



El Colegio de la Frontera Sur

Estudio de la composición química de los depósitos superficiales de la Península de Yucatán

TESIS

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DEDICATORIA

*Para Majito,
te fuiste demasiado pronto y dejaste un vacío en
nuestras vidas, pero me dejaste un par de valiosos
regalos por los que siempre estaré agradecida.
Espero que nos volvamos a encontrar algún día.*

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RESUMEN

El mapeo geoquímico en México hasta la fecha no ha sido concretado, siendo uno de los faltantes la Península de Yucatán, región biogeográfica ubicada en el suroeste de México que posee características geológicas que la diferencian del resto del país. Este trabajo describe los valores de fondo ambientales y la distribución de once diferentes elementos mayores y trazas (Ca, Fe, Ti, K, Mn, Cu, Pb, Sr, Zr, Rb y Nb) en los depósitos superficiales de la Península de Yucatán, con una densidad del muestreo de 1,600 m², mediante FRX, en el contexto geoquímico regional en escala 1:2,500,000. La metodología seleccionada demostró ser efectiva para revelar las tendencias de distribución de los elementos con los valores de fondo de Ca (0.64-27.78 %), Fe (0.16-9.05 %), K (0.13-1.72 %), Ti (0.09-1.29 %), Cu (5-146 ppm), Mn (158-3,770 ppm), Nb (4-62 ppm), Pb (9-94 ppm), Rb (20-181 ppm), Sr (29-1,537) y Zr (73-662 ppm). Se distinguieron algunos patrones coincidentes que sugieren la correlación entre elementos, como el caso del Ti, el Fe y el Nb, los cuales además expresan una relación inversa al Ca. En elementos como el Nb, Zr, Cu, Pb, Rb y K se observaron los valores más altos cargados hacia la zona noroeste de la PY. El mapeo geoquímico de la PY obtenido revela las diversas áreas de oportunidad para continuar las investigaciones, tales como la descripción del contexto geoquímico regional y las aplicaciones en áreas como la agricultura, salud, contaminación y paleoecología.

Palabras clave: suelo; sedimentos superficiales; kriging; valores de fondo ambientales; FRX.

INTRODUCCIÓN

Hasta el día de hoy, se ha descrito en términos de geoquímica aproximadamente el 25% de la superficie terrestre. China, Estados Unidos y Australia han sido los líderes en caracterización geoquímica de su territorio (Caritat et al. 2018), aunque también es notable el esfuerzo de muestreo realizado en el continente Europeo (Caritat et al. 2008; Demetriades et al. 2010; Smith et al. 2013; Wang y CGB Sampling Team 2015). En el continente americano, representantes de los Gobiernos canadiense, estadounidense y mexicano acordaron en el año 2001, generar conocimiento sobre la distribución elemental de sus territorios. En respuesta a esta necesidad, se fundó el proyecto *North American Soil Geochemical Landscapes Project (NASGLP)*. En el año 2010, Estados Unidos de América finalizó de manera exitosa el proyecto titulado *Soil Geochemical Landscapes of the Conterminous United States (SGL)*. Como resultado, se generó una base de datos de 45 elementos químicos y minerales con una densidad de muestreo de 1/1,600 km² (Smith et al. 2013). Sin embargo, el acuerdo trinacional no se concretó de acuerdo con lo planteado debido a la salida de Canadá, y a que México no ha publicado resultados (Caritat et al. 2018).

El Servicio Geológico Mexicano (SGM), el Instituto Nacional de Estadística, Geografía e Informática (INEGI) y la Universidad Autónoma de San Luis Potosí (UASLP); establecieron un equipo de trabajo con la finalidad de crear mapas nacionales de geoquímica. En los años 2008 y 2009 publicaron los resultados de un estudio piloto realizado a lo largo de la zona conocida como el altiplano Potosino, a partir del cual se probó y propuso la metodología de mapeo en al cual se basa el presente trabajo (Chiprés et al. 2008, 2009).

La Península de Yucatán posee características ambientales que la diferencian de otras regiones de México y el mundo. Se considera una provincia biogeográfica por su historia geológica, expresada en su paisaje cárstico y los efectos de su alta permeabilidad y disolución, la hidrología casi totalmente subterránea, además de las condiciones tropicales que imperan (Bautista et al. 2005; Torrescano-Valle y Folan 2015). Esta combinación única de condiciones es un factor que ha propiciado un sistema peculiar al que se han adaptado un gran número de organismos vivos. Por lo

tanto, comprender la disposición de los elementos mayores y trazas, así como la dinámica entre el suelo y los componentes con los que está vinculado, es esencial para el diseño de medidas de conservación, aprovechamiento de recursos y ordenamiento del territorio.

Es pertinente asumir que la larga historia de ocupación humana y uso del territorio en la región, ha tenido un efecto sobre las condiciones geoquímicas originales del suelo y otros regolitos. Muchas sustancias producto de actividades humanas tienen la capacidad de transportarse largas distancias y depositarse en ambientes aparentemente prístinos. Debido a esto, se considera que es sumamente complicado conocer los verdaderos valores naturales de los elementos. Al hablar de mapeos geoquímicos, es importante distinguir entre los conceptos: “valores de fondo naturales”, que se refieren a las condiciones originales del suelo, y los “valores de fondo ambientales”, que describen las condiciones que han sido perturbadas en proporciones desconocidas (Reimann y Garret 2005). Los valores de fondo ambientales describen los rangos en los que se pueden encontrar actualmente los elementos, para lo cual se adoptan metodologías que permiten que se asemejen lo más posible a los valores de fondo naturales.

Las actividades humanas modifican los ciclos naturales de los elementos en la Tierra. En consecuencia, es de urgente necesidad conocer los valores de fondo de elementos críticos en los diferentes componentes del ambiente, con el objetivo de fortalecer los mecanismos de planeación, manejo y saneamiento ambiental (Négrel et al. 2019). El mapeo geoquímico de valores de fondo ha probado ser de utilidad para el monitoreo de elementos potencialmente dañinos para la salud humana en zonas urbanas (Romic y Romic 2003; Wei y Yang 2010; Demetriades et al. 2018), esto debido a que existe una alta correlación entre la concentración de los elementos en la sangre humana y la superficie de la Tierra (Hamilton et al. 1973). Debido a esto, la información geoquímica también se ha empleado para temas agrícolas (Thornton 1980; Bhuiyan et al. 2010; Esmaeili et al. 2014).

Los mapeos geoquímicos son esenciales para la identificación de anomalías en el suelo, las cuales conducen hacia yacimientos minerales de interés para extracción y aprovechamiento (Boyle 1982; Reis et al. 2001; Yaylali-Abanuz et al. 2012; Zhao et al.

2015). Otra aplicación importante de los estudios geoquímicos es en la reconstrucción de ambientes pasados, en disciplinas como paleoecología y arqueología (Koulikova 2005; Oonk et al. 2009; Amorim-Costa et al. 2013 Beverly et al. 2018; Roy et al. 2018). La presente investigación tiene como objetivo conocer los valores de fondo ambientales y describir la distribución elemental en los depósitos superficiales de la Península de Yucatán, para explorar en el contexto geoquímico regional los patrones de distribución. La tesis se encuentra conformada por una introducción, que señala algunos antecedentes importantes sobre el tema de estudio, seguida por el artículo científico obtenido como resultado de esta investigación, el cual fue sometido a una revista para su publicación. Posteriormente se presentan los principales resultados y conjeturas a manera de conclusiones, junto con la descripción de las áreas de oportunidad identificadas en el rubro. Finalmente se detallan las fuentes de la literatura citada y se anexan los mapas de geoquímica obtenidos, en su versión a colores.

ARTÍCULO CIENTÍFICO SOMETIDO PARA PUBLICACIÓN

CONCENTRATIONS AND DISTRIBUTIONS OF MAJOR AND TRACE ELEMENTS IN SURFACE SEDIMENTS ACROSS THE YUCATAN PENINSULA, MEXICO

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Abstract

National geochemical mapping in Mexico to date has not been completed and the Yucatan Peninsula, located in southwestern Mexico, has geological characteristics that differentiate it from other regions. This work describes the environmental background values in the superficial deposits of the Yucatan Peninsula with a sampling density of 1,600 m² and the distribution of eleven different major and trace elements (Ca, Fe, Ti, K, Mn, Cu, Pb, Sr, Zr, Rb and Nb) by XRF in the regional geochemical context at a scale of 1:2,500,000. The selected methodology proved to be effective in revealing element distribution trends with background values of Ca (0.64-27.78%), Fe (0.16-9.05%), K (0.13-1.72%), Ti (0.09-1.29%), Mn (158-3,770 ppm), Pb (9-94 ppm) and Sr (29-1,537). Some coincident patterns were distinguished that suggest the correlation between elements, as in the case of Ti, Fe and Nb, which also express an inverse relationship to Ca. For elements such as Nb, Zr, Cu, Pb, Rb and K, the highest values were observed in the northwestern part of PY. The distribution maps evidence areas for new research to continue the description of the regional geochemical context and applications in the area of agriculture, health, contamination and paleoecology.

Key words: soil; surface sediments; kriging; background values.

1. Introduction

Systematic geochemical mapping is considered as one of the available methods to document changes in chemical element levels in materials occurring near the earth's surface (Demetriades et al. 2010). In addition, low-density mapping is a tool with a suitable cost/benefit for recognizing environmental background values of the soil surface, as it reveals distribution patterns that match those of mappings conducted at higher sampling densities (Smith & Reimann 2008; Garret et al, 2008; Birke et al. 2015). Négrel et al. (2019) have demonstrated the utility of low-density mapping to identify areas of interest (Xie et al. 1989; Demetridades et al. 2010; Reinmann & Caritat 2017). It is of particular importance to know the abundance of trace elements because some are essential micronutrients for plants and animals, so their concentration is a factor that must be considered in the allocation of land uses for conservation or agriculture and livestock areas (Maskall & Thornton 1991; Ferreira Da Silva et al. 2009; Jacinto Oliveira et al. 2018).

Terrestrial geochemical characterization in China, the United States, Australia and the Europe region comprise approximately 25% of the Earth's surface (Caritat et al. 2008; Demetriades et al. 2010; Smith et al. 2013; Wang & CGB Sampling team 2015; Caritat et al. 2018). The origin of mapping is closely related to mining interests. It's essential application for the identification of mineral deposits of interest for extraction and exploitation is now recognized (Boyle 1982; Reis et al. 2001; Yaylali-Abanuz et al. 2012; Zhao et al. 2015). Geochemical mapping is also useful for monitoring elements potentially harmful to human health (Romic and Romic 2003; Wei and Yang 2010; Demetriades et al. 2018), shown by high correlation between the concentration of elements in human blood and the earth's surface (Hamilton et al. 1973).

Human occupation and land use have had an effect on the original geochemical conditions of soil and other regolith (such as sediments from water bodies or floodplains). Substances resulting from human activities have the ability to be transported long distances and deposited in apparently pristine environments. Because of this, it is extremely difficult to know the true natural values of the elements. There are two terms that are still in scientific discussion, "natural background values" to refer to

original conditions and "environmental background values" to describe conditions that have been disturbed to unknown extents (Reimann and Garret 2005). Human activities, such as resource extraction, industry and waste generation, modify the natural cycles of elements on Earth. Consequently, there is an urgent need to know the background values of critical elements in the different components of the environment, with the objective of strengthening environmental planning, management and remediation mechanisms (Négrel et al. 2019). Geochemical mapping projects use methodologies to minimize anthropogenic influence, although this does not mean that it is possible to know what conditions were like before the disturbance. Environmental background values describe the range of elemental concentrations resulting from the heterogeneity of conditions within a specific region (Reimann and Garret 2005).

