Journal of Environmental Management 241 (2019) 138–148

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Determining of risk areas due to exposure to heavy metals in the Toluca Valley using epiphytic mosses as a biomonitor

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ARTICLE INFO

Keywords:
Bioindicators
Biomonitor
Geostatistical analysis
GIS
Heavy metals
Risk area

ABSTRACT

The work aim is to identify the risk areas by exposure to Cr, Cu, Pb and Zn in the Metropolitan Zone of Toluca Valley (MZTV) using the mosses *Fabriona cilaris* and *Leskea angustata* as a biomonitors, geostatistical interpolation and multi-criteria evaluation by analytical hierarchy process. The results from the estimation of the enrichment factors (EF) showed that Pb is the heavy metal with the highest values, followed by the Zn, Cu and Cr. The EF obtained for all heavy metals show that there is a moderate to high anthropogenic enrichment. The above indicates that in the MZTV there are emission sources that contribute (significantly) in the amount of Cr, Cu, Pb and Zn accumulated in the biomonitor. Combustion processes, vehicle emissions, biomass burning, brick kiln emissions, agricultural and livestock activities, manufacturing industry and re-deposition by the action of the wind, were identified as the main heavy metals sources in the MZTV. Risk maps showed the high and medium risk areas are located in sites with poor urban vegetation coverage and close to highways and industrial parks. Low risk areas are located in sites with high urban vegetation coverage. The method used for identifying risk areas is a rapid and low-cost evaluation tool can allow local government environmental agencies to define public policies on air pollution control.

1. Introduction

The accelerated growth of the world population, particularly in developing countries, has accelerated the urbanization and industrialization processes of metropolitan areas around the entire planet. These processes generate several pressures in the environment, the most important being air pollution due to the burning of fossil fuels and various industrial activities.

Pollutants such as greenhouse gases, toxic substances (benzene, toluene, xylene), particulate matter and heavy metals, are released indiscriminately in the air with serious consequences for the environment and people. Heavy metals are important components of air pollution due to their high toxicity, easy dispersion, but above all because of their persistence and bioaccumulation in the ecosystem (Koz et al., 2012; Turkyilmaz et al., 2018a), such characteristics that increase the health risks for the inhabitants of urban centers.

For example, several studies have shown that the exposure to high levels of heavy metals concentration increases the risk of adverse effects on human health by damage to central and peripheral nervous system, lungs, kidneys and liver, or even death (Shaban et al., 2016; Zeng et al., 2016). A long exposure to low concentrations of heavy metals is related to symptoms such as nose and throat irritation, cough, dyspnea and asthma (Koedrith et al., 2013). Studies such as Zeng et al. (2016) indicate the presence of heavy metals such as Pb, Cd and the other heavy metals in particulate matter (2.5 μm) may be related with the increase in respiratory symptoms such as cough, phlegm and dyspnea, as well as asthma in children. These health effects demonstrate the importance of monitoring heavy metals in urban centers. Exposed population health studies and identification of risk areas can be limited due to the high costs of environmental monitoring and the complexity of analytical

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https://doi.org/10.1016/j.jenvman.2019.04.018
Received 16 November 2018; Received in revised form 2 March 2019; Accepted 7 April 2019
Available online 15 April 2019
0301-4797/

methods used in the heavy metal's quantification (Anicic et al., 2009; Abril et al., 2014; Sevik et al., 2018).

The use of passive organisms (bioindicators) with high capacity to accumulate metals is an ideal low-cost alternative for environmental monitoring. Plants, mosses, lichens, among others are examples of organisms used for environmental biomonitoring (Hermens et al., 2008; Carvajal et al., 2010; Dzierżanowski et al., 2011; Schreck et al., 2012; Turkyilmaz et al., 2018b; Malikova et al., 2019). The bioindicators are able to take up heavy metals from soil, rainwater and air and accumulate them into their tissues (Shahid et al., 2017; Sevik et al., 2018). Currently, plants and mosses are being successfully used to determine the concentration of heavy metals in different cities around the world (Trujillo-González et al., 2016; Liang et al., 2017; Lazo et al., 2018). Mosses are the most used in small and medium scale and its use for biomonitoring was proposed in the late 1960s (Rühling and Tyler, 1968). Mosses have been applied in studies of metal deposition (Martins et al., 2012; Zarazúa-Ortega et al., 2013; Schnyder et al., 2018) and radionuclides (Krmar et al., 2013; Wattanavatee et al., 2017; Malikova et al., 2019), both in Europe and in the rest of the world.

The Metropolitan Zone of Toluca Valley (MZTV) is the fifth largest metropolis in Mexico. This zone has serious environmental pressures caused mainly by population growth, economic activities and demand for public services and energy (GEM, 2012; GEM, 2012). In this context, in the recent years, a study of the heavy metal's atmospheric deposition (K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr and Pb) by means of the biomonitoring with *Fabriona cilaris* and *Leskea angustata* was carried out. The analysis of heavy metals concentration in mosses was carried out by inductively coupled plasma optical emission spectrometry (ICP-OES), total reflection X-ray fluorescence spectrometry (TXRF), atomic absorption spectrometry and neutron activation analysis (Zarazúa-Ortega et al., 2013; Caballero-Segura et al., 2014; Mejía-Cuero et al., 2015; Macedo-Miranda et al., 2016). Results showed *Fabriona cilaris* and *Leskea angustata* are useful for atmospheric biomonitoring, and analytical methods used are suitable to quantify heavy metals in the particulate matter. The next step is to identify the risk areas by exposure to heavy metals in the MZVT, in order to evaluate the strategies of the federal government's environmental programs, as well as to contribute to develop of new public policies to reduce the heavy metals emission sources, which have not been considered in the current environmental programs. The identification of risk areas can be carried out in different ways, for example, using Geographical Information Systems (GIS), dispersion models, among others. The use of GIS is a simple and powerful tool to evaluate the spatial distribution of heavy metals through geostatistical interpolation processes (Koz et al., 2012; Cetin et al., 2018; Pan et al., 2016); these processes are widely used by managers and planners in the management and planning of different natural resources (Criado et al., 2017). GIS technology and mathematical methods by multi-criteria analysis allow decision makers solve the problem of site selection and achieve the most suitable site (Li et al., 2017a, b). The combination of GIS and multi-criteria methods has been used successfully in different environmental, urban and geophysical applications (Criado et al., 2017; Li et al., 2017a, b; Sadeghi and Karimi, 2017; Srivanit and Selanon, 2017).

In this context, this work aims to identify the risk areas by exposure to Cr, Cu, Pb and Zn in the ZMVT, using: a) The mosses *Fabriona cilaris* and *Leskea angustata* as a biomonitor, b) geostatistical interpolation and c) evaluation multi-criteria using Analytical Hierarchy Process (AHP).

