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Study of the Distribution of Heavy Metals in the Atmosphere of the Guanajuato City: Use of Saxicolous Lichen Species as Bioindicators

Estudio de la distribución de metales pesados en la atmosfera de la ciudad de Guanajuato: uso de especies de líquenes saxícolas como bioindicadores

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Abstract

The atmospheric deposition of some heavy metals was investigated using saxicolous lichen species (*Xanthoparmelia mexicana* (Gyeln.) Hale, *Xanthoparmelia tasmanica* (Hook. f. & Taylor) Hale, *Caloplaca aff. brouardii* (B.deLesd.) Zahlbr, *Caloplaca aff. ludificans* Arup, and *Aspicilia* sp), samples were collected from three zones (rural, suburban and urban) along the Guanajuato city, during the months of October-November 2012, April, July, and October 2013 and January 2014. Lichen samples were analyzed using the Inductively Coupled Plasma Mass Spectrometry technique. The concentrations of heavy metals in lichen samples from the *Xanthoparmelia* species ranged from (96.21 μg g^{-1}) for lead (Pb), (95.10 μg g^{-1}) for zinc (Zn), (58.40 μg g^{-1})for vanadium (V), (105.15 μg g^{-1}) for Chrome (Cr), and (48.93 μg g–1) for Niquel (Ni). *Caloplaca* species (92.42, μg g^{-1}) for lead (Pb), (172.97 μg g^{-1}) for Zinc (Zn), (53.51 μg g^{-1}) for vanadium (V), (91.23 μg g^{-1}) for copper (Cu), respectively, and Aspicilia sp (612.91μg g^{-1}) for lead (Pb), (72.24 μg g^{-1}) for zinc (Zn), (56.25 μg g^{-1}) for vanadium (V), (18.24 μg g^{-1}) for copper (Cu). The statistical significance of between Co-V, Ni-Cr, Ni-Co, Sn-Zn, Co-Cr, Zn-Th, Sn-Th and Co-Zn concentrations confirmed anthropogenic sources mainly due to emissions from vehicular traffic, fossil fuel combustion correlations, solid waste disposal and other local anthropo-

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genic activities. Pollution indices were additionally calculated by heavy metals concentrations in order to use lichens in Guanajuato city as bioindicators of air pollution. The concentration of these metals was observed to be in higher range as maximum values of Pb, Zn, V, and Cu reported from the lichen samples for the suburban and urban zones in Guanajuato city. The accumulations of Ni and Cr from both zones are similar in concentration. The contamination factors or the pollution index factor and the pollution load index criteria revealed high levels of Be, Cu, Co, Zn, Pb, and Th in *Caloplaca* species and *Aspicilia* sp., while *Xanthoparmelia* species show higher values only in Be, Sb and Pb. The results revealed that the most sensitive lichens were *Aspicilia* sp., with the highest levels of Pb. The results obtained reveal important contributions towards understanding of heavy metal deposition patterns and provide baseline data that can be used for potential identification of areas at risk from atmospheric heavy metals contamination in the region. The use of saxicolous lichens provide a cost–effective approach for monitoring regional atmospheric heavy metal contamination and may be effectively used in large scale air pollution monitoring programmer.

Keywords: lichens, heavy metal pollution, indicator, Guanajuato city.

Resumen

En este estudio se analizaron la concentraciones de algunos metales pesados encontrados en la atmosfera de la ciudad de Guanajuato, empleando para ello, especies de líquenes saxícolas (Xanthoparmelia mexicana (Gyeln.) Hale, Xanthoparmelia tasmanica (Hook. f. & Taylor) Hale, Caloplaca aff. brouardii (B.deLesd.) Zahlbr, Caloplaca aff. ludificans Arup, and Aspicilia sp) recolectados en tres zonas (rural, suburbana y urbana) a lo largo de los meses octubre-noviembre de 2012, abril, julio y octubre de 2013, así como enero de 2014. Las muestras de líquenes se analizaron usando la técnica de espectrometría de masas de plasma acoplado inductivamente. La concentración de metales pesados en las muestras de los líquenes de la especie de Xanthoparmelia van de (96.21 μg g^{-1}) para plomo (Pb), (95.10 μg g^{-1}) para zinc (Zn), (58.40 μg g^{-1}) para vanadio (V), (105.15 μg g^{-1}) para Cromo (Cr) y (48.93 μg g^{-1}) para Niquel (Ni). Caloplaca especie (92.42, μg g^{-1}) para plomo (Pb), (172.97 μg g^{-1}) para Zinc (Zn), (53.51 μg g^{-1}) para vanadio (V), (91.23 μg g^{-1}) para cobre (Cu), respectivamente, y Aspicilia sp (612.91μg g^{-1}) para plomo (Pb), (72.24 μg g^{-1}) para zinc (Zn), (56.25 μg g^{-1}) para vanadio (V), (18.24 μg g^{-1}) para cobre (Cu). La estadística entre las concentraciones de Co-V, Ni-Cr, Ni-Co, Sn-Zn, Co-Cr, Zn-Th, Sn-Th and Co-Zn confirma una fuente antropogénica, principalmente debida a las emisiones del tráfico vehicular, combustión y actividades antropogénicas locales. Los índices de contaminación se calcularon, con la finalidad de utilizar los líquenes estudiados como indicadores de calidad del aire en la ciudad de Guanajuato. Se observaron valores altos en Pb, Zn, V y Cu. La concentración de Ni y Cr en ambas zonas son similares. Los factores de contaminación o el factor de índice de la contaminación y los criterios de índice de contaminación, revelaron niveles elevados de Be, Cu, Co, Zn, Pb y Th en las especies Caloplaca y Aspicilia sp., mientras que las especies Xanthoparmelia muestran los valores más altos solo en Be, Sb y Pb. Los resultados revelaron que el liquen más sensible fue la Aspicilia sp, con los niveles más altos de Pb. Los resultados obtenidos revelan importantes contribuciones para la comprensión de los patrones de deposición de metales pesados y proporcionan a su vez datos de referencia que pueden utilizarse para su posible identificación de zonas de riesgo. El uso de líquenes saxícolas ofrece un enfoque rentable para el monitoreo de la contaminación por metales pesados en la atmosfera y pueden utilizarse con eficacia en la vigilancia de la calidad del aire.