In Mexico, the publication of the National Geochemical Atlas has not yet been achieved and the multiple mappings had approaches with social, geographic and environmental themes (SEMARNAT, 2006; INEGI n.d.). However, Chiprés and collaborators (2008, 2009) have developed the geochemical mapping methodology for the central portion of the country. The present research aims to know the environmental background values and describe the elemental distribution in the surface deposits of the Yucatan Peninsula, and to explore the regional geochemical context of the distribution patterns.

2. Study area

The Yucatan Peninsula (YP) is located in southwestern Mexico and has environmental characteristics that differentiate it from other regions of Mexico. It is considered a biogeographic province because of its geological history and its a karstic landscape of high permeability and dissolution. The hydrology is almost entirely underground, in addition to the tropical conditions that prevail (Bautista et al. 2005; Torrescano-Valle and Folan 2015). Climate is mostly warm and humid ($Awo(x')$, Awo , $Aw1(x')$, $Aw2(x')$, $Aw2$, $Am(f)$), with small arid and semiarid areas ($BS1(h')w$ y $BSo(h')(x')$) in the northwest part of the YP (CONABIO 2008a). Humidity levels goes from arid (BW) and semiarid (BS1) in the Norwest coast to subhumid ($w0$, $w1$ y $w2$) towards the southeast (CONABIO

2008b). This unique combination of conditions has fostered a peculiar system to which a large number of organisms have adapted.

The landscape is composed by alluvial, lacustrine, littoral, paludal, and sandstone from the quaternary, Miocene limestone, Pliocene and Oligocene limestone-conglomerate, Eocene limestone-marl and Paleocene limestone-gypsum (Bautista et al. 2011). The superficial deposits of the YP are grouped into four geomorphological landscapes or subregions: (1) karst subregion, which is the predominant landscape of the region, where neotectonic activity is combined with rock dissolution; (2) karst-tectonic subregion, where high hills and elevations are found, because of inactive tectonic activity; (3) fluvio-palustrine subregion, which describes low areas of periodic flooding with processes of accumulation and hydromorphism; and (4) littoral subregion, which is the transition zone between the ocean and the continent where processes associated with wave dynamics, tidal and littoral drift occur (Bautista and Palacio 2011). Environmental conditions have given origin to 4 groups of soils: sandy, along the coast; organic, developed in wetlands, in the central part are the plain soils (distinctive by its red color) and mound soils (normally black) (Estrada-Medina et al. 2019). On these subregions, Leptosol, Gleysol, Phaeozem, Vertisol, Cambisol, Luvisol and Nitisol soils are developed in a higher proportion (Bautista et al. 2015; Fragoso-Servón et al. 2017; Palma-López et al. 2017). This variability in soils is caused by intrusion of marine sediments, volcanic material and African dust, that are mixed with the local karstic sediments (Cabadas et al. 2010; Das et al. 2013).

2. Materials and Method

2.1 Sampling

Sample collection was carried out based on the methodology recommended by Chiprès et al. (2009) and Smith et al. (2009). Each sample represents a cell within a 40 by 40 km grid in the territory of the Yucatan Peninsula and samples were randomly extracted within each cell (Fig. 1). Composite samples were collected from the top layer of sediment/soil in the first 5 cm, after removal of leaf litter and the first 5 cm of material

(Salminen et al. 1998, Cicchella et al. 2013). Samples were collected at sites with as little human impact as possible, so that environmental background values could be determined. The sampling density was 1/1,600 km² and the scale of the resulting maps was 1:2,500,000. One duplicate was taken randomly every four cells for quality control. Ninety-two samples and 24 duplicates were collected, which covered 98% of the proposed cells. Based on the field observations, a database was constructed with information on the characteristics of each sampling site, such as vegetation type, dominant plant species, relief, elevation, soil type, color and moisture, rockiness, conservation status and surrounding activities.

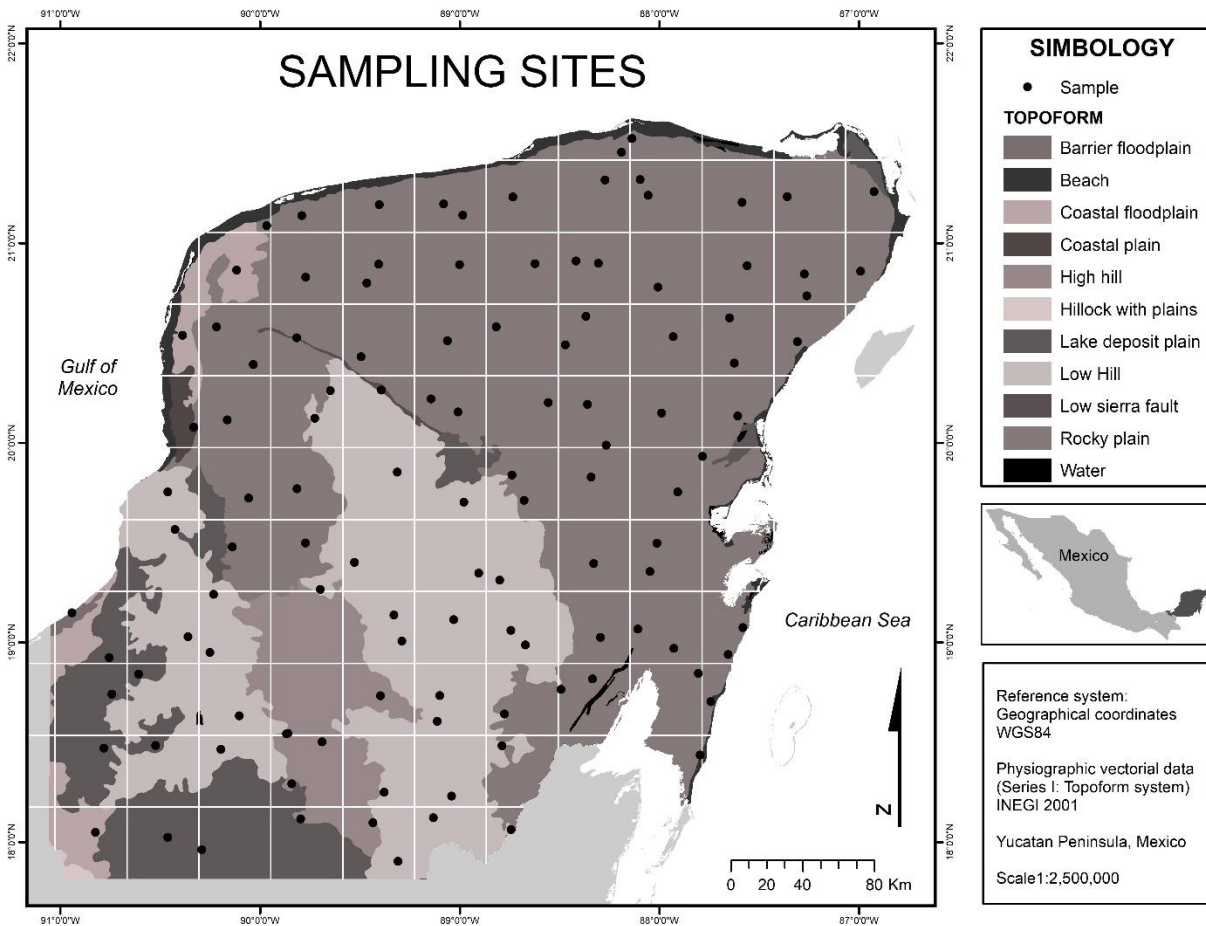


Fig. 1 Location of sampling sites across the Yucatan Peninsula for the geochemical mapping of some elements in surface deposits.

2.2 Geochemical analysis

Samples were dried in a convection oven at 65°C, ground in an agate mortar to a fine texture and prepared for analysis following the recommendations of Mejía-Piña et al. (2016). Eleven major and trace elements Ca, Cu, Fe, K, Mn, Nb, Pb, Rb, Sr, Ti, Zr were quantified with Thermo Scientific Niton XL3t 600 X-ray fluorescence equipment. In order to reduce the percentage of error, the samples were analyzed random and duplicate measurements were considered in each reading batch to determine the precision error. All data were corrected using as reference the UNAM Institute of Geology standards IGLs1-1, IGLa1, IGLD-1, IGLgb-3, IGLsy-1, IGsy-4, IGLsy-2, IGLc-1, as well as Es-2 Black Shale Estonia 2000, Es-4 Dolostone EST 1A, NIST 2709a PP 180-649, NIST 2702, CCRMP TILL-4PP180-649 and QC USGS SAR-M 180-673. In addition, the precision and accuracy of the readings were calculated for each element.

The Thermo Scientific Niton XL3t 600 equipment can read up to 29 different elements, however, only 11 elements are addressed in this paper due to the lack of appropriate reference materials for a matrix such as the YP. The present study evidenced the need for more reference materials for this kind of materials.

2.3 Data analysis

A statistical exploration of the data was carried out to obtain the mean, median, minimum, maximum, standard deviation and mean absolute deviation (Table 1). Boxplots were made with software R version 4.1.0. ggplot2 pack (Wickham 2016). Figure 2 shows the boxplots corresponding to these values.

The database was transformed with base 10 logarithm and georeferenced using ArcMap software version 10.3 (Esri, 2015). To obtain continuous geochemistry data, geostatistical interpolation tools were applied. The parameters were adjusted to suit the trends of each element and to obtain models with the lowest possible error. The interpolation method used was ordinary Kriging (Chiprés et al. 2009; Smith et al 2013; Caritat 2018; Négrel et al. 2019). The data estimated by each model were evaluated by the cross-validation method, considering a confidence value of 95 %.

4. Results and discussion

Less than 1% of the samples showed concentrations of all elements below the detection limit, except for Cu (4.3%, n=5 (see Table 1 of supplements for detection limits). Half of the limit value was assigned during interpolation for elements with values below the detection limit of the instrument (Reinmann and Filzmoser 2000; Zhang et al. 2005). The accuracy of the instrument was maintained with an error below 5 % except for Mn (8.79 %), Sr (5.49 %), Nb (10.46 %) and Pb (9.68 %) (Supplementary Table 1).

Table 1. Basic statistics of the concentrations of the elements Ca, Cu, Fe, K, Mn, Nb, Pb, Rb, Sr, Ti, Zr in the surface deposits of YP.