2. Material and methods

2.1. Study area

The study area is located in the central part of the State of Mexico, with coordinates UTM: 2,101,169.25, 2,184,696.55 mN and 399,803.96, 471,183.26 mE as shown in Fig. 1. The area is situated on the top of an elevated plateau, with a maximum altitude of 4340 masl (in "*Nevado de Toluca*" volcano) and of 2640 masl (average) in the central valley region; total surface area of the territory is 2602.76 km^2. In this region two types of climate are observed: sub humid temperate and sub humid semi-cold, with a mean annual temperature between −3 °C and 14 °C (GEM, 1993). Annual rainfall varies between 800 mm and 1200 mm. The study area is under the influence of the trade winds, whose intensity is expressed as weak in the cold season (November to February). The winds predominate from the south to north with a slight curve in favour of the clock hands (GEM, 2007b). The region is characterized mainly by andosols, feozems, vertisols, luvisols and cambisols soil types, and in a smaller proportion by histosols, planosols and regosols soil types (GEM, 1993). Andosols and regosols soils are characteristic of volcanic zones and they are vulnerable to erosion.

The study area is located in the MZTV, which is the second most important urban centre in the State of Mexico and the fifth in the country. This area presents an accelerated demographic growth with a population of 2,172,035 inhabitants and an annual growth rate of 1.8% (INEGI, 2010). The MZVT is formed by 22 municipalities (a political and administrative unit used in Mexico, equivalent to the county in the USA) (GEM, 2010; SEDESOL, 2012). It should be noted that the study area only includes 7 of the 22 municipalities: Xonacatlán, Lerma, Ocoyoacac, San Mateo Atenco, Metepec, Toluca and Zinacantepec, which concentrate a total population of 1,516,996 inhabitants (INEGI, 2010). Additionally, the protected natural areas of "Nevado de Toluca" and "Otomí-Mexica" State Park have been considered.

Economic activity in the region is divided in: a) 3.4% in the primary sector, characterized by seasonal agriculture and extensive livestock; b) 35.9% in the secondary sector, conformed mainly by metalworking industry, textile industry, chemical industry, petrochemical industry, glass and derivatives industry, rubber and plastics industry, electricity generation, mining industry and construction industry; c) 56.8% in the tertiary sector, highlighting food trade, waste management, hotel management, among others (GEM, 2007c).

Factors such as population growth, economic activity, demand for public services and energy, the increase in the vehicle fleet (917,733 vehicles) and the high consumption of fossil fuels (65 peta Joules per year) (GEM, 2007c; GEM, 2012), have caused the MZTV is subject to strong environmental pressures in the biotic and abiotic environment, increasing the risks to health and environment due to air pollution.

2.2. Biomonitor

In order to determine the risk areas due to heavy metals exposure (Cr, Cu, Pb and Zn) in the MZTV, the mosses *Fabriona ciliaris* and *Leskea angustata* were used as biomonitors. In Mexico, studies on the biological diversity of mosses in urban areas and their use in environmental monitoring are scarce. Zepeda-Gómez et al. (2014) carried out a study of epiphytic mosses diversity in the MZVT. The authors identified that *Syntrichia amphidiacea*, *Leskea angustata*, *S. fragilis*, *S. pagorum* and *Fabriona ciliaris* were the species with the greatest ecological weight. The mosses *Fabriona ciliaris* and *Leskea angustata* were identified as the most tolerant species to desiccation and human disturbances. These moss species can be found in most of tree barks of the MZTV.

In this context, epiphytic mosses of the species *Fabriona ciliaris* and *Leskea angustata* were collected during two sampling seasons in the months of August and November that corresponding to the rainy and dry-cold seasons, respectively. The mosses were obtained from 15 different sites that include urban settlements, recreational parks and natural protected areas (Zarazúa-Ortega et al., 2013; Caballero-Segura et al., 2014; Zepeda-Gómez et al., 2014; Mejía-Cuero et al., 2015; Macedo-Miranda et al., 2016). Direction of the winds, urban vegetation cover and biomonitors abundance were considered for the sampling sites selection. The location of the sampling sites is presented in Fig. 1.

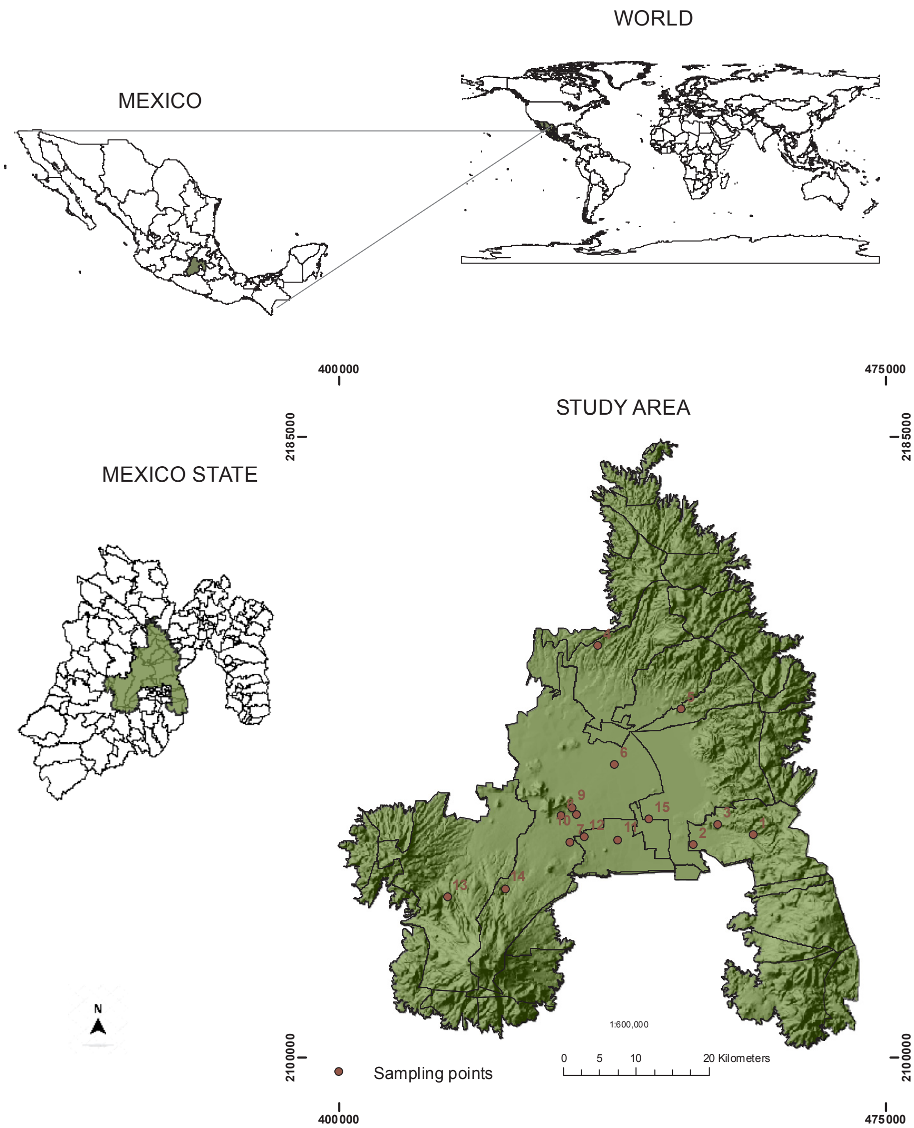

Fig. 1. Study area and moss sampling points.

