

Accepted Manuscript

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PII: S0883-2927(09)00123-1
DOI: [10.1016/j.apgeochem.2009.04.012](https://doi.org/10.1016/j.apgeochem.2009.04.012)
Reference: AG 2050

To appear in: *Applied Geochemistry*

Please cite this article as: Chiprés, J.A., de la Calleja, A., Tellez, J.I., Jiménez, F., Cruz, C., Guerrero, E.G., Castro, J., Monroy, M.G., Salinas, J.C., Geochemistry of soils along a transect from central Mexico to the Pacific Coast: A pilot study for continental-scale geochemical mapping, *Applied Geochemistry* (2009), doi: [10.1016/j.apgeochem.2009.04.012](https://doi.org/10.1016/j.apgeochem.2009.04.012)

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Geochemistry of soils along a transect from central Mexico to the Pacific Coast: A pilot study for continental-scale geochemical mapping

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Abstract

The Mexican Geological Survey (SGM), the National Institute of Statistics, Geography and Informatics (INEGI) and the Autonomous University of San Luis Potosí (UASLP) have established a multidisciplinary team with the objective of creating a national program of geochemical mapping of soils in Mexico. This is being done as part of the North American Soil Geochemical Landscapes Project in partnership with the U.S. Geological Survey and the Geological Survey of Canada. As the first step, a pilot study was conducted over a transect that extends from the Mexico-US border near Ciudad Juarez in the north to the Pacific Ocean in the south. This pilot transect was conducted in two phases, and this paper presents results from the first phase, which sampled soils at about a 40-km spacing along a 730-km transect beginning in Central Mexico and ending at the Pacific Coast. Samples were collected from the A and C horizons at each site and 60 elements were analyzed. This pilot study demonstrates that geochemical mapping based on a 40-km spacing is adequate to identify broad-scale geochemical patterns. Geologic influence (i.e., soil parent material) was the most important factor influencing the distribution of elements along the transect, followed by the influence of regional mineralization. The study also showed that influence by human activities over the transect is minimal except possibly in large mining districts. A comparison of element abundance in the A-horizon with the environmental soil guidelines in Mexico showed that the natural concentrations of the studied soils were lower than the established threshold for soil restoration with the exception of V and As. The former had a median value (75 mg/kg) approximately equal to the value established in Mexico for soil restoration in agricultural and residential lands (78 mg/kg), and the latter had 3 values higher than the 22 mg/kg threshold for soil restoration in agricultural and residential lands. These cases demonstrate the importance of knowing the national- and regional-scale geochemistry of Mexican soils as a support for the decision-making process, particularly for the proper formulation and application of soil guidelines designed to protect human and ecosystem health.

1. Introduction

The natural geochemical variability of the Earth's surface has been altered by different human activities that cause a redistribution of chemical elements in environmental compartments such as soils. Such changes are not well documented in many countries (including Mexico), because knowledge of the natural abundance and spatial distribution of the chemical elements

(geochemical landscapes) of their soils is generally lacking. Without such information about the geochemical distribution patterns of potentially toxic elements, it is difficult to recognize and impossible to quantify changes due to anthropogenic influence. Such information is also critical in determining areas that might exhibit problems in ecosystem or human health caused by enhancements in toxic elements or depletions in essential elements. In order to establish such baseline information, it is necessary to create a national geochemical database of soils in Mexico and to represent the spatial variability of these data through geochemical maps.

Initially, geochemical mapping of soils (and also stream sediments) was used as a tool for geochemical exploration. More recently, geochemical mapping has been applied to environmental studies as a way to identify, analyze and represent anthropogenic impacts (Darnley et al., 1995; Garrett et al., 2008). Now it is considered an essential tool for supporting the decision-making process related to environmental and health risk assessment of contaminated sites (De Vivo et al., 1998; Markus and McBratney, 2001; Rapant et al., 2008). Given the potential environmental and economic uses of the information generated by this type of geochemical study, several projects have been carried out at the national and regional scale in different parts of the world, including those conducted in North America (Shacklette and Boerngen, 1984; Smith et al., 2005), Europe (Vrana et al., 1997; Reimann et al., 2000; Navas and Machin, 2002; Plant et al., 2003; Salminen et al., 1998, 2005; Caritat et al., 2008) and Asia (Xie and Yin, 1993; Ohta et al., 2005; Ujiie-Mikoshiba et al., 2006; Xie et al., 2008). Some of these initiatives have already provided results of environmental and health relevance. For example, the national program of geochemical mapping of China delineated a region of low Se concentrations across the country. A detailed public health analysis of the region demonstrated the presence of two diseases associated with the deficiency of this element: Keshan (chronic cardiomyopathy) and Kaschin-Beck (endemic osteoarthropathy) diseases (Darnley et al., 1995; Selinus and Frank, 2000).

From an even broader perspective than a national scale, it is of interest from both a human health and environmental perspective to define geochemical patterns at continental and global scales. Coordination and cooperation among many different agencies and organizations in many different countries is required to successfully carry out such global-scale mapping. In spite of the logistical problems, diverse international groups have been working on coordinating such efforts. These include the International Geological Correlation Program's Projects 259 and 360 (Darnley, 1990; Darnley et al., 1995); the Forum of European Geological Surveys (FOREGS) Geochemical Baselines Working Group (Salminen et al., 2005); the Task Group on Global Geochemical Baselines (TGGGB) under the auspices of the International Union of Geological Sciences and the International Association of GeoChemistry (Darnley, 1997; Reeder, 2007); and the North American Soil Geochemical Landscapes Project (NASGLP) of the U.S. Geological Survey (USGS), the Geological Survey of Canada (GSC), and the Mexican Geological Survey (Servicio Geológico Mexicano, or SGM) (Smith et al., 2005, 2006, 2009; Smith and Reimann, 2008).

In 2002, the NASGLP was initiated to carry out a soil geochemical survey of North America. The project uses a sampling density of approximately 1 site per 1600 km² (13,500 sites for all of North America) and collects multiple soil horizons at each site. Pilot studies were begun in 2004 to

test sampling and analytical protocols and to optimize field logistics (Smith et al., 2009). These pilot studies included the collection and analysis of samples for organic compounds and microbial characterization. This paper presents the methodologies and results for one phase of the pilot studies conducted in Mexico.

The SGM recognized that the methodologies and experience necessary for successfully carrying out such a national project were dispersed among multiple institutions in Mexico. It would require cooperation between Federal and academic institutions to create a multidisciplinary team that could contribute with its knowledge, experience and opinions for the development of a national geochemical mapping project. The additional institutions invited to collaborate were the National Institute for Statistics and Informatics (INEGI) and the Autonomous University of San Luis Potosí (UASLP).

This multidisciplinary team immediately focused on the task of establishing a work plan that would be compatible with the TGGGB and the NASGLP (by that time pilot studies for the NASGLP were already underway in the USA and Canada), with the ultimate objective of creating a national program of geochemical mapping for the soils of the Mexican territory. The first step was the design of a pilot study consisting of soil sampling along a transect through Mexico that would connect with the pilot study transect across the USA and Canada (Smith et al., 2005, 2006, 2009) and would extend to the Pacific Ocean to the south. This tri-national transect would test and refine sampling and analytical protocols and would ultimately standardize these protocols among the participant institutions at a national level, as well as with the rest of North America. The pilot study transect in Mexico was accomplished in two phases: 1) Central Mexico – Pacific Coast (completed in 2006 and the subject of this paper) and 2) Central Mexico – border with US (completed in 2007).

2. Description of the Mexican pilot transect (phase 1)

The Mexican territory contains a great diversity of topography, climate, geology, soil types, vegetation and land use. The pilot transect was located to cross significant variations in all these factors, with the first phase representing a greater diversity than the second. The phase 1 transect begins in central Mexico, at the north of San Luis Potosi State, in an area known as the Altiplano Potosino. It crosses 3 states to the south (Guanajuato, Michoacán and Guerrero) and ends at the Pacific Ocean, for a total length of 730 km (Fig. 1).

This transect traversed 3 physiographic provinces that included mountains, valleys and coastal areas, and thus crossed a diversity of climates ranging from semiarid to temperate to tropical. Also, the transect crossed a diversity in vegetation zones, influenced by the natural factors mentioned above, including desert vegetation, pine and oak forests, agricultural crops, and rainforests.