Element	Mean	Median	Mínimum	Maximum	Standard deviation	Mean standard deviation
Ca (%)	6.97	4.03	0.64	27.78	6.53	5.31
Fe (%)	3.68	3.52	0.16	9.05	1.73	1.47
K (%)	0.80	0.79	0.13	1.72	0.41	0.35
Ti (%)	0.52	0.51	0.09	1.29	0.24	0.20
Cu (ppm)	27	21	5	146	19	13
Mn (ppm)	1,208	1142	158	3770	557	407
Nb (ppm)	32	32	4	62	12	10
Pb (ppm)	31	33	9	94	13	10
Rb (ppm)	91	87	20	181	36	31
Sr (ppm)	191	82	29	1537	290	175
Zr (ppm)	250	251	73	662	110	84

The concentrations of Ca, Fe, K and Ti are above 10,000 ppm. Mn was found in concentrations between 1,000-10,000 ppm and the concentrations of Pb, Cu, Sr, Zr, Rb and Nb are less than 1,000 ppm (Figure 2, Table 1). The values of Ca (0.64-27.78 %), K (0.13-1.72 %), Ti (0.09-1.29 %) and Zr (73-662 ppm) exhibit larger dispersion compared to Fe (0.16-9.05 %), Mn (158-3,770 ppm), Cu (5-146 ppm), Rb (20-181 ppm), Sr (29-

1,537 ppm), Nb (4-62 ppm) and Pb (9-94 ppm). The asymmetric distributions allowed to transform the data into the spatial scale for the mapping modeling (Fig. 2, 3, 4 and 5). For example, atypical and high Sr concentrations with values between 165-1537 ppm occur in the surface deposits related to the influence of the coastlines of the eastern, northern and western margin of the peninsula (Fig. 5). However, the highest values (>562 ppm) are in the southeast and northwest coasts and the lowest values (29-53 ppm) are in the central part of the YP.

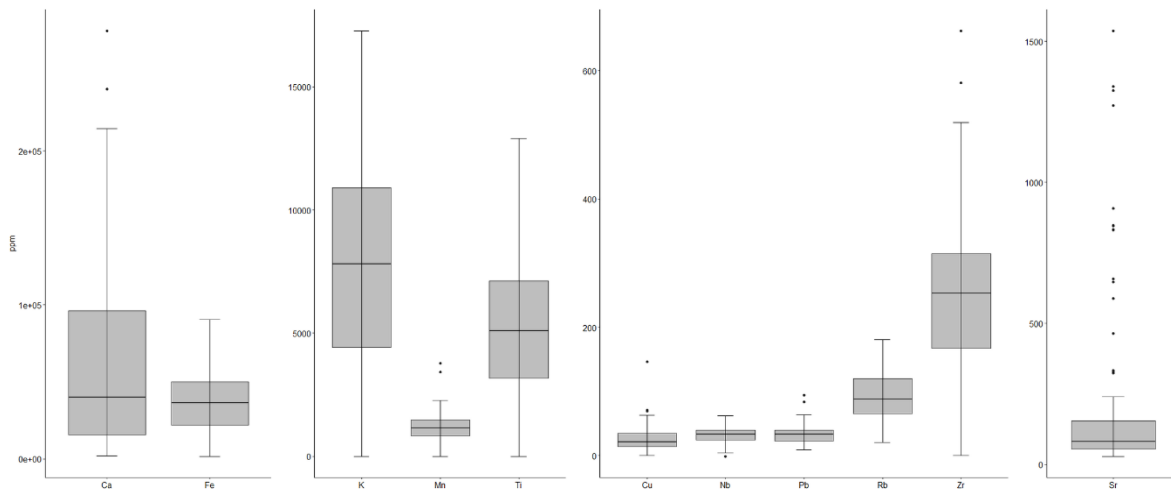


Figure 2. Box plot for the elements Ca, Cu, Fe, K, Mn, Nb, Pb, Rb, Sr, Ti and Zr in the surface deposits of the YP. The concentrations of Ca, Fe, K, Mn and Ti are in % and the other elements in ppm.

4.1 Model Maps

The models were generated with higher quality with the database transformed (with base 10 logarithm) to have a lower error during the cross-validation analyses. Calcium (Ca) was the most abundant element in all samples, with concentrations between 0.64 and 27.68 %, with a median of 4.03 % and the cross-validation of the model resulted in an error of 0.079 (Fig. 3). The map shows a gradient with lower concentrations in the center of the YP, which increase (>12.23%) towards the north coast and south of the study area.

Iron (Fe) is the second most abundant element with the range of concentrations between 0.16 and 9.05 %, with a median of 3.52 % (Fig. 3). The largest gradients in the distribution model with error -0.040, are in the northern and southern part of the PY, while from east to west it is almost constant. The highest values (> 4.58 %) are concentrated in a strip that crosses the central-northern part of the peninsula where Ca is present in lower concentrations and decrease towards the northern coast and south of the study area, with the lowest values in the extreme south.

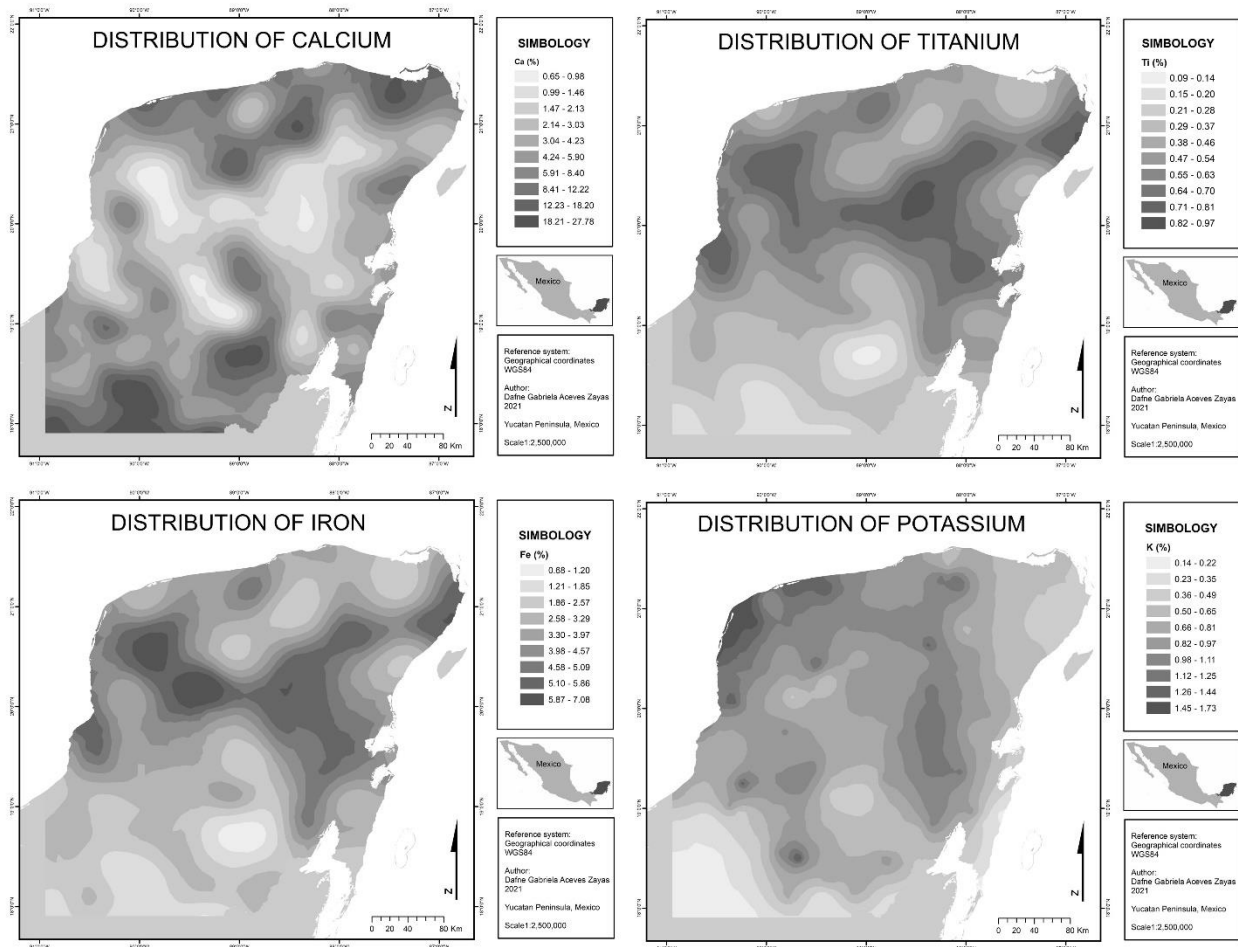


Figure 3. Distribution of the elements Ca, Ti, Fe and K in the surface sediments of the YP.

The distribution patterns of Titanium (Ti, 0.09-1.29 %, median 0.51 %), Niobium (Nb, 4-62 ppm, median 32), and Manganese (Mn, 159-3,770 ppm, median 1,142 ppm) are similar to Fe (Fig. 3, 4 and 5). Model errors for Ti, Nb and Mn were -0.035, -0.059 and -0.013, respectively. The highest concentrations of these elements clustered in a nearly

central horizontal band and in the eastern and western littoral zones. Mn concentrations are observed in a more vertical pattern, with low concentrations in the center and higher concentrations towards the east and west coasts. When compared with the calcium distribution patterns, it is possible to observe an inverse relationship (Fig. 3).

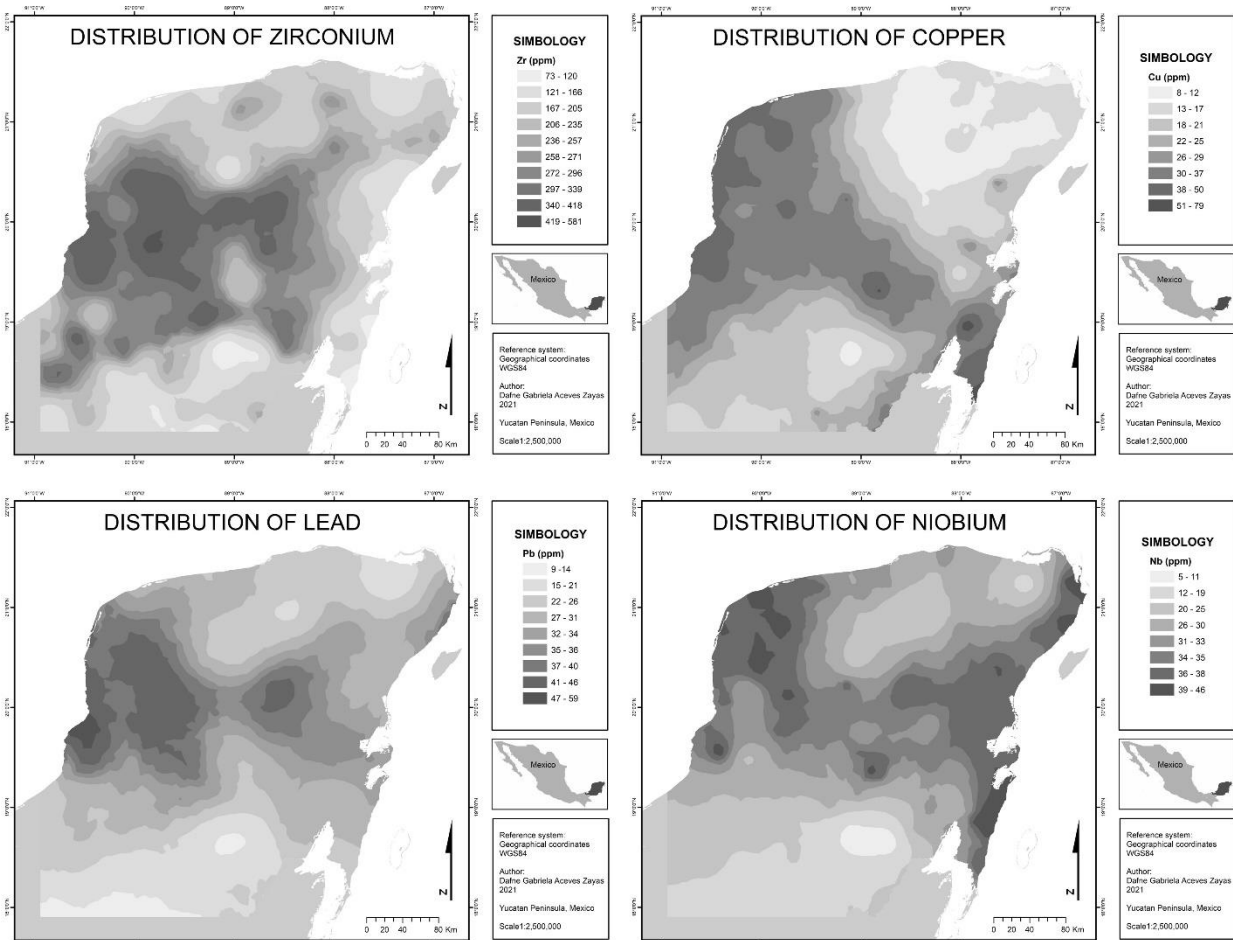


Figure 4. Distribution of the elements Zr, Cu, Pb and Nb in the surface sediments of the PY.