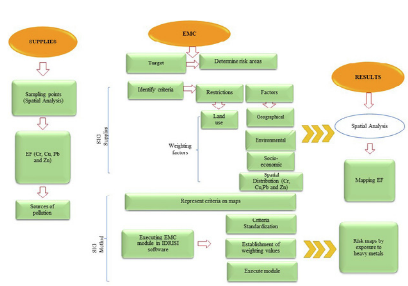

Fig. 2. Description of the process to determine the risk areas due to exposure to heavy metals.

2.3. *Quantification of heavy metals*

The concentration of Cr, Cu, Zn and Pb deposited in the biomonitor was determined by inductively coupled plasma optical emission spectrometry (ICP-OES), following the procedure used by Caballero-Segura et al. (2014). The collected mosses were previously washed with deionized water and then dried at room temperature for 48 h. Subsequently, they were ground and homogenized in an agate mortar. Finally, samples of 0.5 g previously digested in acid solution, were analysed in an ICP-OES (Thermo Jarrel Ash Corporation) model Atomscan Advantage Axial Type. The quantification of heavy metals was carried out under the following analysis conditions: sample uptake of 1.8 mL min^{-1}, auxiliary flow rate of 1.0 L min^{-1}, plasma flow rate 14 L min^{-1}, nebulizer pressure of 207 kPa and generator power of 1150 W. The analysis of the spectra was done by SPEC/PMT 2.1v software.

The results of the Cr, Cu, Pb and Zn concentrations were used to calculate the Enrichment Factor (EF). This factor estimates the enrichment of Cr, Cu, Zn and Pb by natural or anthropogenic sources. Enrichment factors values were calculated using Ti concentration (as conservative element) and equation (1):

$$EF = \frac{{}^{C_M}\!/_{C_{Ti}}\, moss}{{}^{C_M}\!/_{C_{Ti}}\, soil} \quad (1)$$

where C_M is the metal concentration in moss and soil. C_{Ti} is the Ti concentration (conservative reference element) in moss and soil (Sardans and Peñuelas, 2005; Lazo et al., 2018). EF ≤ 2 indicates that the moss does not have metals contributions of anthropogenic origin. EF between 3 and 5 indicates a slight anthropic contribution. EF between 6 and 9 indicates a moderate anthropogenic enrichment. Finally, EF ≥ 10 indicates the metal in the moss is highly enriched and it is coming from an anthropogenic source.

Table 1
Factors, criteria and sub criteria considered in the determination of risk areas due to exposure to heavy metals.

Factors	Criteria	Sub criteria
Environmental	Point sources	Manufacturing industry: Metalworking Textile Chemical Petrochemical Glass and derivatives Rubber and plastic Extractive and construction industry: Extraction of stone materials Brick making
	Mobile sources	Vehicle density: High Medium Low
Geographic	Wind direction	Influenced by the wind Without influence of winds
	Land use	Bare cover Vegetal cover Residential Urban vegetation
	Spatial distribution trends of EF	
Social and economic	Population density	High Medium Low

2.4. Geostatistical analysis

15 sampling points distributed in the study area were used in the geostatistical analysis according to the presence and abundance of the biomonitor. The EF of Cr, Cu, Pb and Zn calculated from the metal concentration accumulated in the moss was used as an indicator variable. The spatial correlation of the EF values of the heavy metals was carried out with the variogram function. The variograms of each one of the variables were calculated in the four spatial directions (0°, 45°, 90° y 135°) and additionally in the horizontal omnidirectional. The experimental variogram was calculated using the semi variogram equation (see equation (2)) (Wackernagel, 1995).

$$\gamma_{(h)} = \frac{\sum_{i=1}^{n(h)} [(Z(x_i) - Z(x_i + h)]^2}{2n_{(h)}} \tag{2}$$

where $\gamma_{(h)}$ is the semi variance, $n_{(h)}$ is the total number of pairs of samples separated by a distance interval *h*. $Z(x_i)$ is the value of the variable in a site *x*. $Z(x_i + h)$ is another value of the sample at the distance *h*, and $n_{(h)}$ is the total number of pairs of samples separated by

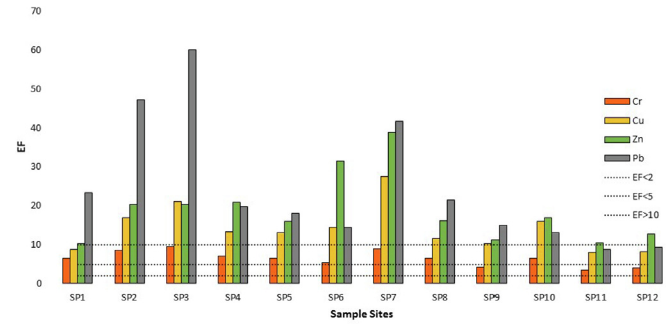

Fig. 4. Cr, Cu, Zn and Pb EF from each one of the sample sites in rainy season.

h. The modelling and adjustment of the semi variograms were performed using the spherical spatial variation model given by the mathematical expression (3). This is the most model used in environmental applications (Burrough, 2001; Lixin and Revesz, 2003; Martins et al., 2012).

$$\gamma_{(h)} = \begin{cases} C_0 + C_1(\frac{3}{2}(\frac{h}{r}) - \frac{1}{2}(\frac{h}{r})^3),\ h \le r \\ C_o + C_1,\ h > r \end{cases} \tag{3}$$

where C_1 is the sill, C_o is the nugget, *r* is the range and *h* is the distance. Finally, the spatial interpolation process of the EF was performed using the ordinary Kriging model (Wackernagel, 1995). The Kriging model estimates the value of the variable *Z* at a point x_i not previously measured, weighting the weights of the variable with its minimum value, as shown in the expression (4).

$$\bar{Z}(x_i) = \sum_{i=1}^{n} w_i Z(x_i) \tag{4}$$

All statistical procedures were performed with the Idrisi software and considering a statistical confidence level > 90%.