2.1. Geology

The 3 physiographic provinces crossed by the transect are the Central Altiplano, the Trans-Mexican Volcanic Belt and the Southern Sierra Madre Range. These provinces present diversity in

lithologies including sedimentary, metamorphic and igneous (extrusive and intrusive) rocks as well as alluvial deposits (Fig. 2). Their principal geological features, as discussed in Calleja (2006) are:

1) Central Altiplano (San Luis Potosí State, Fig. 1): This region is mainly underlain by a thick sequence of continental sediments of Upper Triassic to Middle Jurassic age and marine sediments of Upper Jurassic to Upper Cretaceous age. Together they make up the Central Mexico Mesozoic Basin, which is in turn affected by magmatism ranging from Oligocene to Quaternary age.

2) Trans-Mexican Volcanic Belt (Guanajuato-Michoacán States, Fig. 1): A small and scattered volcanic-sedimentary basement of Late Jurassic to Lower Cretaceous age and of unknown thickness generally underlies a thick lava sequence and deposits of rhyolitic pyroclastic flows of early and middle Tertiary age that represent the southern extension of the ignimbritic province of the Western Sierra Madre Range. Miocene lavas represent the oldest events of the Trans-Mexican Volcanic Belt. Pliocene-Holocene age volcanic features, represented by numerous monogenetic volcanic fields, shield volcanoes, volcanic-tectonic depressions and intrusions of scattered rhyolitic domes, associated with numerous structural lineaments and circular features, occur in the area. Lacustrine sediments are frequently found surrounding the rift zone areas.

3) Southern Sierra Madre Range (Michoacán and Guerrero States, Fig. 1): In this last physiographic province, two different basements coexist. First, a volcanic-sedimentary basement of Upper Jurassic to Lower Cretaceous age named the Guerrero Terrain, which in this region contains siliciclastic marine sediments, carbonate platform sediments, and andesitic units usually metamorphosed to greenschist facies, as well as clastic sediments from continental environments. The second basement, the Xolapa Complex, is composed of igneous and sedimentary rocks metamorphosed to granulite and amphibolite facies, making a thick orthogneissic and paragneissic unit of Precambrian, Paleozoic and Mesozoic ages. Both basements are intruded by numerous Tertiary granitic stocks. Finally, thin beach and tidal sediments have recently been deposited in a narrow strip along the coast.

2.2. Soil types

The most arid and alkaline soils from the entire pilot transect are found in the northern part of the transect in the state of San Luis Potosí. In the higher elevations of this region are found thin soils rich in carbonates, identified as leptosols and regosols. This is also the only part of the transect where soils are found with a high content of secondary gypsum, sometimes cemented due to conditions of high evapotranspiration. These soils are very scarce in the world and are known as epipetric gypsisols.

At about 200 km to the south, the transect enters Guanajuato state, where thin soils are also found at higher elevations but with lower alkalinity. Some soils are cemented with silica at shallow depth (epipetric durisols and albic planosols). The agricultural lands are represented by luvic endoleptic phaeozems. One hundred km farther south, the transect intersects the Trans-Mexican Volcanic Belt (in Michoacán state), which contains very thick and clayey soils. The soils are primarily vertisols, which retain moisture well and have a good natural fertility. In some cases, they

have important concentrations of carbonates, but their primary quality is their elevated salinity caused by the excessive use of agrochemicals and irrigation waters.

In Michoacán and Guerrero states, thin soils are present in the mountains. Between the mountains and the coast of Guerrero, the most acidic soils in all the study area occur (in contrast with the northern part of the transect), most notably those containing kaolinitic clays, which are very vulnerable to erosion caused by deforestation.

The southernmost portion of the transect crosses the coast of Guerrero. Regosols occur in the high-elevation areas; young soils of fluvial origin, known as eutric fluvisols, occur in the middle elevations; and low areas contain soils of lacustrine origin, with high salinity due to marine influence (molic solonchaks). This is also the only region where coastal sandy soils (eutric arenosols) are found.

2.3. Land use and resource activities

The northern and central part of the transect is located over one of the most productive and important regions of the country, which includes the states of San Luis Potosí, Guanajuato and part of Michoacán. Together, these states represent major activities in agriculture, cattle ranching, commerce and industry. This region has several cities of regional importance including Matehuala, San Luis Potosí and Celaya, which have populations ranging from 80,000 to 1 million (INEGI, 2000). The southern part of the transect is less developed, with only medium- and small-sized towns.

Also of note is the important historical mining activity in the north and central regions of the transect. Mining has been conducted there since Mexico was a Spanish colony and represented an extremely important factor in the economic development of the states of San Luis Potosí and Guanajuato and for the northern part of Guerrero and Michoacán. There were important mining areas in the Altiplano Potosino (Au, Ag, Cu, Sb, Hg, Zn), the central area of San Luis Potosí (Au and Ag), the northern and western portions of Guanajuato (Au, Ag, Hg), the eastern part of Michoacán and the northwestern part of Guerrero (Ag, Cu, Sb). Ore deposit types range from veins to skarns, but only a small number of mines are currently in operation (SGM, 1996). However, the influence of mining on the region is evidenced by the development of important cities near ore deposits and mineral processing facilities and by the presence of the residues from past mining processes (e.g., tailings) that are now of environmental concern.

Advancing toward the coast, mining activities in the vicinity of the transect decrease, with some limited exploitation of Au, Cu and Ag in the mountainous areas of Michoacán and Guerrero, as well as some Au, Ag, Pb, Zn and W prospects distributed over this region (SGM, 1996).

Farming, ranching and industrial activities are important in some parts of the transect. The region known as El Bajío (the temperate lowlands of Guanajuato) is famous for its agricultural crops (corn, wheat, chili and other vegetables) and also its chemical, petrochemical, automotive, electronics and food industries. This area of agricultural and industrial development extends from Guanajuato to San Luis Potosí, in contrast with the mountainous areas of Michoacán and Guerrero.

3. Methodology

3.1. Sampling

The sampling design for the transect is based on the global geochemical reference network (GRN) (Darnley, 1997; Darnley et al., 1995). The GRN consists of a series of 160 x 160 km cells over the land surface of the Earth (approximately 5000 cells in total), and was established as a framework for global geochemical mapping. About 100 of the GRN cells are in Mexico and, for the purposes of national-scale geochemical mapping, each of these cells have been divided into sixteen 40 x 40 km subcells, resulting in approximately 1600 subcells for the country. For each of the 19 national subcells encompassing the transect (Fig. 1), a 1-km-wide latitudinal strip was chosen at random. The sample site was selected within each strip on the basis of the most representative landscape within the most common soil type (Smith et al., 2005, 2009). The site was also chosen to represent minimal anthropogenic influence. At 1 in 4 of the national subcells, a separate 1-km-wide latitudinal strip was randomly selected. Within this strip, a site was selected where two separate suites of samples were collected approximately 10 m apart. This resulted in a total of 24 sites for the transect.

Twelve of the selected sites were near sites where soils had been collected by INEGI during 2002-2004 in the course of their project to create a national soils map of Mexico. The sampling protocols used by INEGI were similar enough to the defined transect protocols that samples from the INEGI archives could be used. Thus, only 12 new sites had to be sampled along the transect.

The sampling procedure consisted of excavating a pit until reaching either the C horizon or consolidated bedrock to expose the entire soil profile. Samples were then taken from each soil horizon (O, A, B, and C) identified by INEGI specialists. For each sample, roots and large rocks were removed, and approximately 2 kg of soil was collected. The samples were kept in plastic bags and were labeled with the date, number of the cell and the corresponding horizon. At the same time, a field sheet was filled out with the characteristics of the soil profile and its landscape, including latitude and longitude coordinates and the date. The landscape and the soil profile were documented prior to sampling by a series of digital photographs.

Almost all the sites had well-developed soils with the presence of a C horizon. Nevertheless, there were some special cases such as the presence of thin soils over bedrock. In these situations, it was not possible to sample the C horizon. In order to give continuity to the data, sampling of the parent rock was done as a proxy for the C horizon. For deep alluvial soils, the C horizon was represented by a sample from about a 20-cm range at a depth of about 1.5 m.