Cu is found in concentrations between 5 and 146 ppm, with a median of 21 ppm. The highest concentrations are found on the western coast of the PY, occupying a portion of the center until reaching the coast of the Caribbean Sea, in the region known as Costa Maya (Fig. 4). The error in the Kriging model was 0.050. A similar distribution pattern is observed for Pb, the highest concentrations are located as a horizontal strip in the center of the region, with a greater load towards the western side. In addition, an increase in concentrations is observed in the Cancun area (Fig. 4). The values are

between 9 and 94 ppm with a median of 31 ppm and a model error of -0.048. Zr also reveals some similarity with the distribution of Cu and Pb, with higher concentrations towards the west coast and center of the PY, but without reaching the east coast (Fig. 4). It presents values between 73 and 662 ppm and a median of 251 ppm. The error in the model was -0.054.

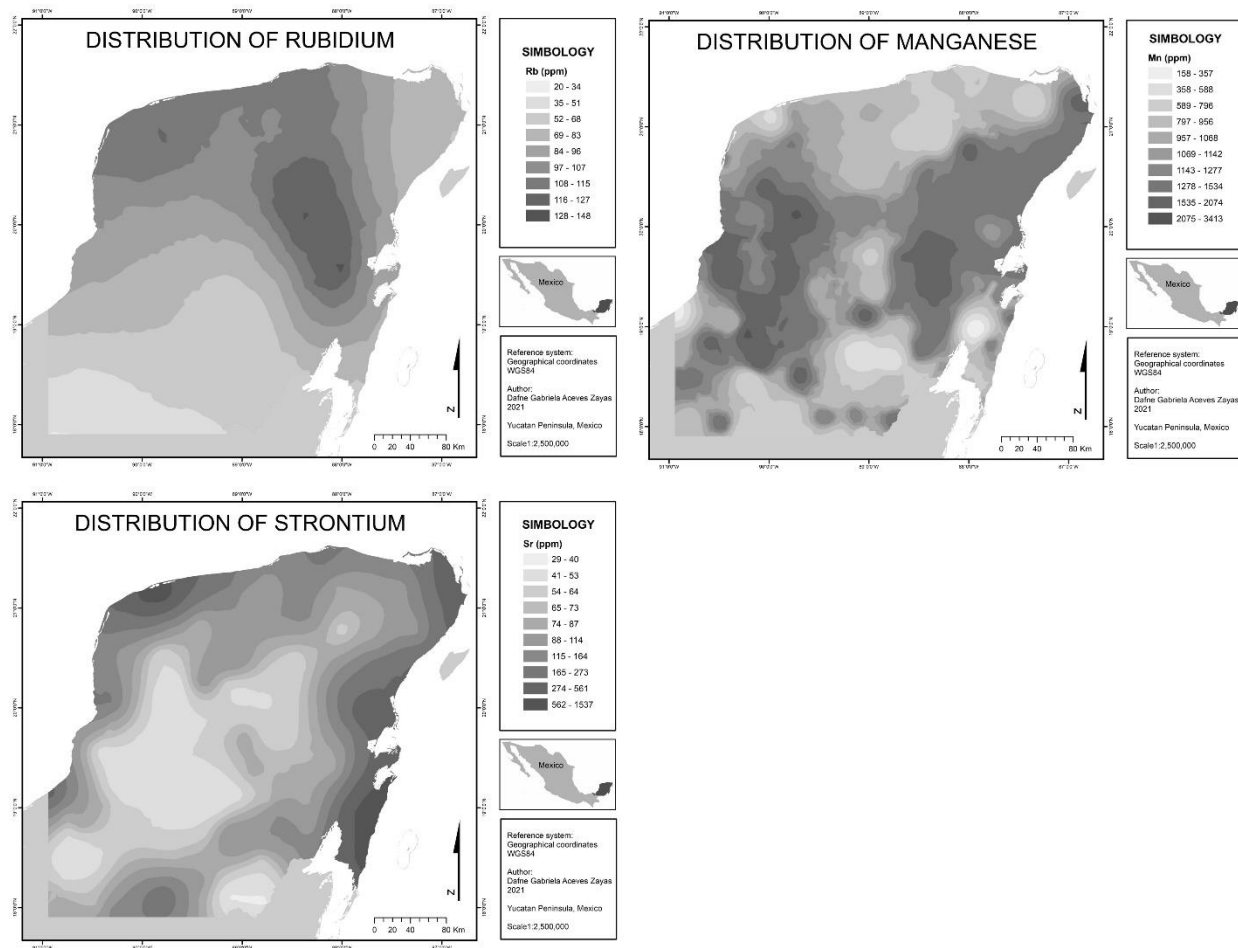


Figure 5. Distribution of the elements Rb, Mn y Sr in the surface sediments of the PY.

Potassium (K) was found to range between 0.13 and 1.72 %, with a median of 0.79 % (Fig. 3). The highest concentrations are observed at the edge of the northwest coast and in a strip parallel to the east coast. The model error was estimated to be -0.024. The highest Rb concentrations extend from the northwest towards the center of the Caribbean Sea coast, while the highest values are found towards the south-southwest, the model error was -0.0359). These range from 20 to 181 ppm, with a median of 87

ppm (Fig. 5). The Sr map shows a trend in concentrations towards the coasts, while the lowest concentrations are found in more continental areas, the model error was 0.044. The highest concentration values reach 1,537 ppm and the lowest 29 ppm, with a median of 82 ppm (Fig. 5).

By contrasting the environmental background values of the PY with those of other regions, such as the Altiplano Potosino (AP), located in central Mexico (Chiprés et al. 2008), it is possible to distinguish differences between the concentration ranges in which the elements are distributed. For example, in all elements, except K, ranges with higher limits are observed in the PY than in the AP. The most notable differences were in the values of Fe, Mn and Zr. This contrast is due to the fact that different environmental conditions are found in each region, which influence the geological processes that give rise to the surficial deposits. In the PY, a karst landscape with little relief and forests can be found in a warm climate, while in the AP the relief is more rugged, igneous and sedimentary rocks can be found in semi-arid to temperate climate, and vegetation from scrubland to pine forests.

On the other hand, there is a preliminary study on geochemistry of PY, however, this was conducted with a smaller number of sites and on surface sediment samples from water bodies (Roy et al. 2018). When comparing those values with those of the present study, it was detected that Ti and Fe were found with wider ranges and higher means in the soil study (Ti sediments: 0.01-0.76 %, Ti soils: 0.09-1.29 %; Fe sediments: 0.01-3.12 %, Fe soils: 0.16-9.05 %). This could be due to the fact that there is a greater amount of samples in areas with outcrops of siliciclastic rocks such as shales and sandstones. The opposite occurred with Ca and Sr, which we observed in wider ranges and higher averages in sediments (Ca sediments: 0.40-37.70 %, Ca soils: 0.64-27.78 %; Sr sediments: 27-4,059 ppm, Sr soils: 29-1,537 ppm). It is possible that the Ca difference is due to an enrichment in the lake sediments due to the accumulation and weathering of biological fragments such as shells of aquatic animals. A comparison of Ca distribution with groundwater flow shows a possible effect of dilution and transport of the element along with the water current (Bauer-Gottwein et al. 2011).

The distribution of Sr reveals a pattern coincident with the age of rocks, the youngest rocks and sediments of Miocene and Pliocene age are located on the shores of the YP together with the highest concentrations of Sr. The age of the rocks increases in a southwesterly direction where the Paleocene rocks with the lowest values of the element coincide (SSP 1989). In addition, it is possible to observe that Sr concentrations are lower as the altitude of the terrain increases (Bauer-Gottwein et al. 2011). It is proposed to continue with this type of research to explore how the concentrations of the elements are related to each other and to environmental factors such as rock type, soil, climate, vegetation and water flows. This information may be useful to understand the natural geochemical processes of the tropical karst region and the dynamics of the cycles of the most important elements at present.

5. Conclusion

In the context of geochemical modeling for Mexico, the sample collection design with 98 % of the cells (40 by 40 km) covering a total area of 129,225 km² proposed in the experimental design could be sampled, and the XRF laboratory analyses were effective to explore and understand the distribution patterns of environmental background values for the elements Ca, Cu, Fe, K, Mn, Nb, Pb, Rb, Sr, Ti and Zr in the Yucatan Peninsula. The elements with the highest abundance (up to >1% or 10,000 ppm) were Ca, Fe, Ti and K compared to Mn (158-3,770 ppm). The concentration of the remaining elements such as Cu, Nb, Pb, Rb, Sr and Zr were less than 1,000 ppm.

In the 1:250,000 scale distribution maps, similar trends were observed for Fe, Ti, Nb and Mn, with distributions in almost equal patterns and an inverse correlation with Ca. On the other hand, unique distribution patterns were observed for Mn, K and Rb, and others with notably influenced by environmental factors, as in the case of Sr which is found in higher concentration on the coasts due to the influence of the coastline.

The concentration ranges described for each element are the first approach to the knowledge of the environmental background values for the YP and are a contribution to the national soil geochemical mapping project. However, it is possible to improve the

coverage of the samples with smaller cells and with complementary sampling at these sites. The creation of standards for the region, the expansion of mapped elements, such as Bi, Cd, Cr, Mo, Ni, Zn and evaluation of the concentrations of the rarer elements, e.g. As, Ba, Co, Pd, S, Se, Sn, V, by means of other measurement techniques such as induced plasma spectrometry (ICP) or conventional X-ray fluorescence (XRF) equipment could improve the background values and distribution maps. For potentially harmful elements, such as As, Cd, Co, Cr, Hg or Sn, it is suggested to consider analyses with a higher sample density (Smith and Reimann 2008) to evaluate the contamination or public health problem. In the case of elements of agricultural interest, it would be more appropriate to work with regional scale sampling.

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SUPPLEMENTARY

Table 1. Quality control parameters.

Element	BDL (%)	EDC (%)	Precision (%) [*]	Accuracy (%) ^{**}	Precision by batch (%)	DL (ppm)
K	0.85	17.09	3.92	-4.78	0.37-4.74	-
Ca	0	0	3.19	19.71	0.47-7.94	0.050 [*]
Ti	0.85	0	4.20	11.97	0.21-7.96	0.016 [*]
Mn	0.85	1.71	8.79	24.73	0.77-7.00	0.085 [*]
Fe	0	0.85	1.22	15.02	0.39-6.34	0.010 [*]
Cu	4.27	0	4.24	-	2.22-13.83	35
Rb	0	0	4.74	-9.48	0.98-10.07	10
Sr	0	11.11	5.49	-10.71	0.22-6.58	11
Zr	0.85	0.85	2.34	-23.21	0.07-17.93	15
Nb	0	0.85	10.46	-	0.15-19.92	-
Pb	0	6.84	9.68	29.80	1.01-23.03	13

BDL (Data below detection limit), EDC (Extrapolated data in correction), DL (Detection limit of the equipment).