2.5. Risk areas

Fig. 2 shows the procedure to determine the risk areas by exposure to Cr, Cu, Pb and Zn in the MZVT. As shown in the figure, the construction of the risk map was carried out by Multi-Criteria Decision Making (MCDM) analysis, which is a weighting method based on analytical hierarchy process (AHP). The AHP is able to perform a prioritization or weighting of each element of the hierarchy in an efficient and rational manner (Li et al., 2017a, b). This type of mathematical analysis is used successfully in complex processes of identification of sites where there are different solution alternatives, for example, in environmental applications (Giulia et al., 2015), urban planning

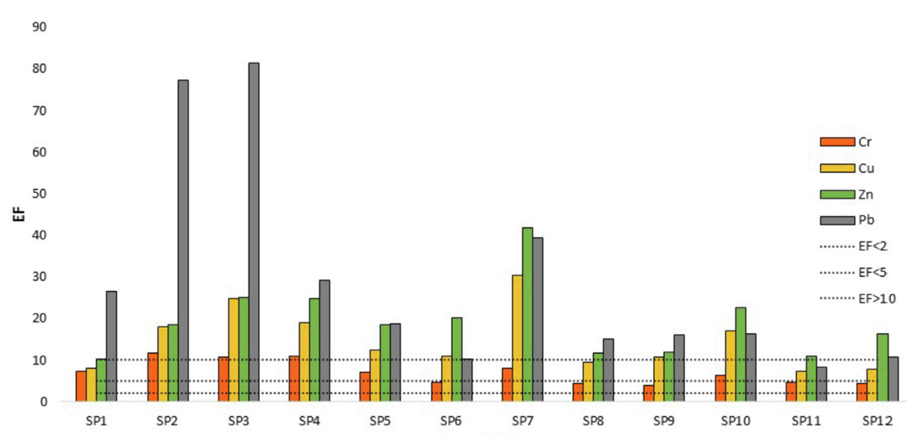

Fig. 3. Cr, Cu, Zn and Pb EF from each one of the sample sites in dry-cold season.

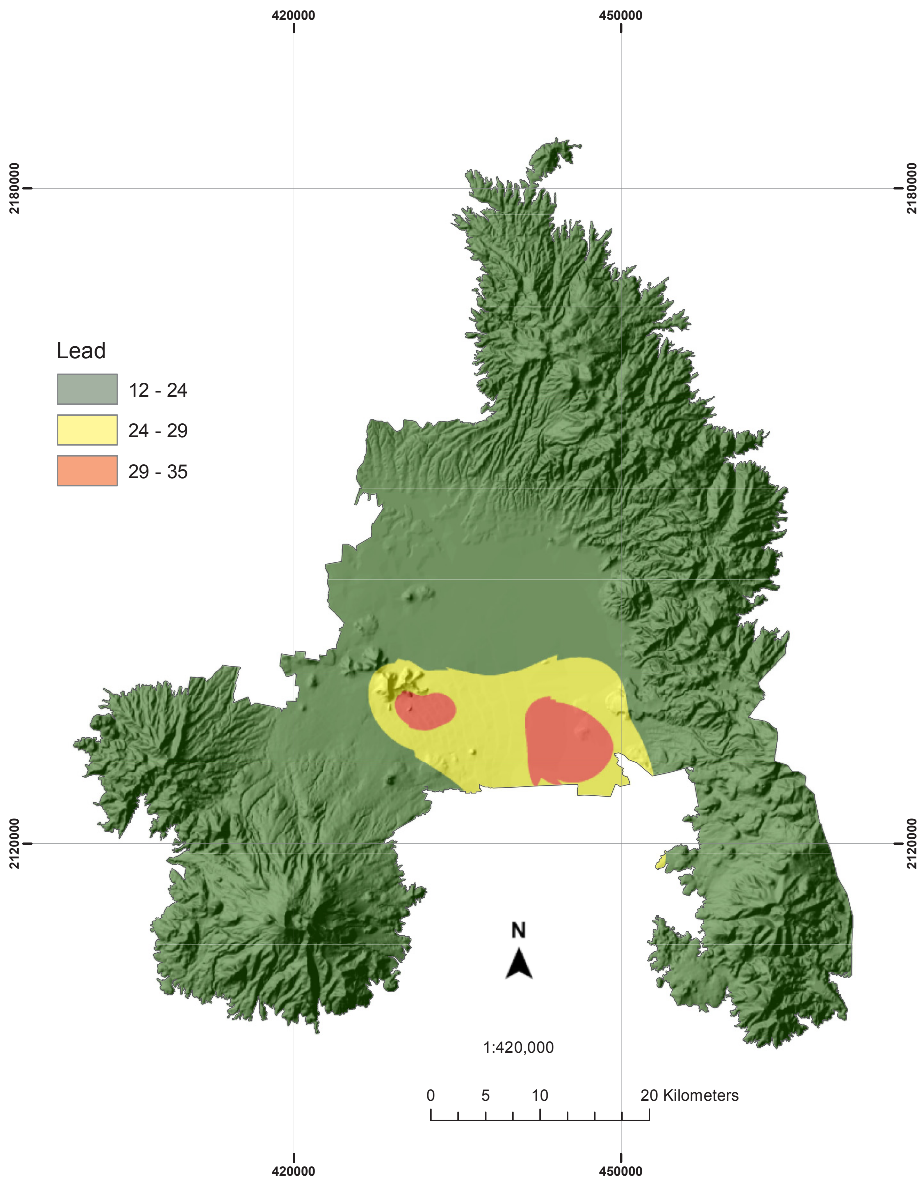

Fig. 5. Spatial distribution of Pb enrichment factors, in the study area (9.83% of maximum error of the prediction model).

(Criado et al., 2017; Srivanit and Selanon, 2017), groundwater vulnerability assessment (Kumar et al., 2017), among others.

The first step was to define the objective of the analysis; in our case it was to identify the risk zones due to exposure to airborne heavy metals. Then, the factors, criteria and sub criteria were defined; in Table 1 each of these are presented. The factors *a) geographical*, *b) environmental* and *c) socio-economic* were selected. Each factor was divided into some criteria and each criterion was divided into some sub criteria.

a) Geographical factor

The EF spatial distribution, winds direction and land use were the geographical factors considered. In this study, land use was considered in four categories: urban settlements, bare ground, urban vegetation and vegetation covert. These geographical elements influence the resuspension, transport and dispersion of heavy metals (Schreck et al., 2012; Smolyakov et al., 2017; Lazo et al., 2018).

b) Environmental factor

The potential emission sources were considered as environmental factors: mobile and point sources. This consideration is based on the fact that the study area has a high industrial activity and a high vehicular density. The manufacturing and construction industry were identified as points sources. The vehicular density was considered as a mobile source (GEM, 2007c; GEM, 2012).

c) Socio-economic factor

The population density of the study area was considered as a socioeconomic factor, the above means that a high population density is more vulnerable to exposure by heavy metals (Koedrith et al., 2013; Shaban et al., 2016; Zeng et al., 2016).