3.2. Sample preparation and chemical analysis

For this study, only samples of the A and C horizons (top and subsoils) were prepared and chemically analyzed. The O and B horizons were stored for future studies. The samples were air-dried at 35 °C and then disaggregated by hand and sieved to <2 mm. Each sample was then homogenized and split into 3 representative portions: one for chemical analysis, one for the analysis of physical and chemical soil properties (e.g., color, pH, organic matter content), and one

for archival storage. The samples for chemical analysis were pulverized with a mechanical agate mortar to $<75\ \mu\text{m}$, and then homogenized. All the samples were randomized prior to chemical analysis to avoid confusing spatial variation with any possible systematic bias (Smith et al., 2005). A near-total decomposition using an acid mixture ($\text{HNO}_3\text{-HF-HCl-HClO}_4$) was used to dissolve the samples prior to analysis by a certified commercial laboratory (ALS-Chemex, Canada). Sixty major and trace elements were determined by a combination of inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) (Table 1). Many of the analyzed elements are important for environmental or public health (e.g., As, Pb and Hg), while others are of economic interest (e.g., Ag, Cu, and Zn) or represent elements of new importance to the field of environmental geochemistry (e.g., rare earth elements).

3.3 Quality control

To evaluate the precision of the chemical analyses, duplicates of randomly selected samples (5% of the total) were prepared and submitted to the laboratory as independent samples. The relative percent difference (RPD) between duplicates was calculated, setting a maximum acceptance criterion of 20% (Chirenje et al., 2001), which was satisfactorily achieved for almost all the analyzed elements with the exception of Ag, Ge and Se. In addition, the accuracy was evaluated using a certified standard reference material (NIST 2709 San Joaquin Soil) and an internal standard provided by the USGS (USGS SONE-1). These standards were randomly included within each batch of samples (equivalent to 10% of the total number of samples), and the accuracy was acceptable if the analytical recovery was between 80 and 120% (Chirenje et al., 2001). This criterion was met for almost all elements, with the exception of Cr and Tl (78% in both cases) and Zr (30%). On the other hand, the USGS SONE-1 had unacceptable recoveries for Se (400%). Additionally, the precision for the specific analysis of the standards was evaluated using the coefficient of variation (also known as relative standard deviation), using a criterion of $\text{CV}<20\%$, which was achieved by all the elements.

The quality control results were used to define which elements were suitable for data analysis. Additionally, an element was not considered for data analysis if more of 25% of the results were reported below the limit of detection (e.g., Re). For elements with less than 25% of the values below the detection limit, the nondetects were adjusted to one-half the limit of detection for purposes of statistical calculations (Reimann and Filzmoser, 2000; Zhang et al., 2005). After these processes, Re and Se were discarded from the data set, thereby reducing the number of reported elements to 58. In spite of their slightly low recoveries, Cr, Nb and Tl were included in the data analysis because of their importance from an environmental perspective.

3.4. Spatial analysis

The first step in spatial analysis was the integration of all the available and generated information in a geographic information system (GIS) using Arcview 9.0 (ESRI). The GIS incorporated the georeferenced sampling points; digital layers of soil type, land use, climate and geology; vector-based data of streams, urban areas, industries, mines and roads; and terrain elevation models.

4. Results

4.1 Statistics

Table 2 shows descriptive statistics for the 58 elements grouped by A and C horizons. Similar values for the mean and median indicate that some elements resemble a normal distribution (e.g., Bi, Cr, Hf, In and Pb), which was verified by checking their skewness and histogram. The rest of the elements presented a right-skewed distribution, similar to lognormal, but logarithmic transformations improved the distribution only in a few cases.

A Tukey boxplot (Kurzl, 1988) was generated for each element. Figure 3 shows these plots for selected elements of environmental interest. Although a detailed statistical analysis was not performed because of the small number (24) of sample sites, it was possible to obtain a general view of the geochemical behavior of the elements in soils of the transect by the use of correlations between soil horizons and their visualization in geochemical maps (Figs 4 and 5) or using correlations between elements (Figs 6 and 7). A scatter plot for each possible elemental association was generated, and a Spearman correlation analysis between all the variables was performed. This non-parametric technique was selected because of the absence of normal distributions and the presence of outliers for several elements, as shown by the Tukey boxplots.

4.2 Spatial representation

The geochemical results are represented in map form by points that increase in size as the concentration of the mapped element increases. The size of the points represents concentration ranges (classes) established from the boxplots. For this study, 5 classes were used: 1) $\leq 25^{\text{th}}$ percentile, 2) $25^{\text{th}} - 75^{\text{th}}$ percentile, 3) 75^{th} percentile to the value below the lowest outlier, 4) the lowest outlier to the value below the limit for extreme outliers, and 5) extreme outliers. Some elements did not exhibit outliers and extreme outliers, so those classes are not shown on some of the maps. For the maps of 8 elements in the A and C horizons in Figures 8 and 9, each point is shown at the center of the sampling cell rather than at its actual location. For cells with duplicate samples, the mean concentration was used for spatial representation.

5. Discussion

Preliminary analysis using the non-parametric Mann-Whitney test indicated little difference between the geochemistry of the A and C horizons except for Ag, Hg, P and Pb. These 4 elements show a higher concentration in the A horizon that may be attributed to human activities (e.g., Hg and Pb from industrial emissions). On the other hand, elevated concentrations occur in subsoils for some elements not generally influenced by human activities (e.g., Sr, Nb and the rare earth elements (REEs)). The Tukey boxplots in Figure 3 may be divided into two groups. The first group consists of elements having very similar distributions in both horizons (As, U and V), and therefore indicating a likely predominant geologic influence. The second group is made up of those elements that show a larger range of data and/or the presence of more outliers in the A horizon than in the C horizon, as shown by Ag, Hg, Cd, Cu, P and Pb.

Correlation analysis also demonstrates the association between element concentrations in A and C horizons (Fig. 4). In addition to the 4 elements shown in this figure, other elements with a strong linear relationship between the two horizons are Al, As, Bi, Co, Fe, Ga, Ti and REE's ($r > 0.80$). This behavior indicates the influence of soil parent material (bedrock) on patterns of geochemical distribution. For example, REE concentrations (represented by Tm in Figs 4 and 5), are generally highest in those areas underlain primarily by extrusive igneous rocks and lowest in areas underlain by sedimentary rocks (sandstones and limestones) (Fig. 5).

Other A-C related groups are represented by Fe, Co, Ti and V (Figs 6 and 7), which probably exhibit a geochemical control related to the presence of Fe oxyhydroxides in soils (Kabata-Pendias and Pendias, 2001; Myers and Thorbjornsen, 2004); and by As, Sb and Bi that show good correlation between both soil horizons, but have very low geochemical associations with other elements. This absence of geochemical correlation for particular elements may be attributed to the influence of mineralized areas (Zhang and Lalor, 2003). The presence of concentrations associated with possible mineralization is also represented by the outliers and extreme outliers in the box plots for elements in this group.

The identification of other large-scale factors with possible influence over the geochemical landscape of the transect was done using concentration distribution maps. The spatial distribution of As, Sb and Cd in Figures 8 and 9 are examples of probable influence by mineralized zones. The Altiplano Potosino (first 3 cells of the transect, from N to S) is well-known for the presence of Ag, Pb, Cu, Sb and Hg deposits (SGM, 1996). Many of these deposits contain associated As and Cd, resulting in elevated natural concentrations of these elements in the surrounding areas (Chiprés et al., 2008). The presence of these mineralized zones is reflected by the relatively high concentrations of these elements in the A and C horizons of soils from this region. Proceeding south along the transect, the concentrations of As and Sb decrease, with one site having an elevated concentration near the center of the state of Guanajuato (only observed in the A horizon because of absence of data for the C horizon from that site). This, again, is probably associated with known deposits of Hg and Sb (with associated As). Cadmium also shows lower levels south of the Altiplano Potosino area. South of the Guanajuato area, Sb and As show lower concentrations with the exception of a cell along the border of Michoacán and Guerrero. This site is underlain by sedimentary rocks that are intruded by rocks of andesitic composition and is located near ore deposits of Ag, Sb, Cu and Zn (SGM, 1996). It was expected that the geochemical patterns for these elements would be controlled to a large extent by the regional geology, basically by the difference between the igneous rocks from the central and southern part of the transect and the sedimentary rocks in the northern portion. However, this was not the case, as was previously seen during the correlation analysis. So, it is very possible that the mineralized areas in the north played an important role in masking this expected behavior.