^{*} Calculated with 5 repetitions of the standard CCRMP TILL–4PP 180-646.

^{**} Calculated with 5 repetitions of the standard NIST2709a.

^{***} Expressed in percentage.

CONCLUSIONES

El diseño de colecta de muestras, los análisis de laboratorio y el proceso de modelación probaron ser efectivos para la creación de mapas de distribución de los elementos y la determinación de los valores de fondo ambientales en la Península de Yucatán. La colecta cubrió el 98 % de las celdas planteadas (40 x 40 km) y a partir de ello se crearon modelos de 11 elementos (Ca, Fe, K, Ti, Cu, Mn, Nb, Pb, Rb, Sr y Zr) que describen un área de 129,225 km² a escala 1:2,500,000, con una densidad de muestreo baja (1/1,600 km²). Se demostró que, a pesar de contar con limitado número de muestras, la densidad de colecta fue suficiente para revelar los patrones de distribución y los rangos en los que varían las concentraciones de los elementos en los depósitos superficiales, puesto que es una escala adecuada para estudios regionales.

Se identificaron cuatro elementos mayores: Ca (0.64-27.78 %), Fe (0.16-9.05 %), K (0.13-1.72 %) y Ti (0.09-1.29 %); un elemento menor: Mn (158-3,770 ppm); y seis elementos traza: Cu (5-146 ppm), Nb (4-62 ppm), Pb (9-94 ppm), Rb (20-181 ppm), Sr (29-1,537 ppm) y Zr (73-662 ppm).

Los mapas revelaron patrones de distribución coincidentes en algunos elementos, como es el caso del Fe, Ti, Nb y Mn, los cuales a su vez presentan una relación inversa a la distribución del Ca. Por otra parte, se observaron algunos elementos con patrones de distribución únicos, como el K y el Rb, otros elementos con una relación notable con factores ambientales, como es el caso del Sr y la zona costera. Estas observaciones dan paso a interrogantes sobre cuáles son las correlaciones entre los elementos, y entre estos y los factores ambientales como la geología, la precipitación, la escorrentía, el clima y la vegetación. La interpretación de estas correspondencias es un área de oportunidad que podría generar información de utilidad para conocer la dinámica de los elementos en los ciclos biogeoquímicos de zonas cársticas y tropicales.

Otra área de oportunidad identificada fue la necesidad de crear materiales de referencias con matrices de composición similar a las observadas en la Península de Yucatán, para poder ampliar el número de elementos detectables de manera confiable por equipos portables de fluorescencia de rayos x, y de esta manera crear mapas de

otros elementos, como Bi, Cd, Cr, Mo, Ni y Zn. Incluso sería posible ampliar aún más el mapeo haciendo uso de equipos convencionales de fluorescencia de rayos x o un espectrómetro de plasma inducido, los cuales permiten conocer las concentraciones de los elementos que se encuentran en las concentraciones más pequeñas, como es el caso de elementos potencialmente tóxicos (As, Co, Cr, Hg y Sn).

La presente investigación es el primer aporte de la región sureste al proyecto de mapeo de la geoquímica de México y revela información inédita que describe una parte de las condiciones actuales de la química de los depósitos superficiales de Península de Yucatán. Dichos avances dan pie para la continuación de la exploración geoquímica del territorio a través de técnicas complementarias y mejoras en el método de estudio.

LITERATURA CITADA

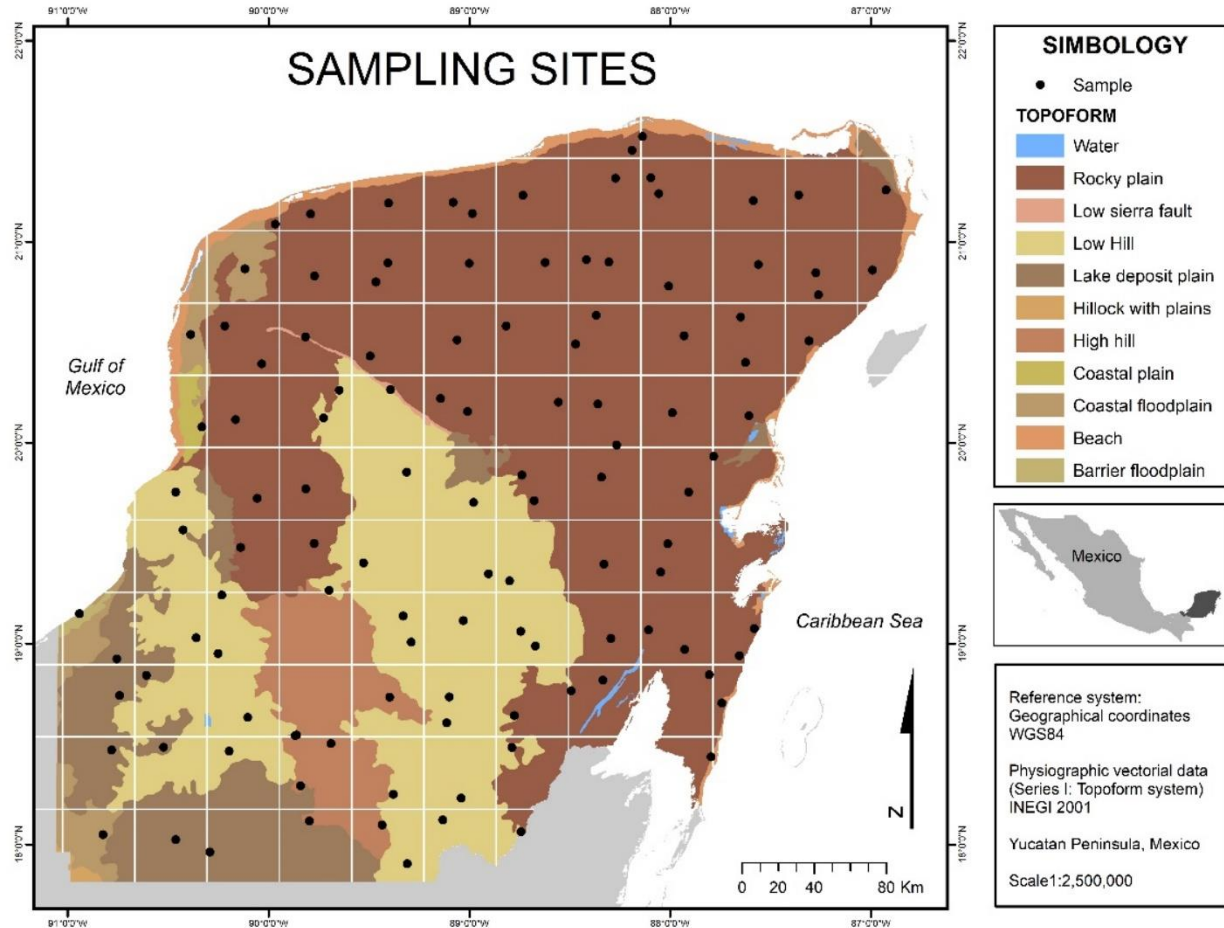
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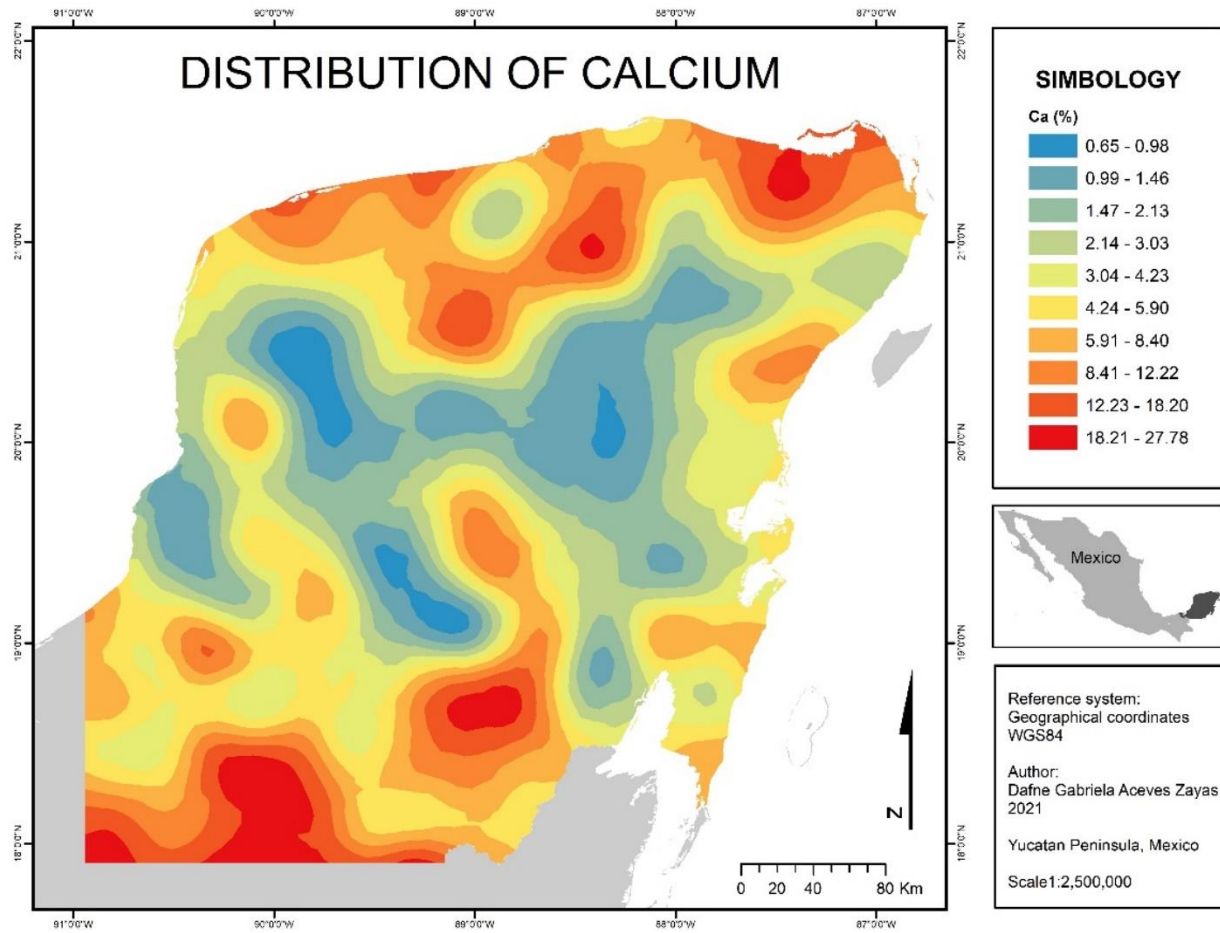
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ANEXOS