After determining the factor, the next step was the criterion weighting. In this work, AHP was used for weighting the criteria. This weighting of factors represents the relationship between the study objective and the decision alternatives. As seen in Table 1, the factors that have more influence in achieving the objective it was assigned a greater weight. Factors with less importance have less weight. The next step was to display the outputs into the risk areas map. Based on the outputs, the risk areas were categorized into: a) High risk, b) Medium risk and c)

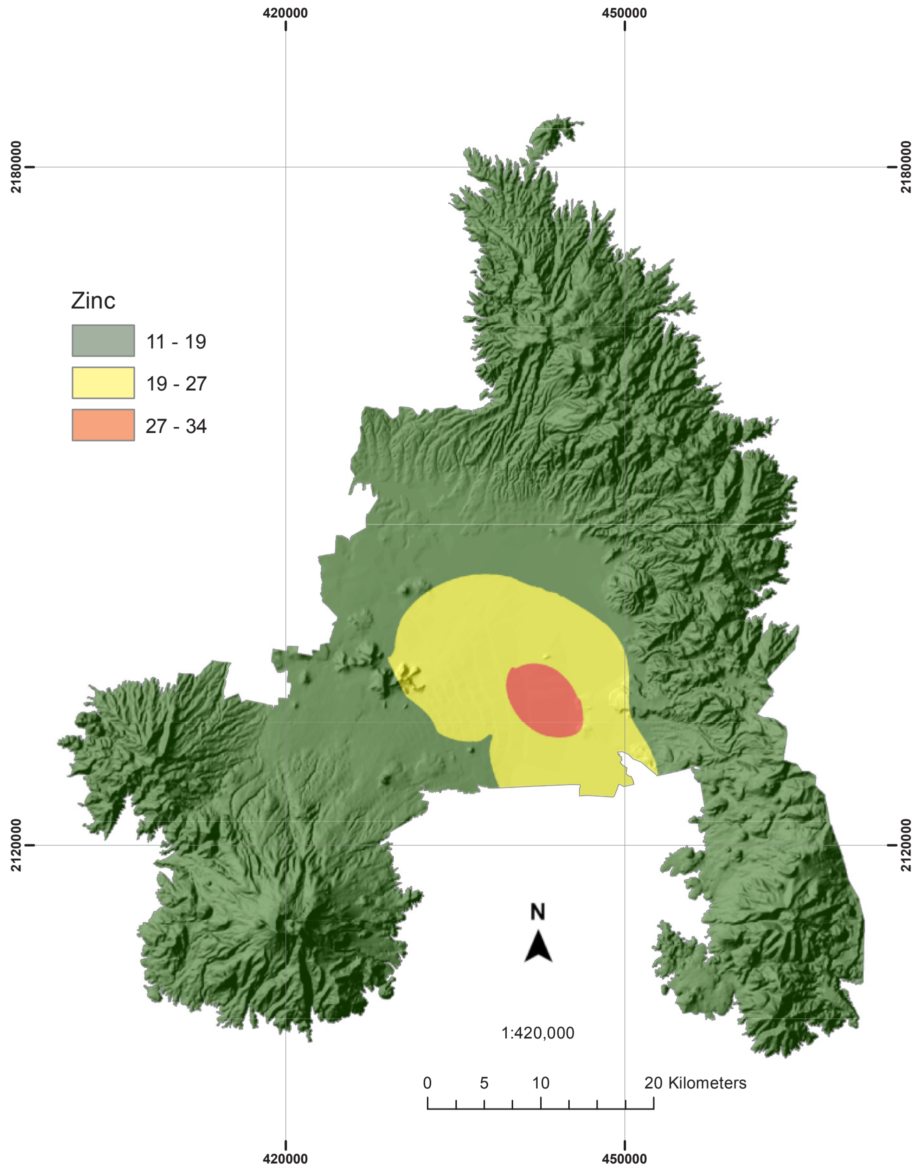

Fig. 6. Spatial distribution of Zn enrichment factors, in the study area (9.11% of maximum error of the prediction model).

Low risk. All inputs and modelling were obtained using the Idrisi software.

3. Results and discussions

Figs. 3 and 4 show the Cr, Cu, Pb and Zn enrichment factors from each one of the sampling sites in the dry-cold season and in the rainy season, respectively. As shown, the highest EF is present in the dry season, in both seasons Pb is the heavy metal with the highest values, followed by Zn, Cu and Cr. The EF obtained for all the heavy metals show that there is a moderate to high anthropogenic enrichment. This last, evidence there are emission sources that contribute significantly in the Cr, Cu, Pb and Zn concentration accumulated in the biomonitor.

3.1. Geostatistical analysis

The knowledge of the heavy metal's spatial patterns and trends through geostatistical analysis is an essential requirement to determine the risk areas. The geostatistical analysis results were visualized in spatial patterns maps using the Idrisi software.

In Figs. 5, 6, 7 and 8 the EF's patterns and trends of Pb, Zn, Cu and Cr are shown. These spatial patterns depend on the geological, environmental, geographical and meteorological characteristics of the study area, as well as the chemical speciation of the metal (Chandrasekaran and Ravisankar, 2015). As shown in Fig. 5, Pb always had EF > 8 in all study area. The spatial tendency of lead coincides with the prevailing winds pattern (SE-NW direction) in the MZVT. The highest Pb enrichment factors (EF > 24) were located in the central part of the Toluca Valley. This Valley is characterized by having an intense vehicular traffic in the primary and secondary roads (121,513 - 23,786 vehicles per day, average annualized) (GEM, 2012). Three anthropogenic sources could contribute to the Pb enrichment in the MZVT: a) combustion processes of food waste, paper, plastics, textiles, rubber, wood and metal melting. b) Plastic and textile industries, as well as metalworking. c) Re-deposition of old Pb coming from leaded gasoline. Next, each of one are discussed.

a) Combustion processes of food waste, paper, plastics, textiles, rubber, wood and metal melting. In the study area, it has been identified at least 6 smelters, 6 waste incinerators and the uncontrolled waste burning to the environment have been identified (DENUE, 2018). Some studies such as the one carried out by Li et al. (2017a, b)