Other elements whose distributions were also influenced by the mineralized regions were Hg and Cu, although the evidence of this phenomenon was less perceptible for the latter element. Mercury showed relatively high concentrations in A-horizon soils from the Altiplano Potosino, associated with the mineralization mentioned earlier. However, these concentrations were not

reflected in the C horizon, composed of weathered sedimentary rocks in these areas. The higher Hg concentrations observed in the A horizon may have an anthropogenic origin, because of the dispersion of this element as a product of mining activity and amalgamation processes during the past 200 a. Continuing along the transect to the south of the Altiplano Potosino, the concentrations of Hg decrease in A-horizon soils developed over extrusive igneous rocks from San Luis Potosí. The following cells with higher Hg concentrations in the A horizon (0.13-0.25 mg/kg) are located near known Ag, Hg and Sb deposits (SGM, 1996). In this part of the transect, the concentrations in the A horizon were similar to those observed in the C horizon.

In the case of Cu, higher concentrations have been reported in igneous rocks than in limestones (Kabata-Pendias and Pendias, 2001). This was not observed in the pilot transect, where soils in the northern part of the transect, dominated by limestones, contained higher Cu concentrations than the cells over felsic rocks at the center of San Luis Potosí and mafic rocks in Guanajuato. Once again, this observation is attributed to the presence of important Cu mineralization in the Altiplano Potosino (SGM, 1996). In the central part of the transect, the concentrations of Cu were similar for both horizons, being lower in the soils formed over felsic rocks than in those formed over mafic or intermediate rocks. The Cu concentration in the A horizon increases near the border between the states of Guerrero and Michoacán, where Cu, Pb, Ag and Zn mineralization has been reported (SGM, 1996). Near the coastal area, Cu again increases in the A horizon and somewhat less so in the C horizon, being attributed to some dispersed Cu mineralization around this area (SGM, 1996).

There are several zones along the transect where Pb mineralization is present, principally in the Altiplano Potosino and Guerrero state (SGM, 1996). However, the spatial distribution for Pb does not clearly delineate these zones. For the transect samples, this element shows a distribution without outliers (Fig. 3), which would be expected as indicators of mineralized zones or anthropogenic activities. Soils formed from extrusive and intrusive felsic rocks generally contain higher concentrations of Pb than soils formed from sedimentary rocks (Kabata-Pendias and Pendias, 2001). However, soils formed over the granites and granodiorites in the southern part of the transect show relatively low concentrations of this element (Figs 8 and 9). Correlation analysis shows a low association between the A and C horizons ($r=0.40$, $p<0.05$), so the geologic factor cannot be considered a determining one for the spatial distribution of Pb. In general, the A horizon has somewhat higher Pb concentrations than the C horizon, which may be attributed to human activities. However, a better understanding of the Pb distribution will be obtained after completion of the second phase of the transect.

Uranium and V do not show a complex distribution (Fig. 3) and they seem mainly related to geologic factors. Uranium has relatively high concentrations in A and C horizons associated with felsic igneous rocks in southern San Luis Potosí and at the coast of Guerrero. Vanadium shows a general increase in concentration in A-horizon soils from north to south. The most obvious factor that could explain this variation is the presence of limestones and extrusive felsic rocks in the northern part of transect, which are expected to have lower concentrations when compared to the mafic rocks from the central part (Kabata-Pendias and Pendias, 2001). The highest V

concentration in A-horizon soils is found at the southern end of the transect, even though the soil parent material consists of intrusive felsic rocks. A possible explanation could be the association of this element with the Au-Ag-Cu mineralization located around this region (SGM, 2006).

Comparison of A-horizon data with the environmental soil guidelines established in Mexico (SEMARNAT, 2007) showed that the median concentrations of the transect soils were lower than the threshold for soil restoration with the exception of V (Table 3). This metal had a median value approximately equal to the value established in Mexico for soil restoration in agricultural and residential lands. Three samples from the transect also had As concentrations in excess of the 22 mg/kg soil guideline (Fig. 3). These cases demonstrate the importance of knowing the national- and regional-scale geochemistry of Mexican soils as a support for the decision-making process, particularly for the proper formulation and application of soil guidelines designed to protect human and ecosystem health. Similar observations have recently been made by Rapant et al. (2008) for Europe.

6. Conclusions

The soil geochemical survey conducted along a 730-km transect through central and southern Mexico represents the first step in establishing a national geochemical database that will provide information to support the decision-making process in many fields, from environmental and public health to mining, exploration and agriculture. In particular, this pilot study demonstrates that geochemical mapping based on a 40-km spacing of sample sites is adequate to identify broad-scale geochemical patterns. Geologic influence (i.e., soil parent material) was the most important factor influencing the distribution of elements over all the transect, followed by the influence of regional mineralization. The study also showed that the influence of human activities over the transect is minimal, with the possible exceptions of local influence from mining and mineral processing. It also can be affirmed that there are some areas in Mexico with natural values of regulated elements (e.g., V and As) that exceed established soil guidelines.

The study also served to test and refine the sampling protocols to be used for the soil geochemical survey of North America. The sample design used for the transect was adequate to map the abundance and spatial distribution of elements at the broad scale and to gain insights on the large-scale geochemical patterns and the processes that led to the observed distributions. This national geochemical background information, along with the data from the ongoing follow-up studies (including bioaccessibility and water-solubility tests for all the transect samples), will be important references for future geochemical, environmental and public health studies in Mexico, including environmental guidelines.

Acknowledgements

The authors wish to thank R.A. Klassen (GSC) and D.B. Smith (USGS) for their reviews that greatly improved the manuscript.

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Fig. 1. Location of the national pilot transect phase 1.

Fig. 2. Simplified geologic map of the study area showing sampling sites of soil profiles and cell duplicates.

Fig. 3. Tukey boxplots of selected elements grouped by soil horizon (A: A horizon, C: C horizon). The outliers are represented by dots and the extreme outliers by triangles. All concentration units are mg/kg.

Fig. 4. Scatterplots of concentrations of 4 selected elements in the soil A horizon versus their respective concentrations in the soil C horizon. The correlation factors from Spearman correlation analysis are also shown ($p < 0.05$). All concentration units are mg/kg except for Ti (%).

Fig. 5. Geochemical distribution of Tm in A (left panel) and C (right panel) horizons from soils along the transect. The simplified geology is also shown.

Fig. 6. Scatterplots of concentrations in A horizon for selected elements. The correlation factor from Spearman correlation analysis are also presented ($p < 0.05$). Concentration units: Al, Ti, and Fe in %; Co, Ga, and V in mg/kg.

Fig. 7. Scatterplots of concentrations in C horizon for selected elements. The correlation factor from Spearman correlation analysis are also presented ($p < 0.05$). Concentration units: Al, Ti, and Fe in %; Co, Ga, and V in mg/kg.

Fig. 8. Spatial distribution of concentrations of selected elements in the soil A horizon across the study transect. The concentration intervals were chosen based on Tukey boxplots.

Fig. 9. Spatial distribution of concentrations of selected elements in the soil C horizon across the study transect. The concentration intervals were chosen based on Tukey boxplots.

Table 1

Lower detection limits (LDL) for the 60 analyzed elements in this study.

Concentrations are in mg/kg.

Element	LDL	Element	LDL	Element	LDL	Element	LDD
Ag	0.01	Eu	0.03	Mo	0.05	Sn	0.2
Al	100	Fe	100	Na	100	Sr	0.2
As	0.1	Ga	0.05	Nb	0.05	Ta	0.01
Ba	10	Gd	0.05	Nd	0.1	Tb	0.01
Be	0.05	Ge	0.05	Ni	0.2	Th	0.2
Bi	0.01	Hf	0.02	P	10	Ti	50
Ca	100	Hg	0.01	Pb	0.2	Tl	0.02
Cd	0.01	Ho	0.01	Pr	0.03	Tm	0.01
Ce	0.01	In	0.005	Rb	0.1	U	0.05
Co	0.1	K	100	Re	0.002	V	1
Cr	1	La	0.2	S	100	W	0.05
Cs	0.05	Li	0.1	Sb	0.05	Y	0.05
Cu	0.2	Lu	0.01	Sc	0.1	Yb	0.03
Dy	0.05	Mg	100	Se	1	Zn	2
Er	0.03	Mn	5	Sm	0.03	Zr	0.5

Table 2

Summary statistics of total concentrations in A and C horizons from the Mexican pilot transect phase 1 (N=29 for A horizon and N=25 for C horizon). Concentrations are in mg/kg except where noted .