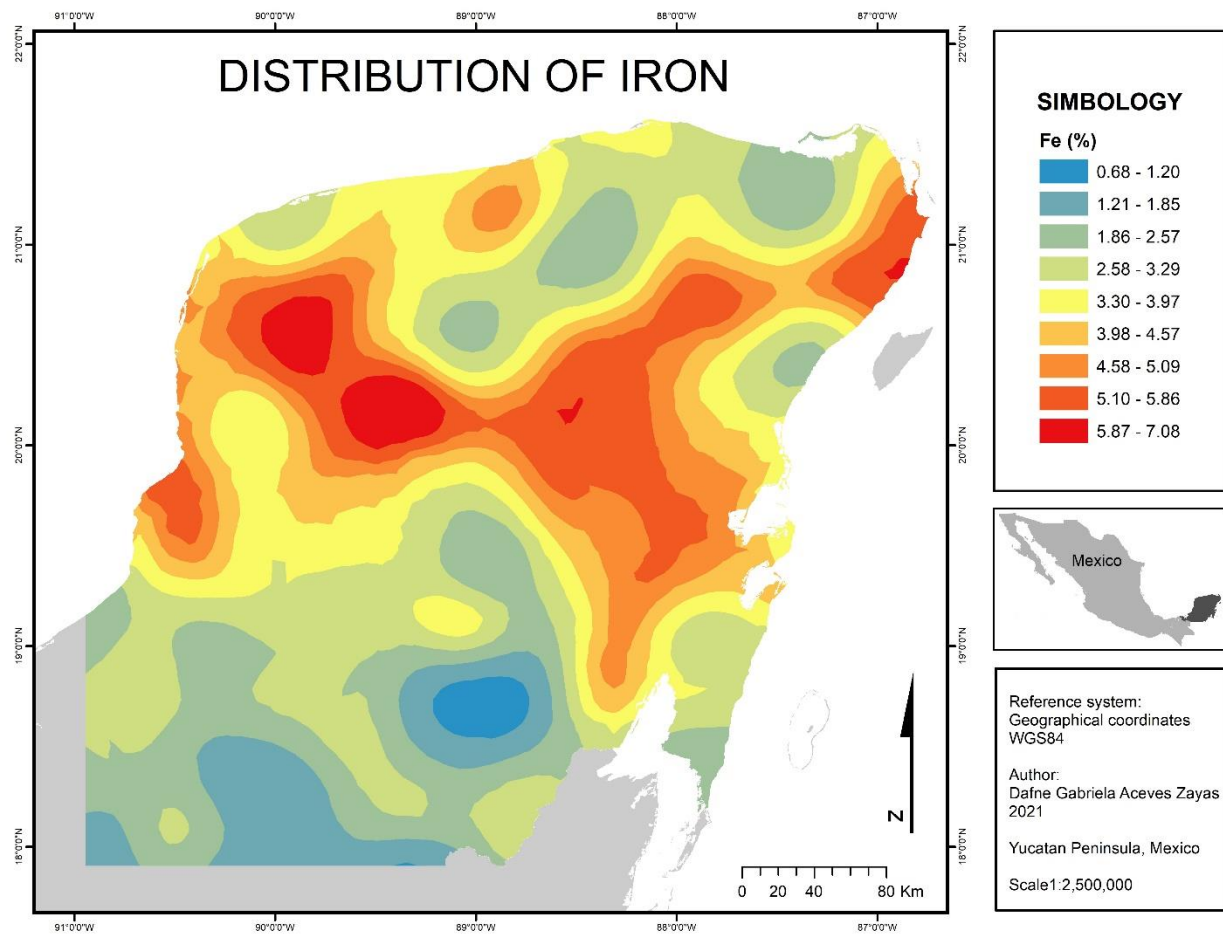
Anexo 1. Mapa de los sitios de muestreo y las topoformas de la Península de Yucatán.



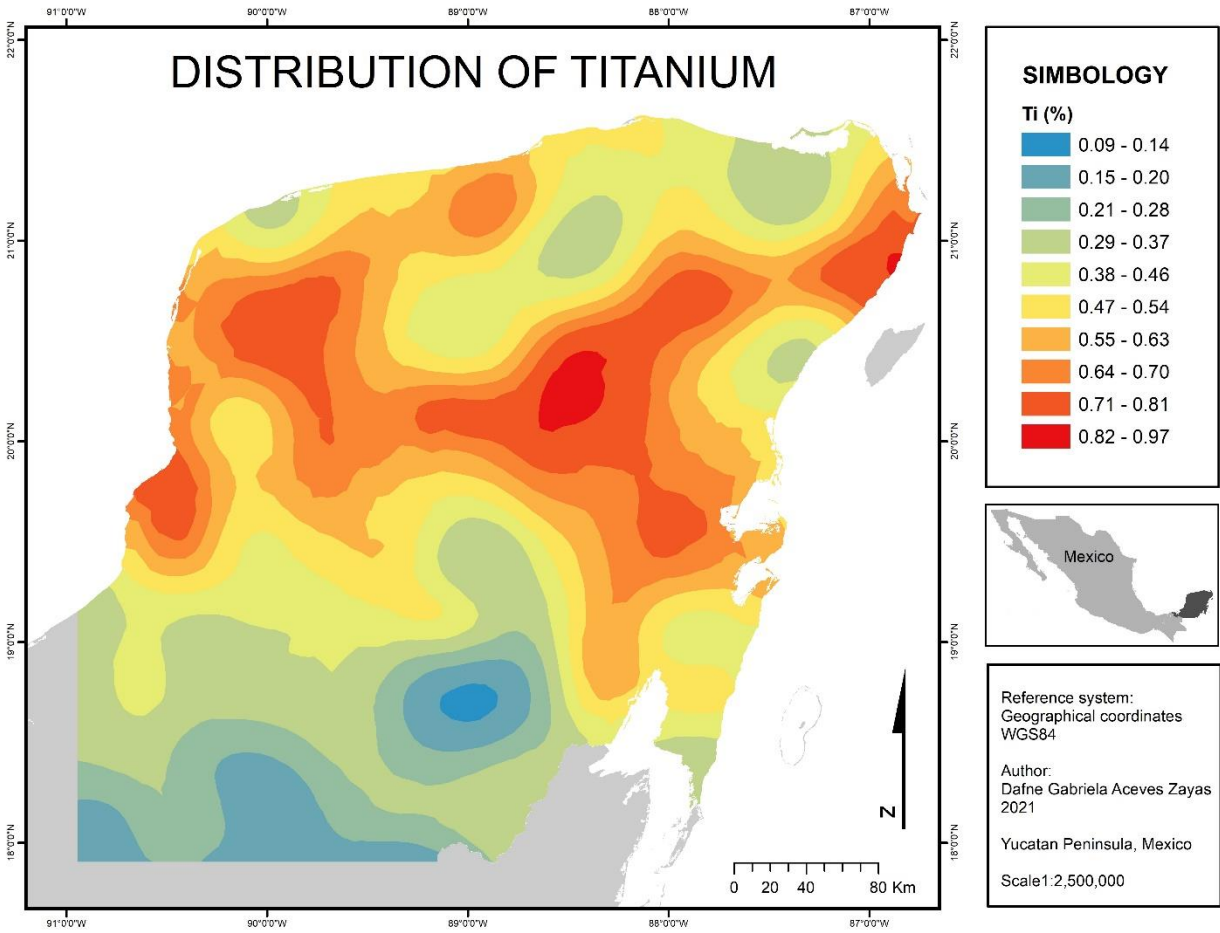
Anexo 2. Mapa de valores de fondo y distribución del calcio (Ca) en la Península de Yucatán.



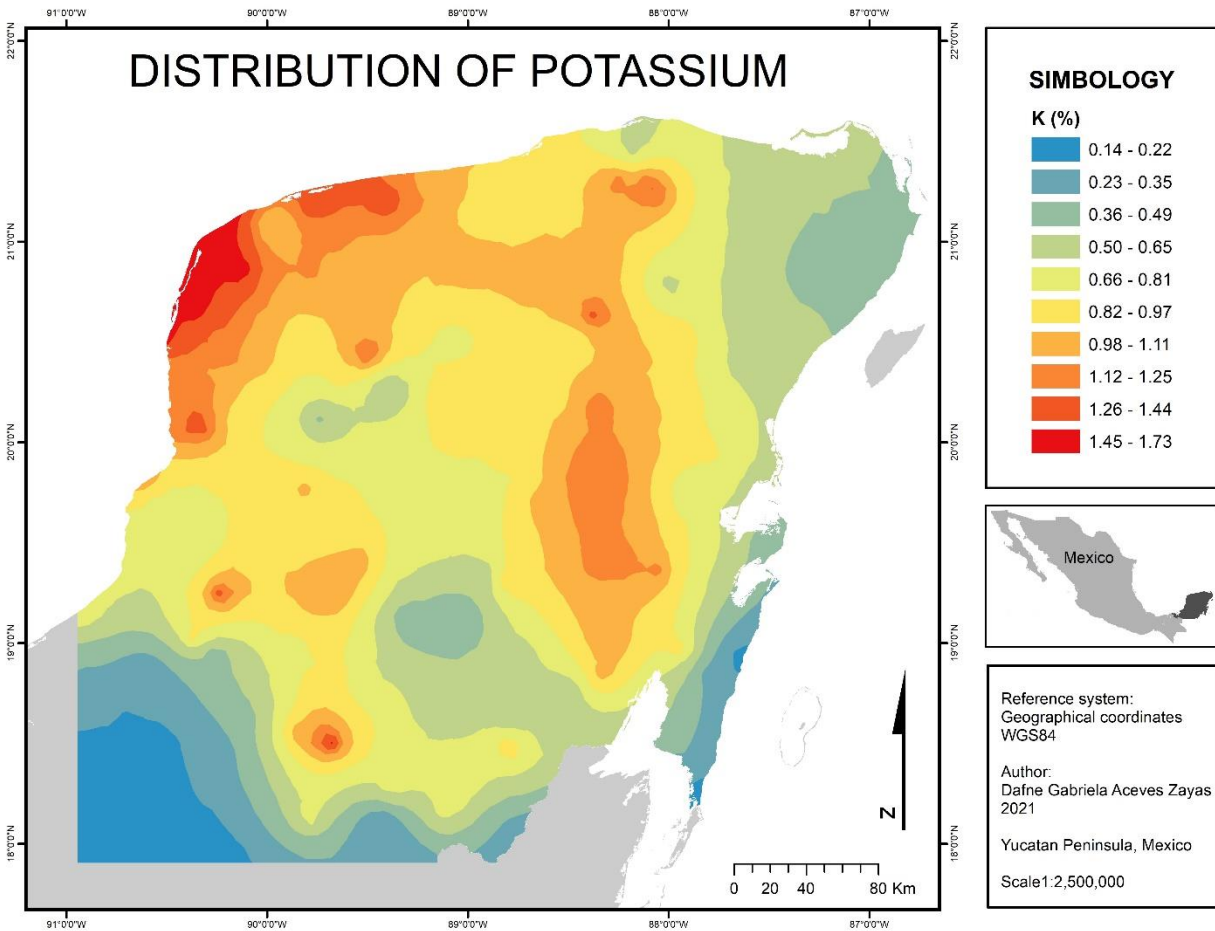
Anexo 3. Mapa de valores de fondo y distribución del hierro (Fe) en la Península de Yucatán.