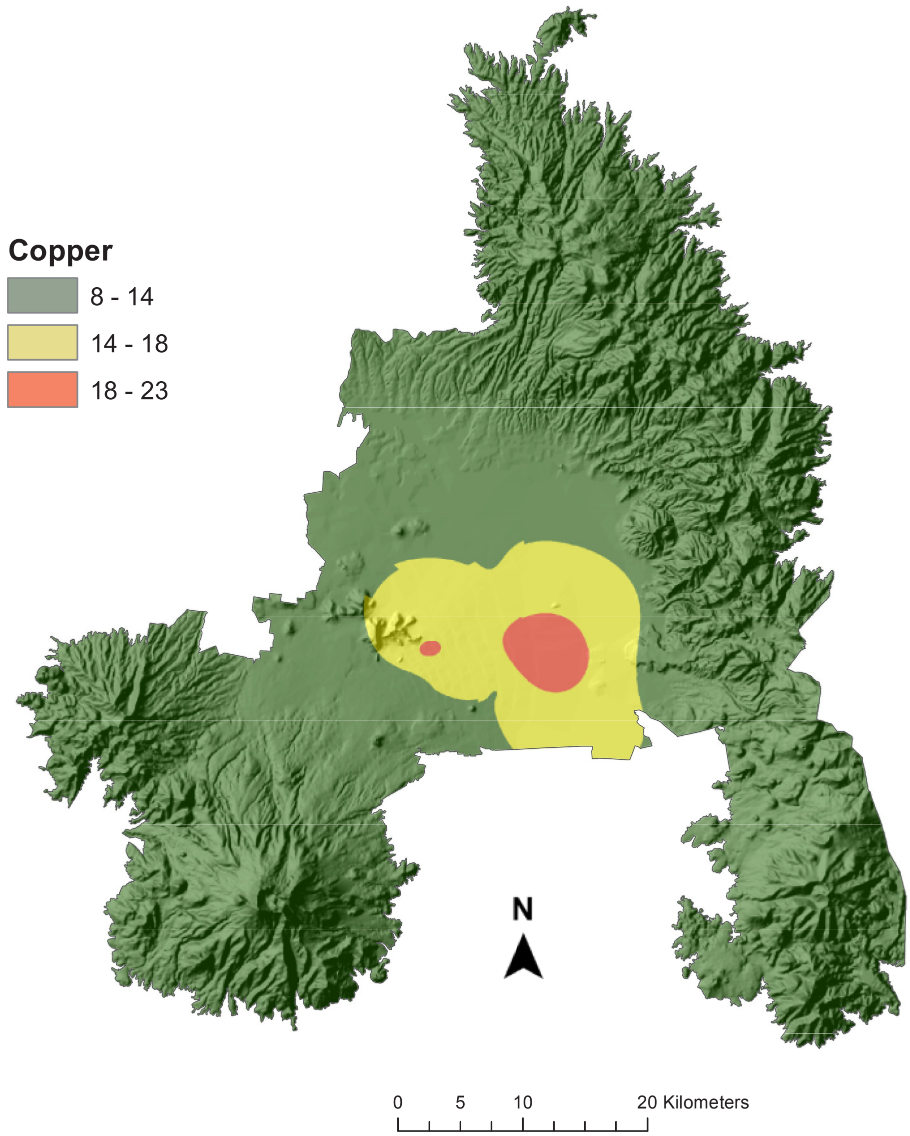

Fig. 7. Spatial distribution of Cu enrichment factors, in the study area (6.39% of maximum error of the prediction model).

suggest as sources of lead: the combustion processes of rubbers, wood, polyethylene bags and polyvinyl chloride (common materials for urban solid waste).

b) Plastic and textile industries, as well as metalworking. According to the National Statistical Directory of Economic Units, in the study area there are around of 835 textile, plastics, glass, paints and metallurgical manufacturing industries (DENUE, 2018).

c) Re-deposition of old Pb coming from leaded gasoline. In Mexico, leaded gasoline was banned in 1990; however, the re-deposition phenomenon of lead has been observed in urban and with traffic areas in other countries (Simonetti et al., 2003; Chrastný et al., 2018). In this context, the re-deposition of lead, in study area, is explained by the existing correlation between the Pb enrichment factors trend patterns, with respect to the prevailing winds patterns.

On the other hand, studies conducted in other regions suggest that the burning of unleaded gasoline and diesel are a Pb contributor to the air in metropolitan zones (Shiel et al., 2012; Yao et al., 2015; Chrastný et al., 2018). These studies estimate 9.6 ng g^{-1} to 17.9 ng g^{-1} (unleaded gasoline) and 29.4 ng g^{-1} to 44.8 ng g^{-1} (diesel), depending on the crude oil used for its manufacture (Yao et al., 2015). Metal baseline studies have to be conducted in the study area in order to determine sources of Pb enrichment.

The map of EF's patterns and trends of Zn is presented in Fig. 6. It is observed the whole study area presents EF $>$ 10, which indicates that the source of the metal is mainly of anthropogenic origin. The highest EF values ($>$ 23) were obtained in the central part of the study area with a spatial distribution pattern associated with the urban high population settlements and with the highest vehicular density. This area is characterized by concentrating a 121,000 average daily annualized vehicular traffic. Also, an EF's spatial distribution similar to the wind pattern is observed (SE-NO direction). Several authors have identified that the major contamination sources of Zn are industrial activities, urban activity and agriculture (Fekiacova et al., 2015). Zn and Zn-compounds are widely used in agricultural fertilizers (McBride and Spiers, 2001; Fekiacova et al., 2015). In this context, the MZVT is characterized to have land uses such as urban settlements, bare ground and different industrial zones (GEM, 2007a; GEM, 2012). Therefore, it can be inferred that in the study area, the industrial activities, combustion of fossil fuels, incineration of municipal waste and agricultural activity due to fertilizer use are the main zinc pollution sources.

Fig. 7 shows the spatial distribution of copper enrichment factors. As shown in the figure, there are EFs between 7.5 and 23 which indicate that copper mainly of anthropogenic origin is accumulated in the