Element	A horizon						C horizon					
	AM ^a	M ^b	Min ^c	Max ^d	SD ^e	MAD ^f	AM	M	Min	Max	SD	MAD
Ag	0.14	0.10	0.04	0.47	0.11	0.04	0.10	0.08	0.02	0.45	0.09	0.03
Al(%)	7.26	7.18	3.67	10.2	1.74	1.33	7.44	7.44	1.58	12.8	2.78	2.24
As	10.2	5.6	1.0	85.6	16.7	3.1	9.3	5.6	2.1	50	10.7	3.2
Ba	490	470	110	890	175	120	547	370	120	2400	471	180
Be	2.41	2.07	0.88	5.71	1.24	0.80	2.84	2.39	0.53	6.85	1.69	0.77
Bi	0.21	0.20	0.03	0.99	0.17	0.04	0.22	0.19	0.04	0.91	0.16	0.05
Ca(%)	3.32	0.69	0.16	16.85	5.22	0.43	6.09	1.06	0.04	29.2	8.88	0.78
Cd	0.27	0.16	0.04	1.08	0.26	0.11	0.21	0.12	0.01	0.95	0.22	0.09
Ce	61	56	27	116	26	15	60	50	15	119	28	18
Co	13.4	9.4	3.0	42.7	11.2	5.7	11.7	7.20	2.00	39.5	11.29	3.70
Cr	70.8	70.0	23.0	164	36.2	22.0	57.5	54.0	10.0	174	40.1	30
Cs	5.89	5.60	1.96	14.1	2.91	1.94	5.84	6.29	1.89	11.1	2.54	1.58
Cu	23.8	16.3	6.9	68.7	17.1	7.7	16.9	13.7	4.7	44.4	11.0	6.3
Fe(%)	3.13	2.80	1.38	6.88	1.41	0.92	2.92	2.28	0.69	7.09	1.74	0.86
Ga	20.2	21.7	9.0	28.6	5.0	2.8	21.4	21.8	3.1	35.1	8.2	6.9
Ge	0.16	0.16	0.08	0.28	0.06	0.05	0.15	0.16	0.05	0.27	0.07	0.05
Hf	4.2	4.0	0.5	8.7	2.5	1.5	4.7	3.6	1.0	12.4	3.3	1.6
Hg	0.09	0.05	0.02	0.55	0.12	0.02	0.04	0.03	0.01	0.15	0.03	0.01
In	0.06	0.05	0.03	0.12	0.02	0.01	0.06	0.06	0.01	0.12	0.03	0.02
K(%)	1.45	1.31	0.39	2.95	0.70	0.46	1.39	1.16	0.19	3.06	0.87	0.55

Table 2 (cont.)

Element	A horizon						C horizon					
	AM ^a	M ^b	Min ^c	Max ^d	SD ^e	MAD ^f	AM	M	Min	Max	SD	MAD
La	29.8	27.0	12.0	56.3	11.9	5.1	30.8	30.7	7.4	77.7	16.0	9.0
Li	34.4	26.9	15.2	84.5	17.4	9.4	38.7	34.1	12.7	87.5	20.0	13.1
Mg(%)	0.59	0.48	0.14	1.33	0.39	0.30	0.53	0.49	0.12	1.03	0.28	0.23
Mn	725	540	39	2420	600	222	507	319	76	2680	577	114
Mo	1.4	1.2	0.6	3.0	0.6	0.4	1.4	1.1	0.4	3.4	0.9	0.5
Na(%)	0.82	0.64	0.07	2.62	0.61	0.36	0.78	0.62	0.05	2.95	0.78	0.43
Nb	15.6	11.8	3.8	41.1	9.7	4.0	17.1	13.0	3.6	57.3	12.3	4.0
Ni	19.8	15.0	4.90	65.5	13.6	6.80	18.7	15.8	3.50	69.0	14.6	9.00
P	442	400	130	920	209	160	318	290	100	1120	209	120
Pb	18.9	18.6	6.9	35.1	7.4	6.5	15.3	14.3	4.0	30.2	6.7	3.5
Rb	93.1	76.4	18.3	189	51.6	29.8	90.1	72.4	7.0	194	52	39
S(%)	0.03	0.02	0.01	0.21	0.04	0.01	4.12	0.02	0.01	101	20.2	0.01
Sb	3.9	0.8	0.2	55.1	10.2	0.5	3.2	0.7	0.2	47.3	9.3	0.3
Sc	11.8	9.2	4.6	32.3	6.8	3.6	11.3	7.7	2.4	34.2	7.8	3.6
Sn	2.96	2.75	1.00	6.90	1.48	1.05	3.17	2.60	0.50	6.90	1.57	0.80
Sr	189	144	41.6	556	136	79.8	225	230	30.9	730	185	131
Ta	1.2	1.0	0.3	3.5	0.8	0.4	1.4	1.0	0.3	4.5	1.0	0.3
Th	9.4	8.6	1.7	23.5	5.1	3.0	10.5	10.4	1.3	23.8	5.5	3.4
Ti (%)	0.40	0.35	0.15	0.87	0.21	0.14	0.37	0.28	0.06	0.95	0.28	0.14
Tl	0.7	0.6	0.1	1.2	0.3	0.2	0.6	0.6	0.1	1.2	0.3	0.2

Table 2 (cont.)

Element	A horizon						C horizon					
	AM ^a	M ^b	Min ^c	Max ^d	SD ^e	MAD ^f	AM	M	Min	Max	SD	MAD
U	2.7	2.1	0.6	13.9	2.5	0.8	2.9	3.0	0.5	5.9	1.5	1.2
V	83.5	75.0	18.0	208	51.3	41.5	75.7	67.0	11.0	216	56.7	43.0
W	1.3	1.3	0.3	2.6	0.6	0.3	1.4	1.3	0.5	3.5	0.8	0.5
Y	24.9	21.5	6.8	55.4	12.5	8.1	28.6	21.9	7.8	74.9	18.3	6.6
Zn	70.5	70.0	25.0	118	26.0	20.0	63.4	65.0	25.0	132	29.2	20.0
Zr	129	127	10.2	314	79.1	42.4	134	114	17.6	334	94.8	60.0
Dy	4.5	3.7	1.6	11.0	2.4	1.3	5.1	3.9	1.3	13.6	3.2	0.8
Er	2.7	2.2	0.9	6.4	1.4	0.9	3.1	2.3	0.8	8.4	2.0	0.6
Eu	1.1	1.0	0.5	2.0	0.4	0.3	1.1	1.0	0.3	2.1	0.5	0.4
Gd	5.6	4.6	2.6	12.0	2.4	1.1	6.0	5.1	1.5	16.1	3.4	1.0
Ho	0.9	0.8	0.3	2.2	0.5	0.3	1.1	0.8	0.3	2.8	0.7	0.2
Lu	0.4	0.3	0.1	0.8	0.2	0.1	0.4	0.4	0.1	1.1	0.3	0.1
Nd	28.6	26.1	14.7	55.6	11.8	6.6	29.4	24.8	6.5	82.2	16.5	6.6
Pr	7.4	6.7	3.3	14.5	3.1	1.5	7.7	7.2	1.8	20.3	4.2	2.0
Sm	5.9	5.2	3.0	12.6	2.5	1.3	6.0	5.0	1.3	16.5	3.5	1.4
Tb	0.8	0.7	0.3	2.0	0.4	0.2	1.0	0.8	0.3	2.5	0.6	0.2
Tm	0.4	0.3	0.1	0.9	0.2	0.1	0.4	0.3	0.1	1.2	0.3	0.1
Yb	2.4	2.1	0.8	5.8	1.3	0.8	2.8	2.2	0.7	7.6	1.8	0.6

^a AM, arithmetic mean; ^b M, median; ^c Min, minimum value; ^d Max, maximum value; ^e SD, standard deviation; ^f MAD, median absolute deviation.

Table 3.

Comparisons of median concentrations in A-horizon for some elements of environmental relevance from the Mexican pilot transect phase 1 against reported soil background values in A horizon from North America and Europe. Data in mg/kg.