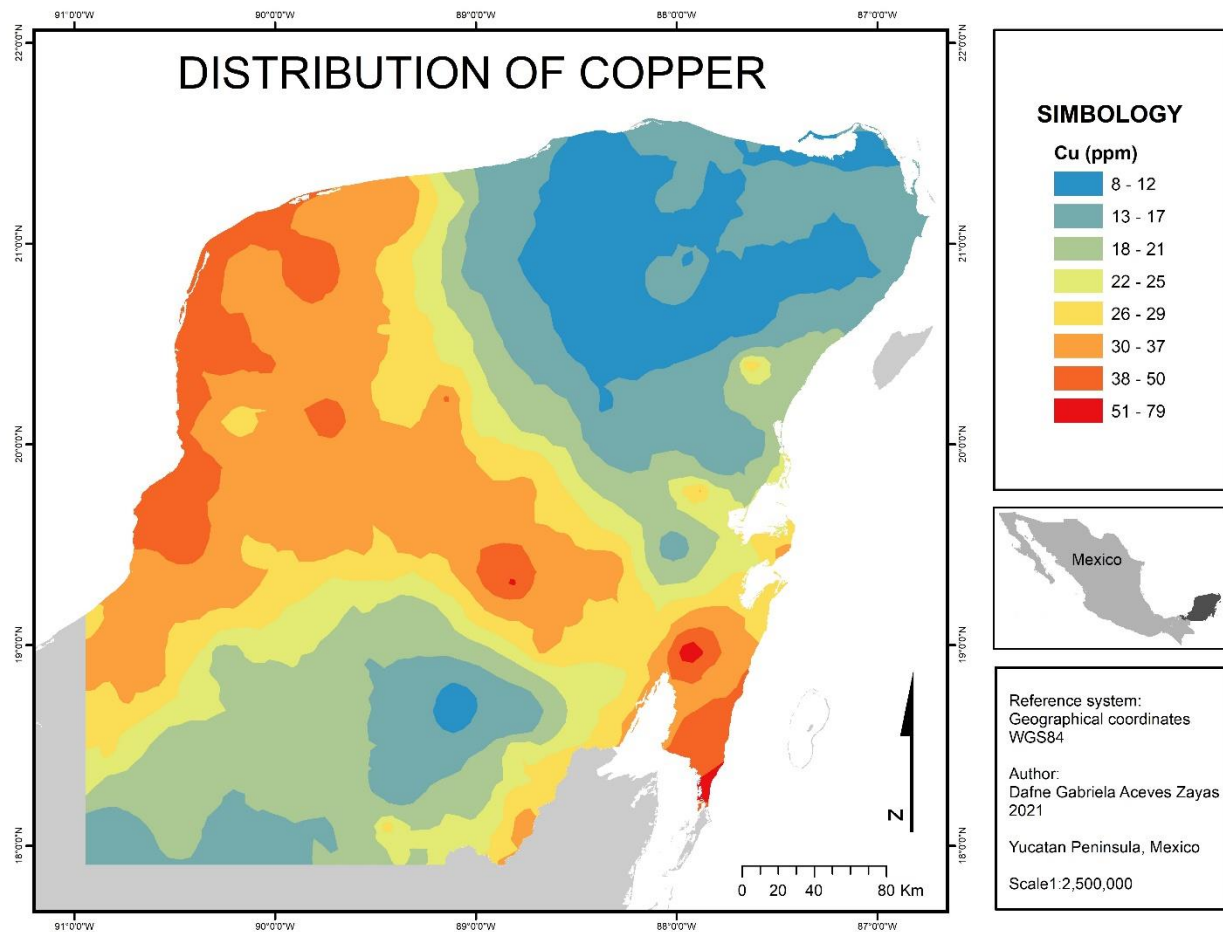
Anexo 4. Mapa de valores de fondo y distribución del titanio (Ti) en la Península de Yucatán.



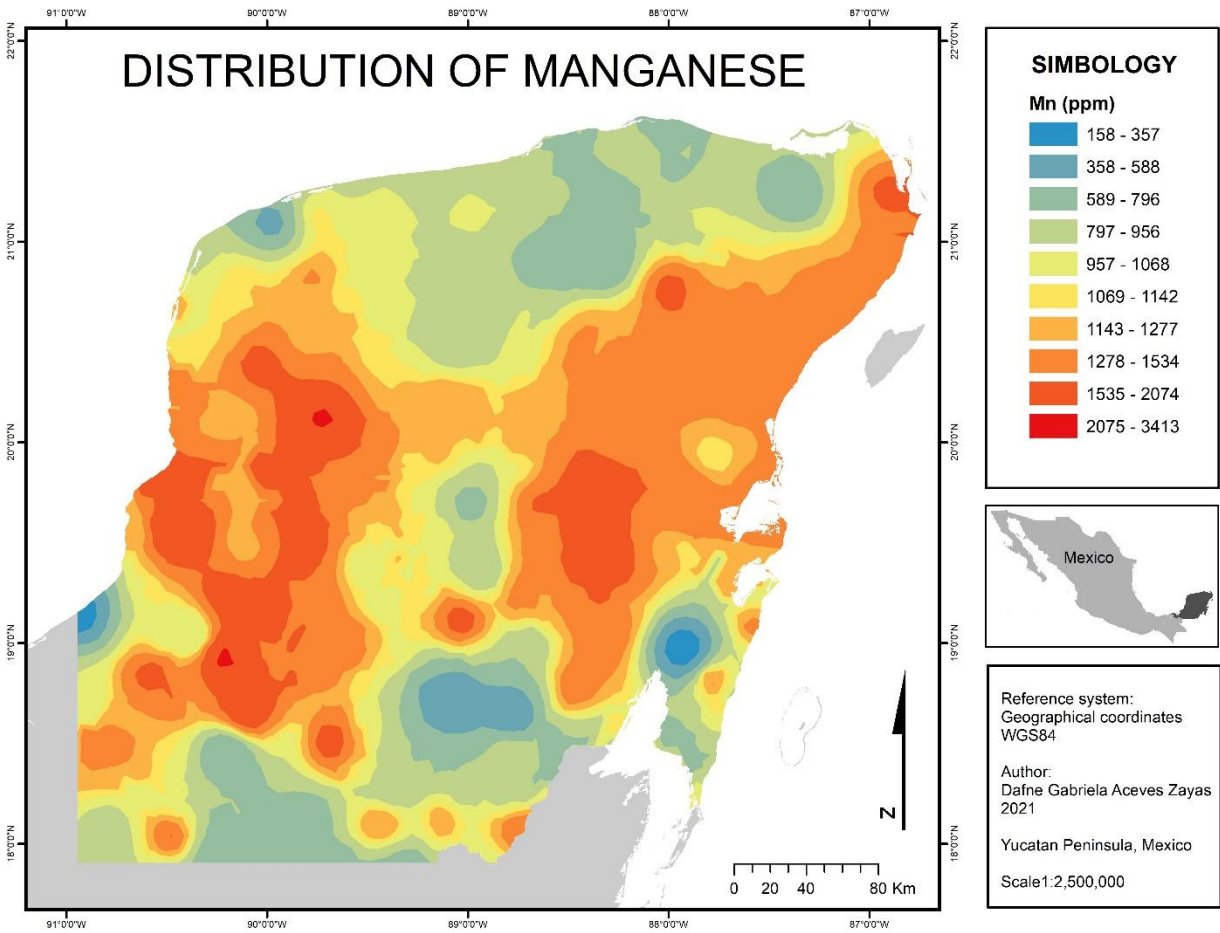
Anexo 5. Mapa de valores de fondo y distribución del potasio (K) en la Península de Yucatán.



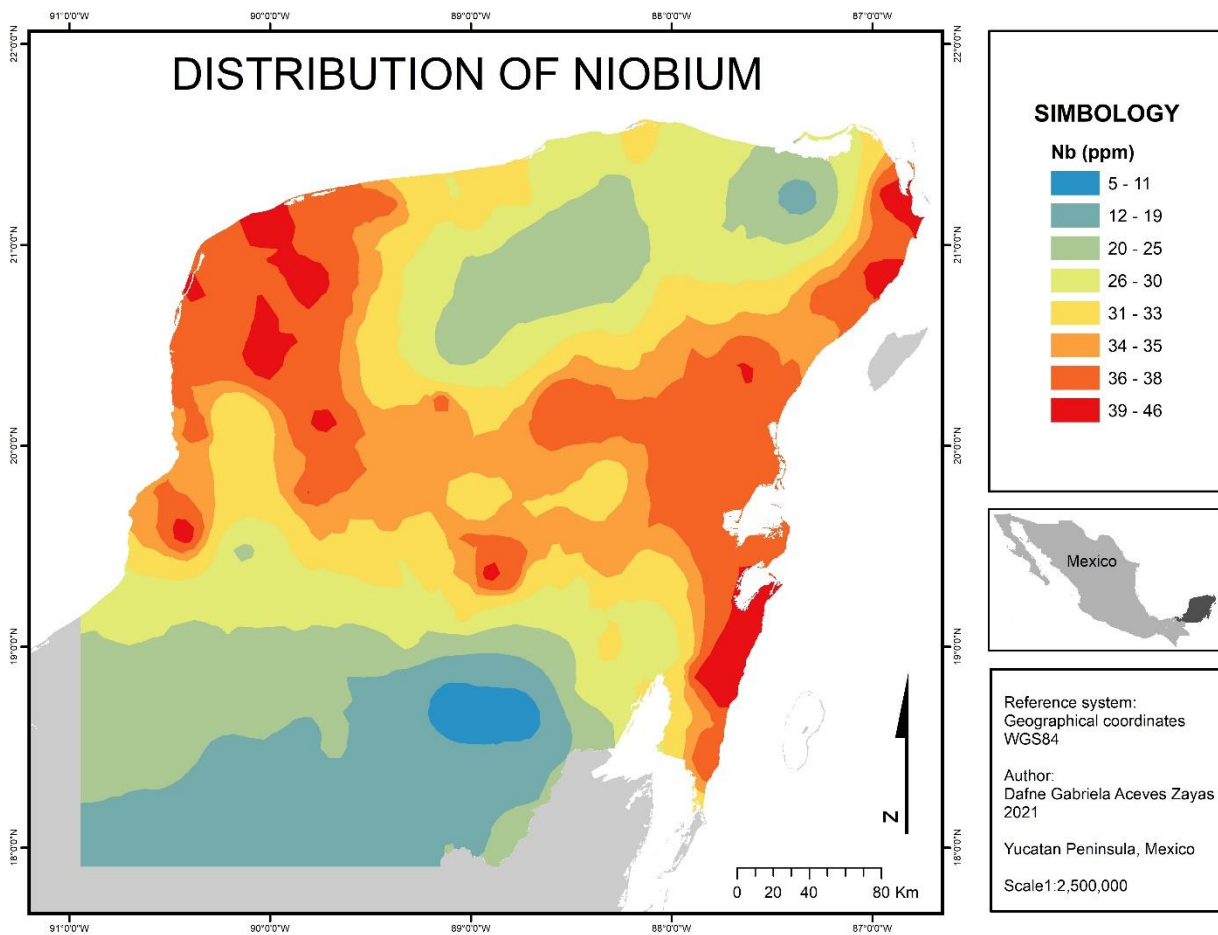
Anexo 6. Mapa de valores de fondo y distribución del cobre (Cu) en la Península de Yucatán.