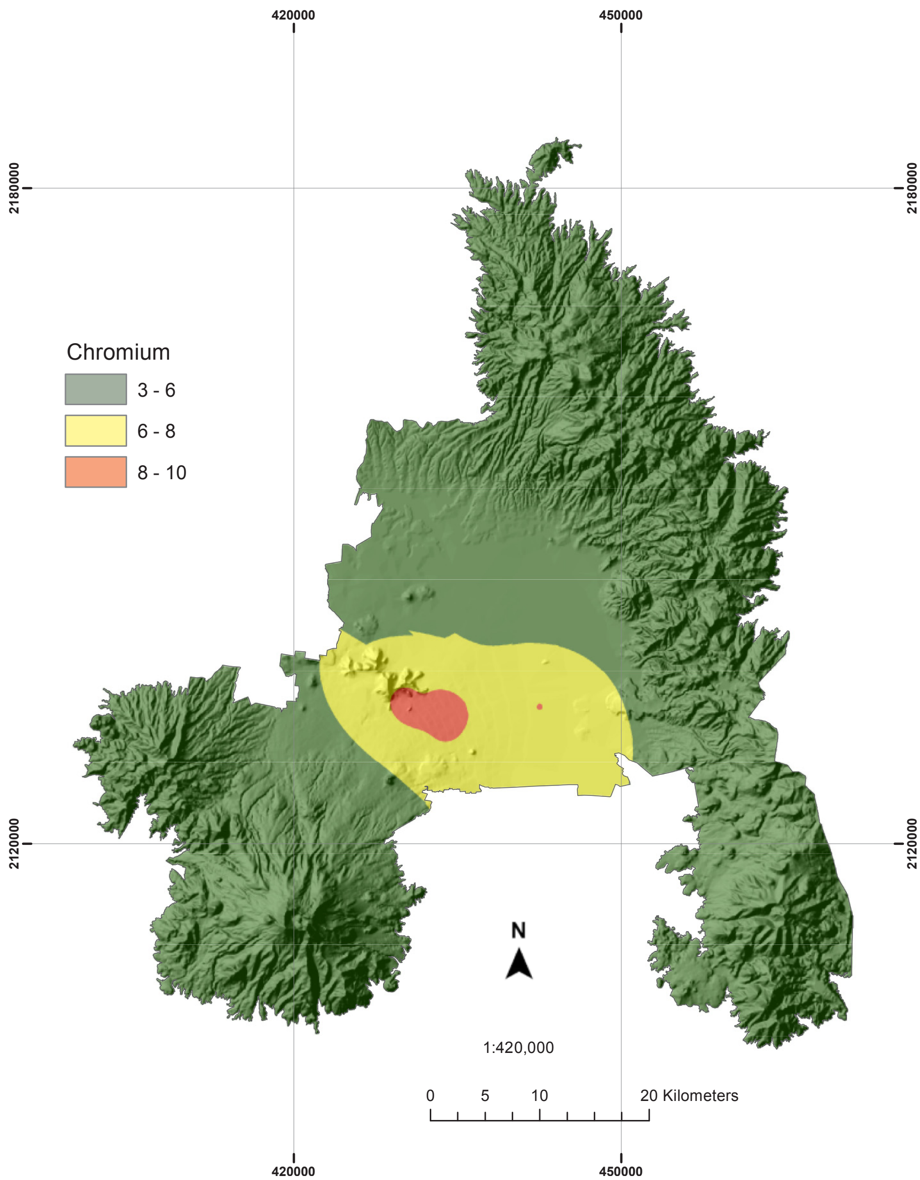

Fig. 8. Spatial distribution of Cr enrichment factors, in the study area (2.31% of maximum error of the prediction model).

biomonitor. The spatial distribution obtained shows the highest enrichment factors (EF > 19) coincide with the sectors of greater economic and industrial activity. A hotspot is observed in the municipalities of San Mateo and Lerma, around the most important highway in the MZTV. The enrichment of Cu can be related with the activities of the automotive, glass, paints and electroplating industries located in the industrial sector of the Lerma municipality (DENUE, 2018). Additionally, it is likely that agricultural and livestock activities in the region could contribute to the enrichment of this metal, as it has been observed in other parts of the world (Mirzaei Aminiyan et al., 2018). For example, authors such as McBride and Spiers (2001) and Pan et al. (2016) have described that fertilizers and pesticides are a significant source of Cu. Also, the cattle slurry can contain significant concentrations of Cu (Pan et al., 2016). In this context, the decomposition of pesticides and fertilizers used in potato crops (in the agricultural and livestock areas of the MZTV) transfer the Cu by runoff and, probably, this metal is re-suspended and deposited by the action of the wind.

Finally, Fig. 8 shows a Cr enrichment probably coming from anthropogenic sources in the MZTV, where the highest enrichment factors (> 13) are in the central portion. Studies performed in other countries have identified that Cr can be associated to combustion of diesel oil (Mróz et al., 2017) and biomass burning, among other industrial activities (Ismail et al., 2012; Wannaz et al., 2012; Abril et al., 2014). In this context, the vehicle emissions, biomass burning as an agricultural practice, as well as to brick kiln emissions could be the main anthropogenic sources of chromium in the area. For example, according to State of Mexico government records, at least 391 brick kilns have been identified in the MZTV (GEM, 2015).

The results from the geostatistical analysis allow establishing the heavy metals distribution in the study area has different spatial patterns that depend on the land uses and emission sources close to the places where the biomonitor was collected.

3.2. *Risk maps*

In Fig. 9 the risk map of exposure to heavy metals is presented. As shown in the figure, the exposure risk was classified into 3 categories a) “High” risk, b) “Medium” risk and c) “Low” risk. In accordance with the results, “High” risk areas are found in small hotspots located in the municipalities of Toluca, Metepec, San Mateo Atenco and Lerma. These hotspots are characterized by settlements of high population density (Toluca with 3412 inhabitants/km^2 and Metepec with 3040

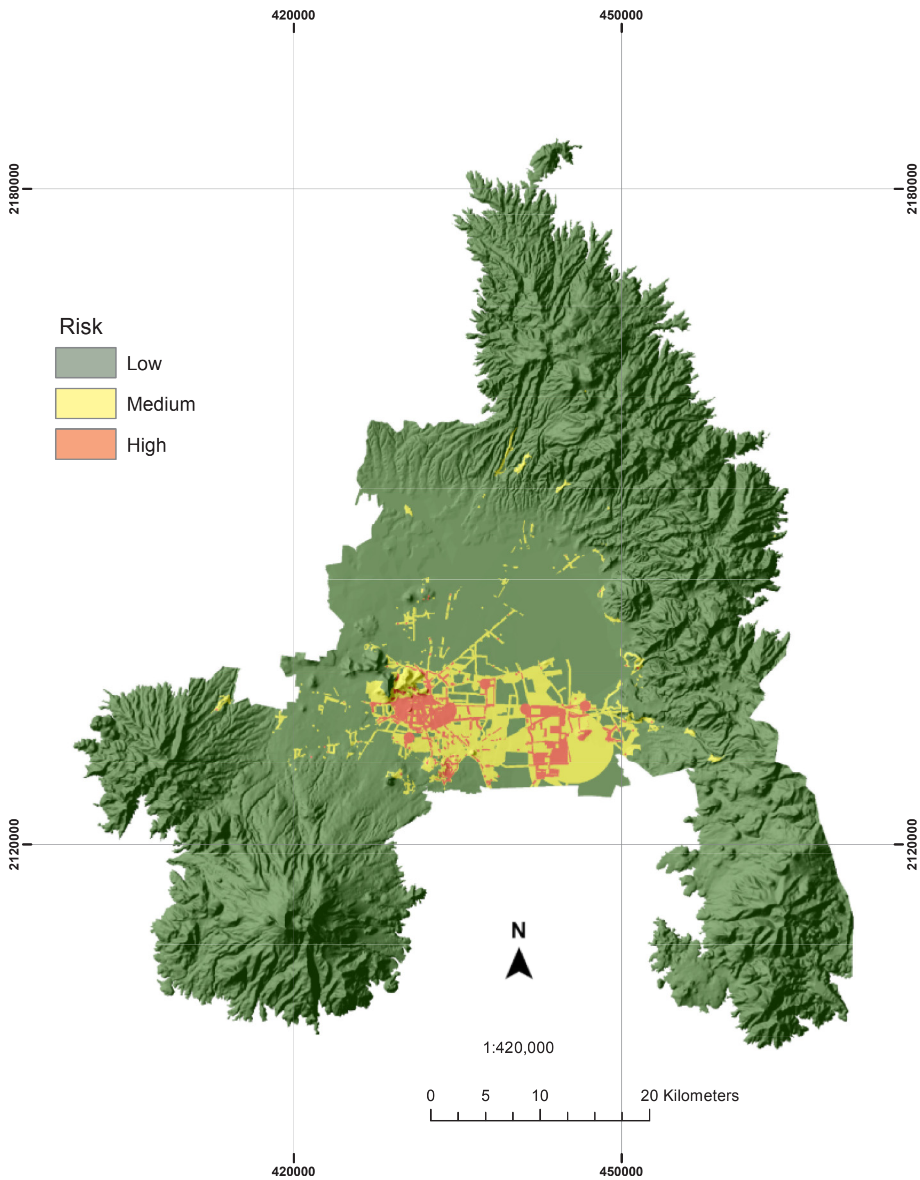

Fig. 9. Risk map of exposure to heavy metals in the study area.

