	Cr	Cu	Fe	Pb	Hg	Ni	Zn
PSS 21A	2 m	7920	2.8	0.19	13	13	6800	136	0.047	3.7	107
PSS 21B	20 m	12200	1.6	0.072	11	4.9	6240	9.1	0.059	3.1	24
PSS 21C	40 m	5550	3.3	0.13	20	9.3	3280	15	0.072	5.5	72
PSS 35A	2 m	3740	1.2	0.15	8.9	3.6	5180	49	0.009	1.5	21
PSS 35B	20 m	5050	1.1	BDL	5.6	4.2	4100	12	0.033	1.4	8.2
PSS 35C	40 m	6850	1.2	BDL	6.1	2.2	5410	3.5	0.013	2.1	5.3
PSS 37A	2 m	12100	2.3	0.13	14	5.8	9200	57	0.019	3.9	33
PSS 37B	20 m	13700	1.4	0.12	10	6.7	8130	21	0.038	4.8	24
PSS 37C	40 m	10500	1.4	0.1	10	5.7	6190	20	0.04	5.2	20
PSS 37D	60 m	13500	2.1	0.23	14	7.1	7960	21	0.038	7	27
PSS 39A	2 m	21800	6.7	0.26	44	19	17000	95	0.038	16	71
PSS 39B	20 m	9800	3.5	0.25	15	8.1	7650	22	0.029	5	48
PSS 39C	40 m	16200	9	0.31	25	13	11600	29	0.039	9.5	81
PSS 46A	2 m	5540	1.5	0.3	8.7	7.1	4650	21	0.008	2.7	60
PSS 46B	20 m	6190	1.1	BDL	4.5	4	3700	4.2	0.028	1.4	9.3
PSS 46C	40 m	6160	2.4	BDL	6.4	6.4	4710	7.1	0.051	2.5	47
PSS 55A	2 m	7230	2.1	0.23	10	7.6	4510	25	0.028	4.6	94
PSS 55B	20 m	8510	2.2	0.17	12	4.4	5390	24	0.019	2.3	72
PSS 55C	40 m	8510	1.9	0.24	11	6.8	5040	19	0.024	3	162
PSS 55D	60 m	5910	1.9	0.22	9.2	5.8	3570	15	0.008	2.7	85
PSS 56A	2 m	6230	3.4	0.15	13	6.5	8600	34	0.01	3.2	45
PSS 56B	20 m	10300	2.1	0.13	12	4.9	5740	20	0.053	3.7	19
PSS 56C	40 m	4850	1.7	BDL	7	4.4	4170	7.4	0.008	2.6	16
PSS 57A	2 m	12400	3.2	0.26	16	11	8260	23	0.021	5.7	108
PSS 57B	20 m	11800	3.6	0.4	17	11	8930	25	0.019	5.4	96
PSS 57C	40 m	7970	2.6	0.2	11	5.9	4620	17	0.021	4	46
PSS 57D	60 m	5970	0.82	0.09	4.7	3.6	3430	5.4	0.011	2.2	24
PSS 58A	2 m	5110	1.1	0.14	6.2	9.8	3480	5.3	0.008	3.6	40
PSS 58B	20 m	15400	2.8	BDL	11	5.1	7700	5.9	0.011	4.5	29
PSS 58C	40 m	10700	2.3	0.091	8.2	5.6	5590	5.5	0.011	3.3	25

Table 16. Trace metal concentrations [mg/kg] as a function of proximity to a road (cont'd).