Element	MMex ^a	MNA ^b	MEu ^c	MCR ^d
Ag	0.1	<1.00	0.27	390
As	5.6	5	7.03	22
Ba	470	528	375	5400
Be	2.07	1.3	<2.00	150
Cd	0.16	0.2	0.15	37
Co	9.4	7.1	7.78	NR
Cr	70	27	60	280
Cu	16.3	12.7	13	NR
Hg	0.05	0.03	0.04	23
Mn	540	489	650	NR
Ni	15	13.8	18	1600
Pb	18.6	19	22.6	400
Sb	0.83	0.6	0.6	NR
Tl	0.58	0.5	0.66	5.2
U	2.1	2.1	2	NR
V	75	55	60.4	78
Zn	70	56	52	NR

^a M Mex, median values in A horizon of soils from the Mexican pilot transect phase 1;

^b MNA, median values in A horizon of soils from USA and Canada (Smith et al., 2005);

^c MEu, median values in A horizon of soils from Europe (Salminen et al., 2005); ^d MCR, NOM-147-SEMARNAT/SSA intervention values for soil restoration in agricultural and residential land use (SEMARNAT, 2007); NR, not regulated.

Fig.1

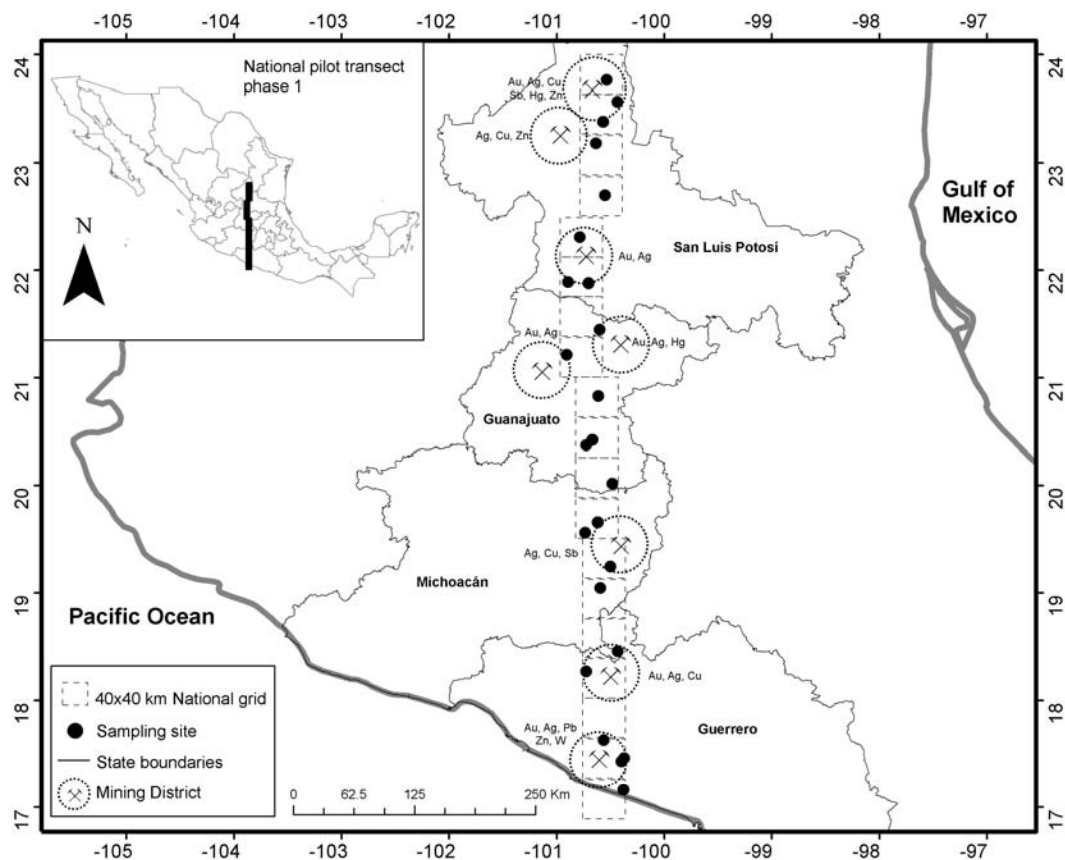


Fig.2

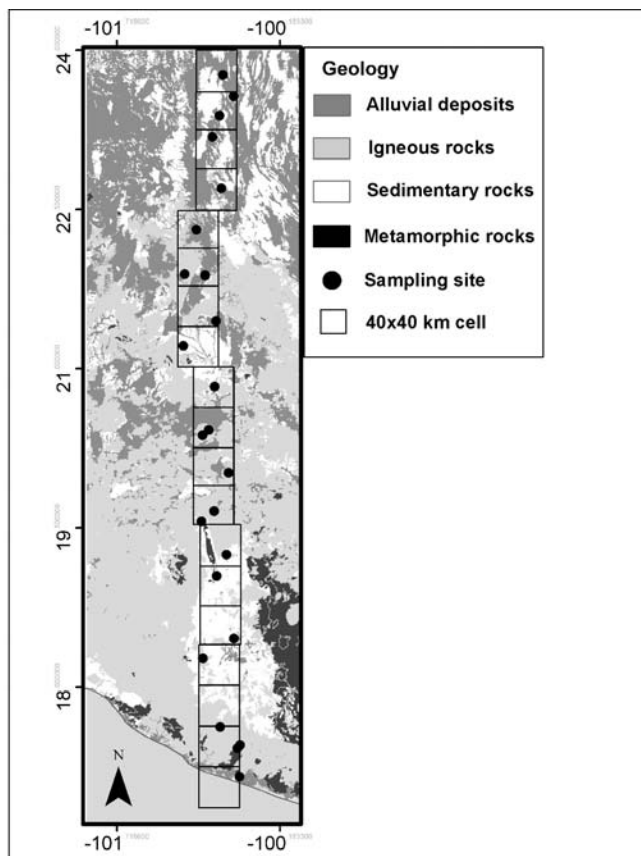


Fig.3

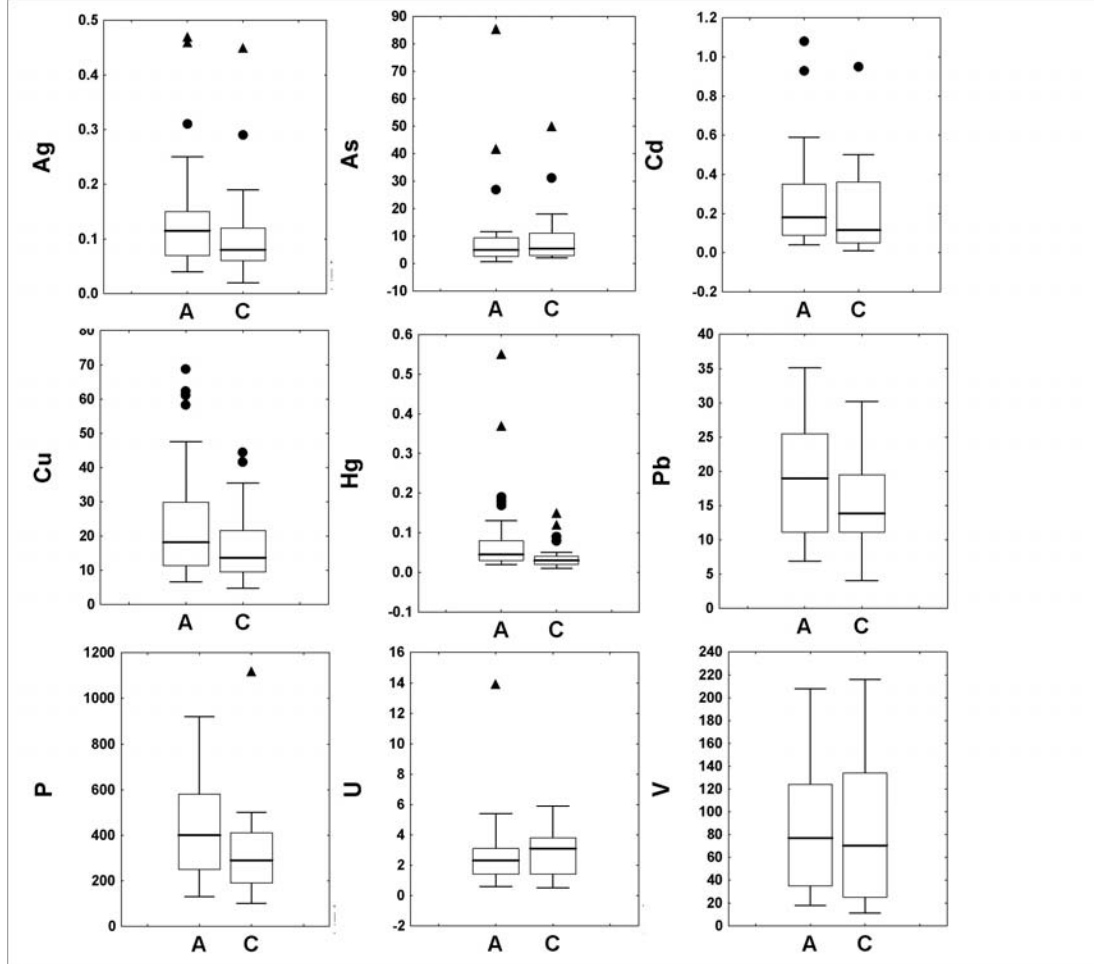


Fig.4

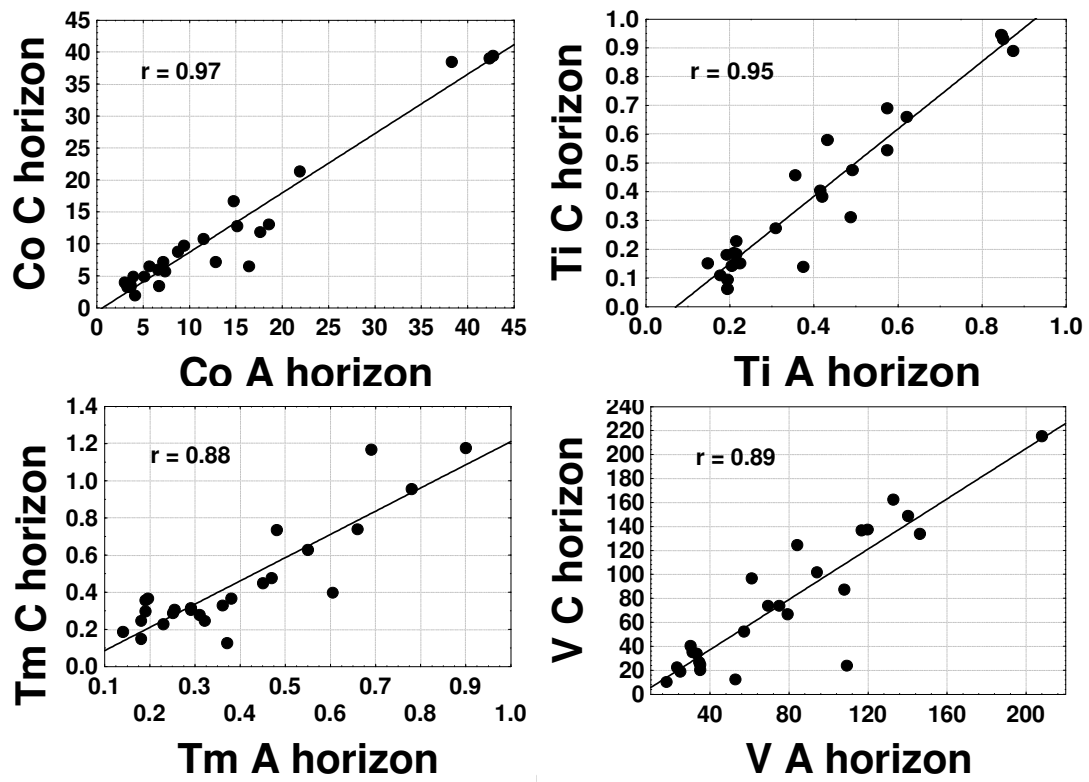
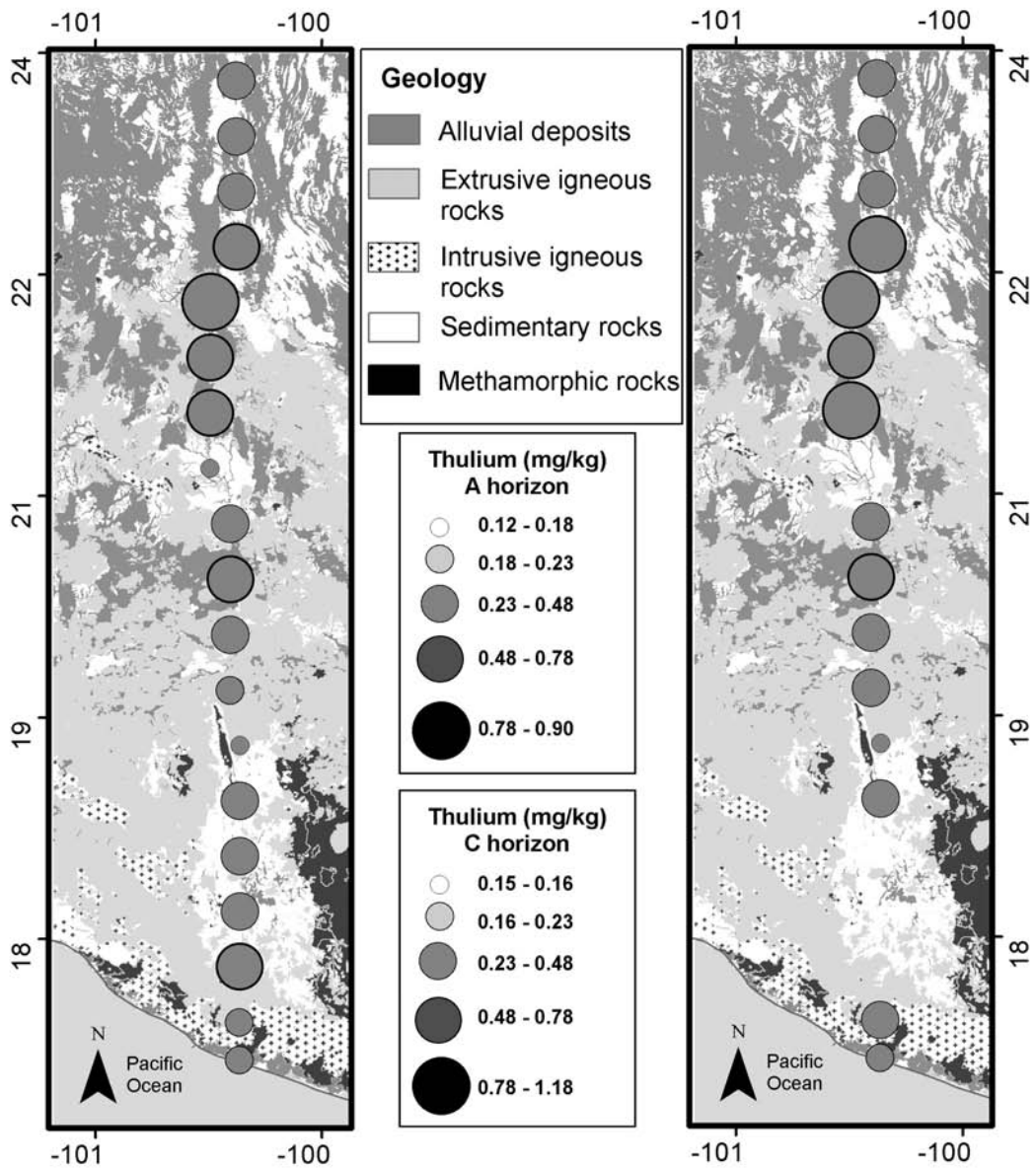
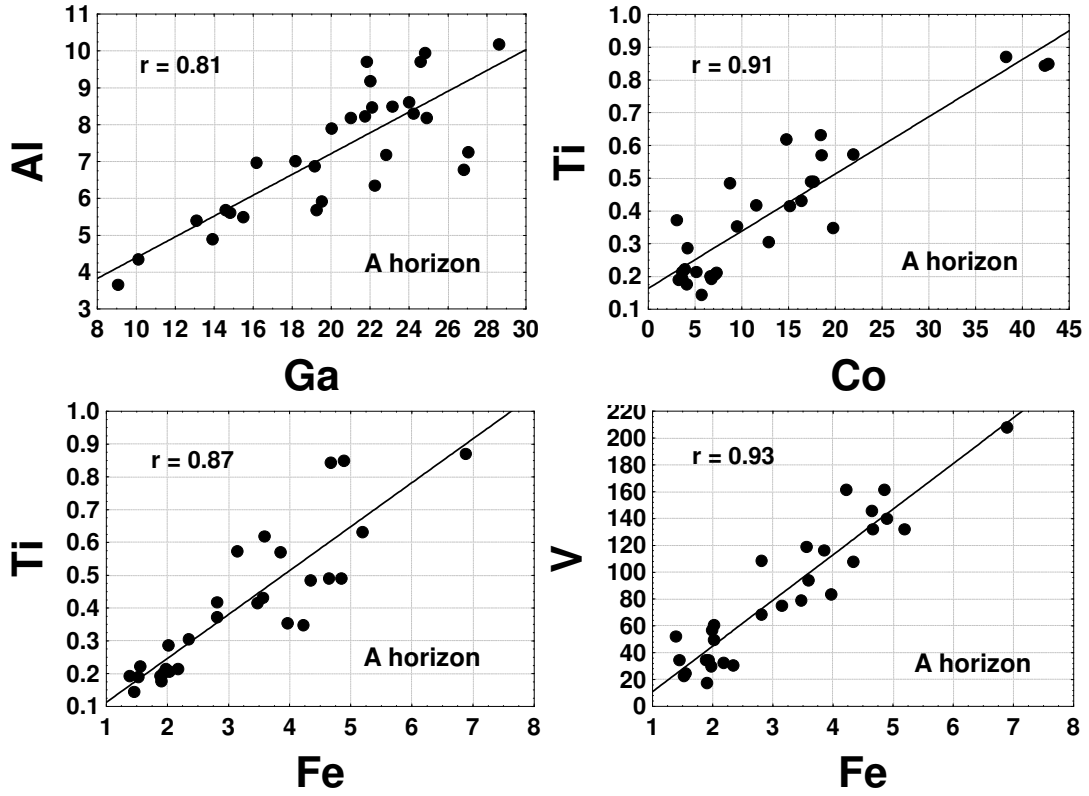