inhabitants/km^2 (INEGI, 2010), and highways with intense vehicular traffic. Additionally, in the municipalities of San Mateo Atenco and Lerma are located the three most important industrial parks in the MZTV: “Toluca 2000”, “El Cerrillo” and “Lerma”. These industrial parks, together with the deposition of the particulate matter, contribute to the environmental pressures increase in the region, as well as the health and the environment risks due to high levels of atmospheric pollution.

The areas identified as “Medium” risk are located in the centre and north of the municipalities of Toluca, north of Metepec, as well as in Lerma and San Mateo Atenco. These sites are characterized by a poor urban vegetation cover (< 9 m^2/inhab). Study developed by Versañez (2014), indicates that 69% of the municipalities territory that make up the study area have insufficient urban vegetation coverage, 16% have poor coverage and only 15% have acceptable coverage. This same study considered as urban vegetation cover acceptable if it has more than 9 m^2/inhab (Versañez, 2014). It should be noted that this vegetation cover includes the vegetation of public parks and gardens, vegetation on roads, trees at the limits of cultivated areas and scattered trees. The poor urban vegetation cover facilitates the dispersion of heavy metals associated to particulate matter and therefore it contributes to the increased risk of exposure to those pollutants (Yang et al., 2005; Scovronick, 2015). It has been shown that urban vegetation cover contributes to the reduction of particulate material released into the atmosphere (Weber et al., 2014; Yang et al., 2015); also offers many social, economic and environmental functions, such as lowering noise, decreasing wind speed, having positive effect on human psychology, producing economic resources and promoting soil conversation, among others (Cetin and Sevik, 2016; Sevik et al., 2016; Turkyilmaz et al., 2018a). The particulate matter can mainly interact with the vegetation by impact, interception and Brownian diffusion (Janhäll, 2015), therefore, it can be established the high risk in this area is principally associated with a low vegetation cover and with the increased pollution sources that were identified in the geostatistical analysis.

The remaining study area can be considered as “Low” risk. This area is characterized by an urban vegetation cover of more than 40 m^2/inhabitant consisting mainly of tree species of oak and pine that serve as natural barriers that intercept the particulate matter.

It should be noted that in the study area, there are no similar studies with which to perform a comparative analysis of the results obtained. However, the general trends observed in the geostatistics analysis and in the risk map are similar to those obtained in other regions of the world, but with other different methodologies (Martins et al., 2012; Trujillo-González et al., 2016; Mirzaei Aminiyan et al., 2018; Turkyilmaz et al., 2018a).

As it has been evidenced, the MZTV has serious environmental pressures caused mainly by the population growth, the economic activities and the demand for public services and energy (GEM, 2007a; GEM, 2012). The environmental pressures have increased the risks to inhabitant's health and the environment due to air pollution. In this context, the Federal and State governments, through the environmental agencies, have established a program to improve the air quality in the Toluca Valley. The goal of this program is to establish strategies in order to reverse the deterioration of air quality by regulating the $PM_{2.5}$, PM_{10}, O_3, NO_2, SO_2 and CO concentrations in the MZTV. Despite government efforts, the concentration of particulate matter has been increasing over time, with the health risks that implies (GEM, 2012). The last has been evidenced by means of our results, which indirectly show an anthropogenic enrichment of heavy metals in the biomonitor used and it also highlights the importance of redefining the regulatory strategies of $PM_{2.5}$ and PM_{10} in order to reduce the risks for exposure to heavy metals in the study area. It should be noted the presented methodology in this paper is a fast and low-cost evaluation tool that could allow to local government environmental agencies to define new public policies on air pollution control. In addition, this methodology could facilitate the identification of social, political and economic groups to act as stakeholders in the development of a participatory and even new air quality management program for the MZTV.

4. Conclusions

The EF results for all the heavy metals show a moderate to high anthropogenic enrichment. This evidence indicates that in the MZTV there are emission sources that contribute significantly in the Cr, Cu, Pb and Zn concentration accumulated in the mosses. The distribution of heavy metals in the MZTV has different spatial patterns that are related with the land uses and the emission sources close to the places where the biomonitors were collected.

The highest Pb EFs (> 20) were located in the central part of the Toluca Valley. Three anthropogenic sources contribute to the Pb enrichment: a) combustion processes of food waste, paper, plastics, textiles, rubber, wood and metal melting; b) plastic and textile industry, as well as metalworking; and c) re-deposition of old Pb coming from leaded gasoline. In the case of Zn, the EF results allowed to establish that the source of metal is mainly of anthropogenic origin. The industrial activities, combustion of fossil fuels, incineration of waste and agricultural activities due to fertilizer use have been identified as sources of heavy metal pollution. On the other hand, the spatial tendencies of Cu showed that the highest enrichment factors are related to the high density of vehicles, as well as the activities of automotive, glass, paint and electroplating industries. In rural zones, the agricultural and livestock activities contribute to the enrichment of this metal. Finally, the vehicle emissions, biomass burning as an agricultural practice, as well as to brick kiln emissions could be the main anthropogenic sources of Cr in the MZTV.

In general, the combustion processes, vehicle emissions, biomass burning, brick kiln emissions, agricultural and livestock activities, manufacturing industry and suspended and deposited particles by the action of the wind, have been identified as the main sources of heavy metals in study area.

The high and medium risk areas are characterized by poor urban vegetation coverage and because it is located close to highways and industrial parks. The low risk area is characterized by high urban vegetation coverage. The poor urban vegetation coverage and the increase in the pollution sources are the main factors that determine the risk category in the MZTV.

The proposed methodology for identifying risk zones has demonstrated been a fast and low-cost evaluation tool and it could help to environmental agencies to define new public policies on air pollution control in the MZTV.

Acknowledgements

This work is part of the projects EDOMEX-2009-C02-132003 from COMECyT and AM-110 from the National Institute for Nuclear Research.

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