sample	dist. to rd.	Al	As	Cd	Cr	Cu	Fe	Pb	Hg	Ni	Zn
PSS 59A	2 m	5110	1.1	BDL	5.9	3.2	3680	26	0.005	1.8	24
PSS 59B	20 m	14400	2.1	0.11	10	6.3	7580	11	0.02	4.1	50
PSS 59C	40 m	9730	1.8	0.087	6.9	8.6	5100	9.7	0.019	3.3	27
PSS 66A	2 m	2310	1.3	BDL	3.9	3.5	2370	3.2	BDL	2.2	34
PSS 66B	20 m	6610	1.9	0.076	6.6	8	3800	4.7	0.008	2.1	23
PSS 66C	40 m	1430	0.56	BDL	1.4	0.48	828	1.6	BDL	0.33	2.3
PSS 76A	2 m	4370	1.6	0.29	9.3	11	3920	47	0.016	4.5	92
PSS 76B	20 m	1020	0.35	BDL	1.9	1.7	983	7.9	0.023	0.84	11
PSS 76C	40 m	1530	0.54	BDL	2.8	0.96	1070	4.5	0.006	1.2	8.5
PSS 77A	2 m	4160	1.1	0.14	7	6	3610	84	0.008	3.3	68
PSS 77B	20 m	1030	0.43	BDL	1.5	1.3	800	10	0.009	0.58	21
PSS 77C	40 m	4420	6.2	0.066	5.6	1.9	3280	3	BDL	0.61	4.4
PSS 77D	60 m	412	15	BDL	15	8.9	328	0.84	BDL	BDL	0.89
PSS 80A	2 m	9220	3.9	0.33	34	14	7710	48	0.013	4.4	108
PSS 80B	20 m	13200	3.6	0.24	21	6.9	9040	114	0.009	3.2	55
PSS 80C	40 m	9020	2.5	0.097	13	5	5650	14	0.007	1.8	80
PSS 91A	2 m	11300	1.9	0.1	10	5	6420	6.4	0.007	2	31
PSS 91B	20 m	9010	1.8	BDL	7.3	3.6	5350	5.8	0.011	1.9	18
PSS 91C	40 m	4030	0.9	BDL	3.4	1.6	2550	3.2	0.005	1.1	5.8
PSS 91D	60 m	3040	0.67	BDL	2.8	1.5	1960	2.3	BDL	0.87	8
PSS 97A	2 m	8330	2.6	0.11	7.3	8.1	5200	35	0.008	3.7	58
PSS 97B	20 m	2810	0.68	BDL	2.6	1.4	1990	7.1	0.03	1	12
PSS 97C	40 m	5340	0.91	BDL	4.2	2.1	3400	6.2	BDL	1.1	7.8
PSS 104A	2 m	4040	0.79	0.075	6.4	3.2	2890	24	0.012	2.2	29
PSS 104B	20 m	4430	1.1	BDL	4.6	3.7	2460	15	0.025	1.8	8.4
PSS 104C	40 m	3660	1.2	BDL	5.5	2.8	2230	9.3	0.023	1.9	19
PSS 116A	2 m	8580	2.2	0.37	15	7.5	6750	111	0.013	3.9	65
PSS 116B	20 m	5860	1.1	BDL	6.4	3.6	3450	14	0.018	3.2	20
PSS 116C	40 m	9080	2.3	0.14	11	7.1	6600	26	0.034	4.5	46
PSS 117A	2 m	9990	2.7	0.35	17	11	7240	48	0.017	6.3	76
PSS 117B	20 m	7010	1.5	0.09	8.5	3.8	5120	25	0.017	2	33
PSS 117C	40 m	17900	4.8	0.27	18	12	13100	37	0.062	11	49
PSS 117D	60 m	8100	2.4	0.12	11	5.5	5790	31	0.032	3.3	52

Table 17. Soil particle size, organic matter content, and pH.