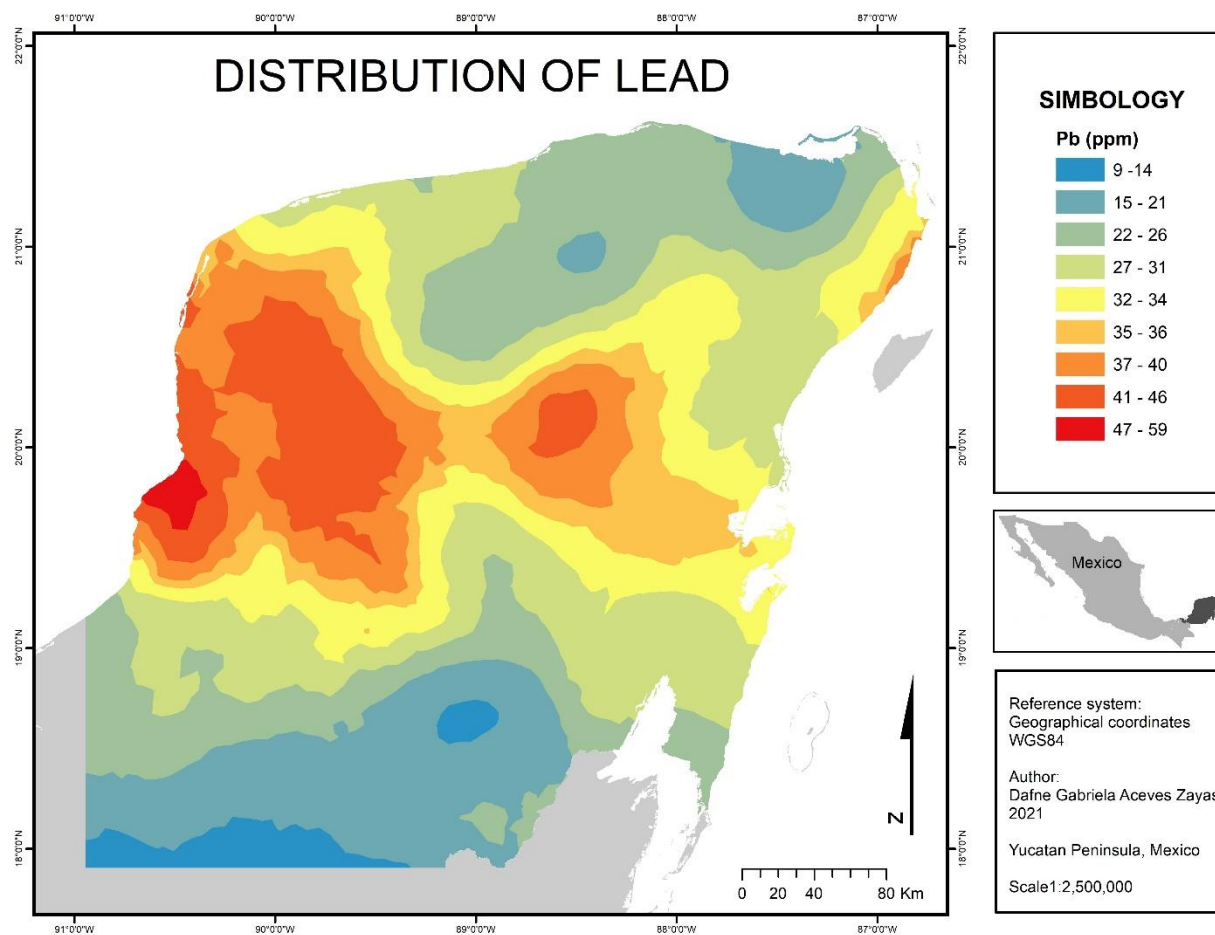
Anexo 7. Mapa de valores de fondo y distribución del manganeso (Mn) en la Península de Yucatán.



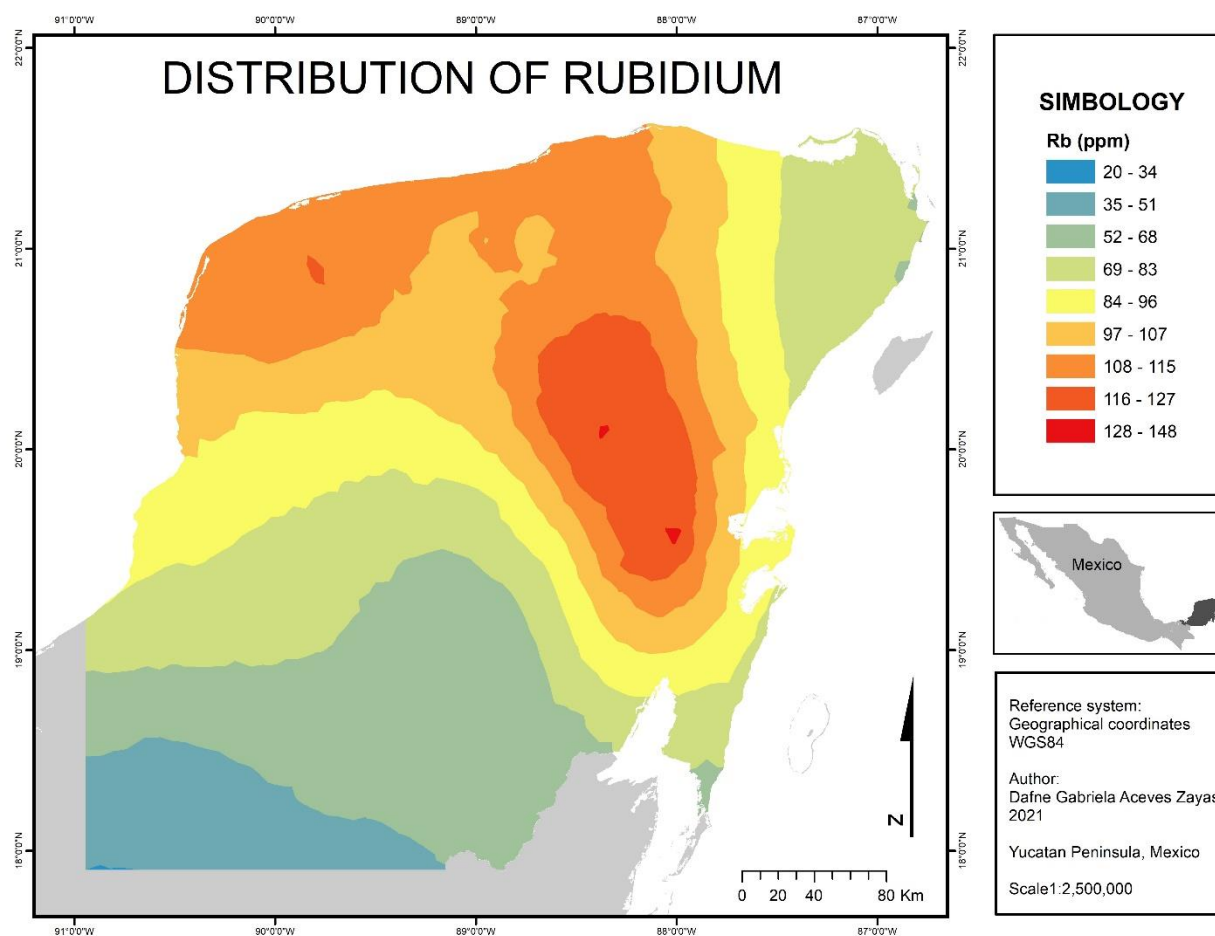
Anexo 8. Mapa de valores de fondo y distribución del niobio (Nb) en la Península de Yucatán.



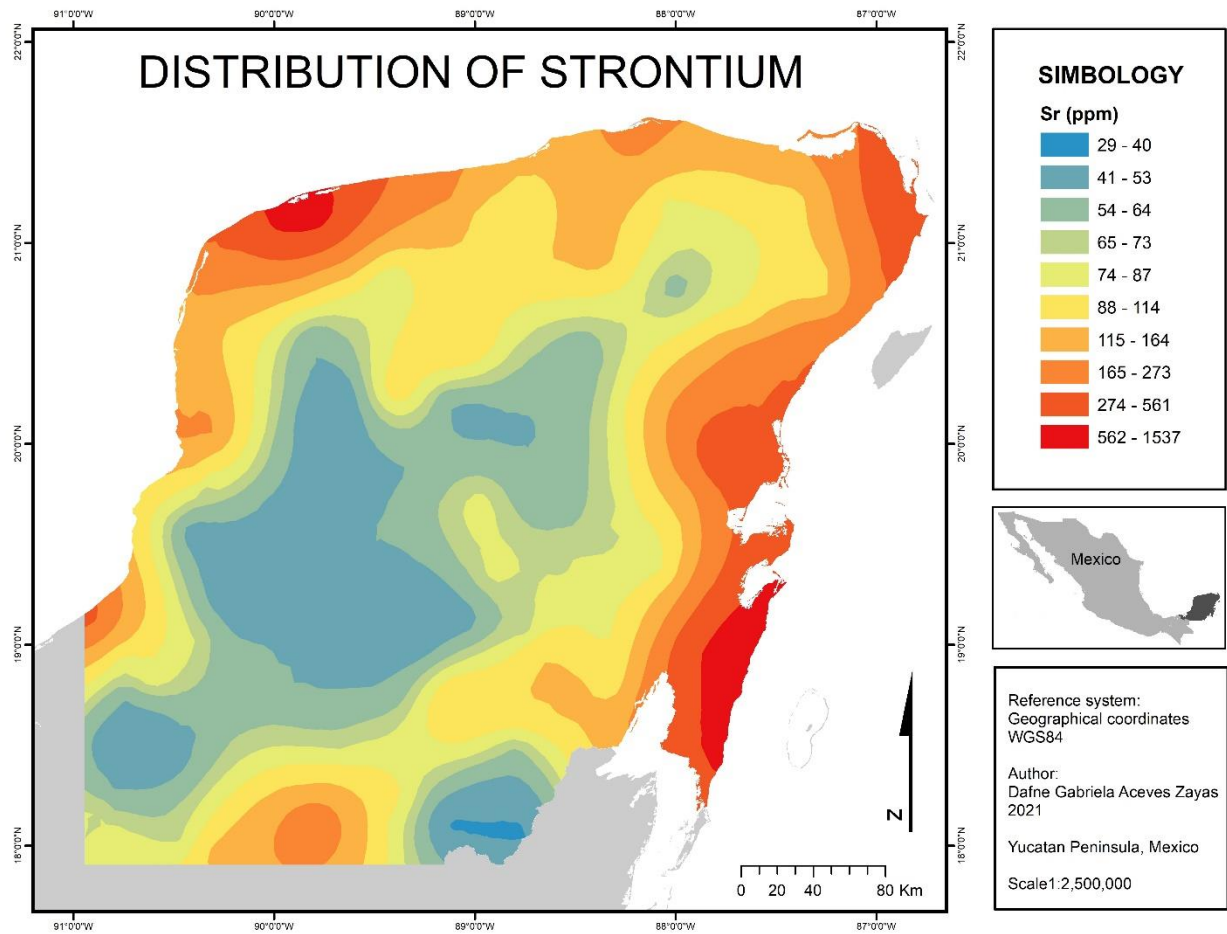
Anexo 9. Mapa de valores de fondo y distribución del plomo (Pb) en la Península de Yucatán.



Anexo 10. Mapa de valores de fondo y distribución del rubidio (Rb) en la Península de Yucatán.



Anexo 11. Mapa de valores de fondo y distribución del estroncio (Sr) en la Península de Yucatán.



Anexo 12. Mapa de valores de fondo y distribución del circonio (Zr) en la Península de Yucatán.