Fig.5



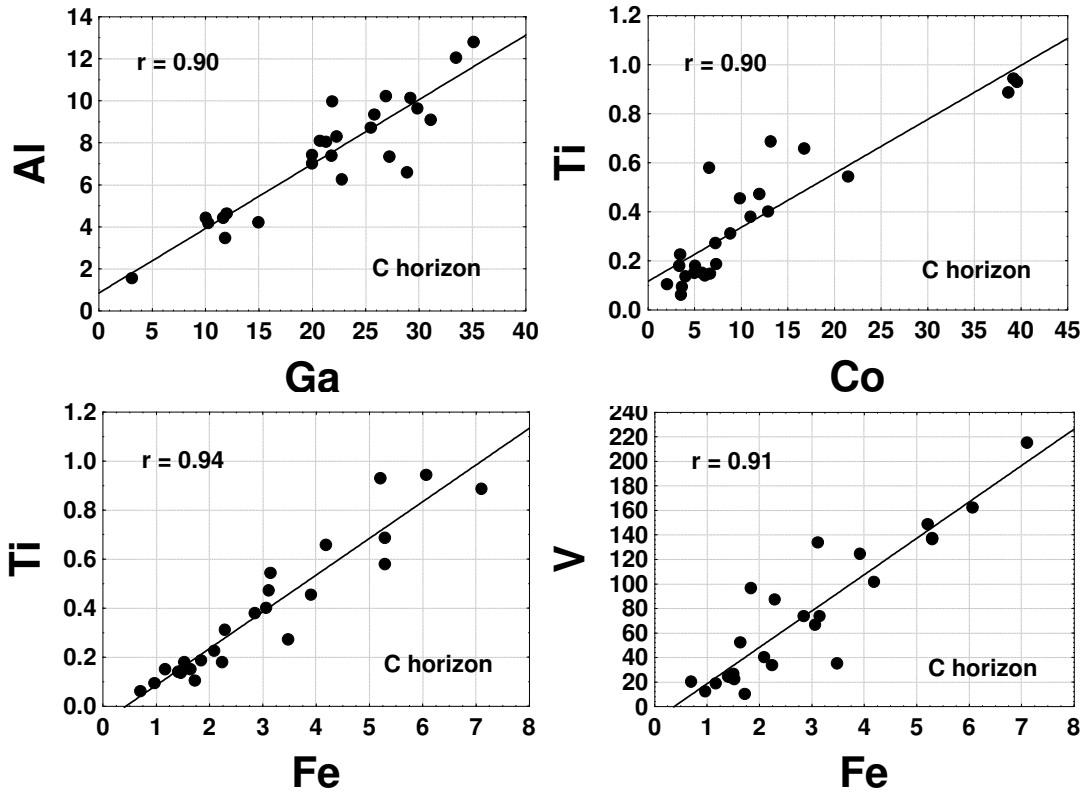
ACC

Fig.6



ACCEPTED MANUSCRIPT

Fig.7



ACCEPTED MANUSCRIPT

Fig.8

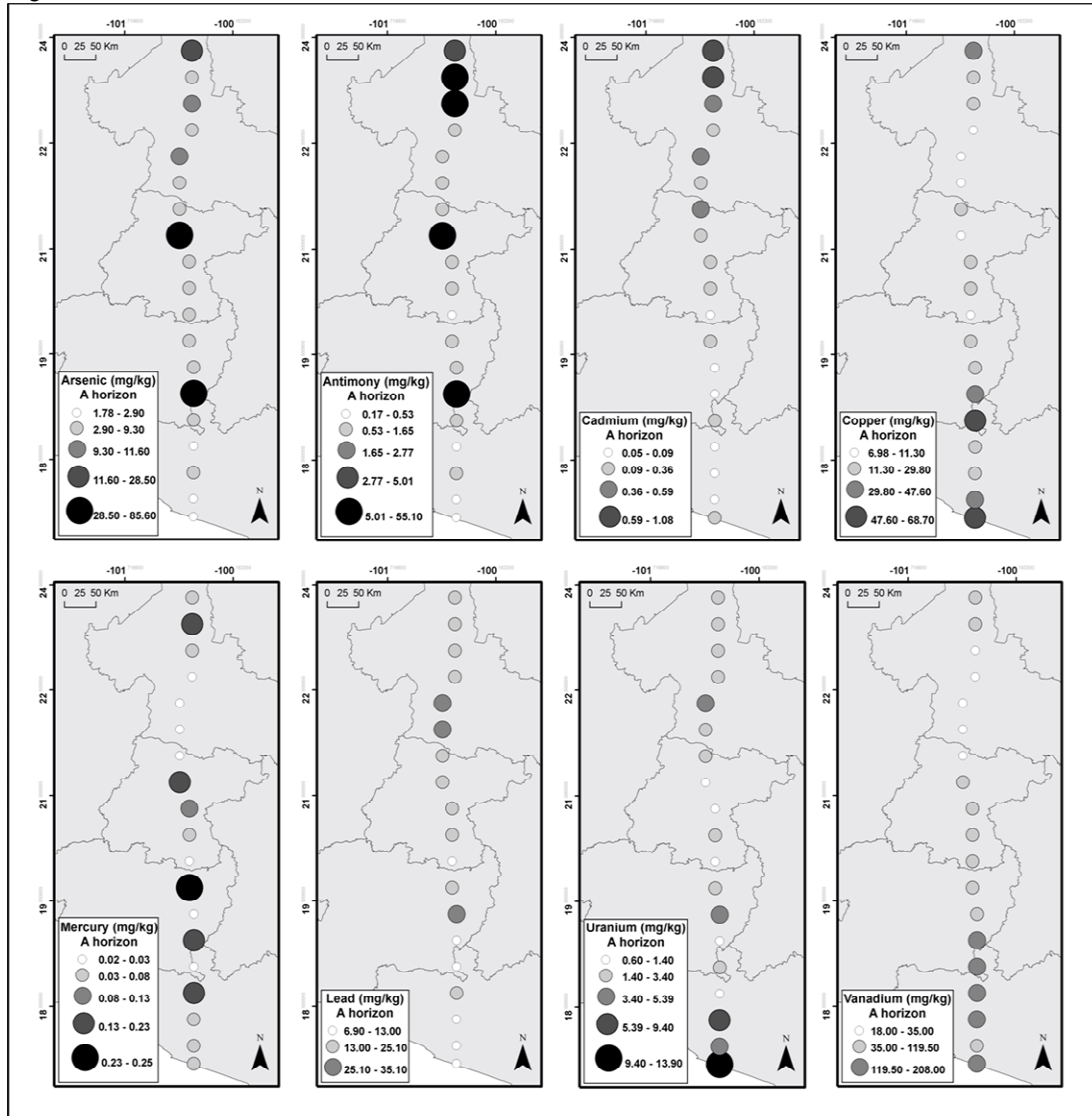


Fig.9