Sample	clay [%]	silt [%]	sand [%]	OM [%]	pH
PSS 01	1.14	10.34	88.52	3.41	5.23
PSS 02	2.05	13.23	84.73	3.10	5.62
PSS 03	1.51	6.29	92.20	2.76	6.60
PSS 04	2.25	10.67	87.09	2.41	6.27
PSS 05	1.19	7.03	91.78	3.64	5.82
PSS 06	1.52	11.11	87.37	3.61	6.15
PSS 07	1.68	9.19	89.14	1.32	5.16
PSS 08	1.09	6.28	92.63	9.64	6.14
PSS 09	1.02	5.17	93.81	2.37	6.24
PSS 14	1.44	4.14	94.42	5.10	5.76
PSS 15	2.35	9.73	87.92	4.80	6.66
PSS 16	1.74	7.77	90.49	1.76	5.91
PSS 17	2.25	10.70	87.05	6.20	5.54
PSS 18	1.03	7.18	91.79	5.05	4.46
PSS 19	0.89	5.27	93.83	2.31	5.40
PSS 20	5.35	11.64	83.01	3.39	6.90
PSS 21	2.13	8.80	89.07	4.96	4.53
PSS 22	1.66	10.61	87.74	9.18	4.95
PSS 23	5.32	9.21	85.47	4.64	4.56
PSS 24	1.40	9.75	88.85	6.84	5.10
PSS 25	1.90	7.93	90.17	4.05	6.11
PSS 26	1.30	4.32	94.38	1.74	5.12
PSS 27	0.95	4.13	94.92	4.85	5.21
PSS 28	2.18	5.63	92.19	4.41	5.23
PSS 29	0.74	3.36	95.90	4.08	4.48
PSS 30	1.40	4.08	94.53	3.76	5.88
PSS 31	4.79	24.34	70.87	5.48	5.19
PSS 32	5.66	28.99	65.35	11.69	5.18
PSS 33	3.62	7.77	88.61	5.44	5.10
PSS 34	2.26	8.64	89.10	4.70	5.35
PSS 35	1.90	13.91	84.19	3.48	4.55
PSS 36	3.27	19.74	76.99	6.76	5.36
PSS 37	5.06	26.13	68.81	8.72	5.26
PSS 38	4.70	26.67	68.63	7.68	4.45
PSS 39	4.44	14.85	80.71	4.20	5.05
PSS 40	2.15	7.69	90.16	5.38	4.89
PSS 41	1.51	6.67	91.83	2.34	5.74
PSS 42	4.10	10.29	85.61	4.40	4.34
PSS 43	2.43	8.96	88.61	1.80	5.15
PSS 44	2.87	11.63	85.49	4.48	7.12
PSS 45	1.65	12.53	85.82	5.77	5.39
PSS 46	0.83	3.51	95.66	3.15	5.01
PSS 47	1.84	7.30	90.86	8.39	4.70
PSS 48	1.98	10.40	87.62	2.97	4.94
PSS 49	1.76	6.67	91.57	2.79	4.26
PSS 50	1.69	9.08	89.23	4.49	4.47

Table 17. Soil particle size, organic matter content, and pH (cont'd).

Sample	clay [%]	silt [%]	sand [%]	OM [%]	pH
PSS 51	5.00	16.63	78.37	6.79	4.54
PSS 52	6.72	22.58	70.70	5.45	5.19
PSS 53	1.46	4.47	94.07	3.55	5.15
PSS 54	1.96	13.27	84.78	7.43	5.61
PSS 55	2.46	6.93	90.61	8.19	5.68
PSS 56	5.83	14.20	79.97	6.30	5.09
PSS 57	5.99	16.96	77.05	7.85	5.14
PSS 58	3.67	13.25	83.08	3.12	6.12
PSS 59	1.71	7.08	91.21	4.91	4.77
PSS 60	3.58	13.56	82.86	8.36	5.24
PSS 61	5.53	19.56	74.92	7.78	6.04
PSS 62	2.00	6.96	91.04	3.39	4.76
PSS 63	1.83	8.29	89.89	4.20	4.44
PSS 64	1.32	3.07	95.62	1.73	5.26
PSS 65	2.05	11.64	86.31	2.95	4.55
PSS 66	1.47	4.04	94.49	2.50	5.52
PSS 67	2.23	6.44	91.33	4.01	5.11
PSS 68	0.81	2.77	96.42	3.54	3.95
PSS 69	2.06	6.72	91.23	1.32	6.77
PSS 70	1.35	3.90	94.75	6.44	4.26
PSS 71	1.02	5.51	93.47	2.37	6.02
PSS 72	0.88	3.67	95.44	7.43	4.52
PSS 73	0.26	3.70	96.04	3.09	4.92
PSS 74	1.48	4.18	94.34	2.20	5.80
PSS 75	1.14	4.49	94.37	3.95	4.66
PSS 76	1.18	2.04	96.78	2.91	6.63
PSS 77	1.92	9.35	88.73	3.18	5.77
PSS 78	0.86	4.99	94.15	3.54	5.18
PSS 79	0.97	5.36	93.66	7.41	5.46
PSS 80	0.49	2.06	97.45	7.65	4.08
PSS 81	2.06	6.11	91.84	1.10	6.93
PSS 82	0.69	2.36	96.94	6.12	4.86
PSS 83	2.25	7.29	90.46	6.66	4.76
PSS 84	1.30	3.74	94.96	2.73	6.35
PSS 85	2.23	10.03	87.74	4.22	5.58
PSS 86	1.56	6.72	91.72	2.72	5.00
PSS 87	1.22	7.61	91.16	1.84	5.80
PSS 88	1.58	5.67	92.75	2.88	5.47
PSS 89	3.12	8.80	88.08	3.43	5.60
PSS 90	1.51	6.44	92.05	6.37	5.20
PSS 91	4.78	11.66	83.56	3.36	5.05
PSS 92	1.55	9.20	89.25	2.16	4.69
PSS 93	1.98	8.85	89.17	6.46	4.78
PSS 94	0.81	2.07	97.11	1.68	5.46
PSS 95	1.80	15.23	82.97	4.65	6.55
PSS 96	2.17	4.56	93.27	2.08	4.77

Table 17. Soil particle size, organic matter content, and pH (cont'd).

Sample	clay [%]	silt [%]	sand [%]	OM [%]	pH
PSS 97	1.38	5.10	93.52	5.99	5.56
PSS 98	1.66	7.51	90.84	2.49	4.91
PSS 99	0.97	4.82	94.20	6.32	4.80
PSS 100	2.22	12.98	84.80	2.98	5.56
PSS 101	1.41	6.06	92.53	2.56	4.75
PSS 102	1.05	9.34	89.62	8.30	3.80
PSS 103	1.28	6.61	92.11	2.50	5.03
PSS 104	2.37	11.06	86.56	3.30	4.87
PSS 105	1.53	7.68	90.80	4.14	4.54
PSS 106	3.20	10.32	86.48	5.22	4.72
PSS 107	1.61	9.57	88.82	4.30	4.91
PSS 108	1.13	8.00	90.87	7.77	4.37
PSS 109	2.16	6.88	90.96	2.23	4.21
PSS 110	2.42	13.47	84.11	4.80	5.42
PSS 111	1.29	13.98	84.74	4.97	4.38
PSS 112	6.97	14.30	78.72	4.26	6.56
PSS 113	4.08	20.15	75.77	8.92	5.18
PSS 114	4.43	7.97	87.60	2.24	5.19
PSS 115	1.29	11.83	86.88	3.17	4.91
PSS 116	1.78	15.76	82.45	3.09	5.91
PSS 117	7.13	25.28	67.59	8.86	4.89
PSS 118	17.97	37.00	45.03	6.45	4.58
PSS 119	7.03	19.03	73.94	6.87	5.18
PSS 120	3.51	14.39	82.10	3.35	5.11
PSS 121	2.25	6.92	90.82	2.12	4.61
PSS 122	2.97	10.85	86.17	3.97	4.80
PSS 123	2.03	7.15	90.82	3.07	4.97
PSS 124	17.51	24.55	57.94	10.82	5.29
PSS 125	3.96	21.51	74.53	4.57	5.14
PSS 126	6.86	23.26	69.87	8.82	5.06
PSS 127	4.07	15.65	80.28	5.09	4.60
PSS 128	13.94	36.68	49.38	17.80	3.84
PSS 129	1.52	4.15	94.33	3.14	4.27
min	0.26	2.04	45.03	1.10	3.80
max	17.97	37.00	97.45	17.80	7.12
geomean	2.08	8.54	86.45	4.15	5.17