***Descriptores**: líquenes, contaminación metales pesados, indicador, Ciudad de Guanajuato.*

Introduction

In the last decades, several studies have shown that lichens are excellent bioindicators of air pollution (Addison and Puckett, 1980; Farner *et al*., 1992; Gries, 1996; Jeran *et al*., 2002; Nash and Gries, 2002; Gartner Lee *et al*., 2006; Kinalioglu *et al*., 2010), mainly due to their susceptibility to the deposition of airborne pollutants in the form of soluble salts and particles (Nimis *et al*., 2002). Lichens accumulate and retain macronutrients, trace elements and metal elements to concentrations that exceed their physiological requirements, tolerating high concentrations of toxic pollutants. The accumulation of elements in lichens occurs by particulate trapping, active uptake of anions, passive absorption of cations and ion exchange Nieboer *et al*. (1978). According to Boonpragob *et al*. (1989) and Garty (2001), the residence of elements in lichens is different for macronutrients, trace elements and metals. The macronutrients are mobile and their concentrations in lichens can change seasonally, whereas trace elements and metals are less mobile and accumulate in lichen species over time with the advantage of metal contents decreasing when air quality improves. Information about atmospheric pollutant levels in industrial and

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mining areas is particularly scarce in Mexico and the use of lichens as bioindicators of atmospheric pollution has received little attention. Mining activities are widely known as the main pollutant source by releasing high concentrations of heavy metals to the environment (Conesa *et al*., 2007). Specifically, mining activities in the Guanajuato city have been developed for over 500 years, constituting the most important economic activity in the region. For the last five centuries, mineral deposits have been utilized to obtain commercial quantities of iron, lead, zinc, copper, gold and silver. Iron is present in oxides (hematite, and magnetite) and sulfides (pyrite); lead and zinc occur in galena and sphalerite, while copper is present in chalcopyrite (Puy *et al*., 2013). No literature on heavy metal pollution in the Guanajuato city is available and neither on the use of lichens as bioindicators for atmospheric trace elements and heavy metal deposition. The objective of this work was the use of saxicolous lichens as bioindicators of atmospheric deposition of trace elements and heavy metals in the city of Guanajuato. Samples were collected at three sites: rural, suburban and urban; the first is considered a pristine area located in the forest known as 'La Bufa' and the remaining two are influenced by anthropogenic activities (Figure 1). Pollution indices, such as contamination factors (CFs) and pollution load index (PLI) were used to determine the pollution state and to assess the possible sources of contaminants. This study can be considered as a basis for future research on air quality monitoring in areas influenced by strong human impact (mining extractions, industry and vehicular emissions).

Materials and methods

Study area

Guanajuato is a city in central Mexico and the capital of the state bearing the same name. The origin and the economic development of the city come from the discovery of mines in the surrounding mountains. The city is located at 2,000 meters above sea level and is characterized by a regional semi-arid climate. Temperature varies from 6 to 20° C in winter and 21 to 32°C in summer. Most of the rainfall occurs between May and September, with a total annual rainfall reaching 700 mm/year. The trees, which generally reach heights of 15 m, are distributed mostly at the summit of the hills where mining has not yet spread. The site was selected due to the anthropogenic activities such as mining, stone crushers, and intense vehicular flow. Lichen specimens were collected in three zones in Guanajuato city:

1. Urban (four sites were sampled: Plaza de Los Angeles (14Q265491-2325649), Belen (14Q265388-2325963), Teatro Principal (14Q265949-2325548) and Universidad de Guanajuato (14Q265748-2325687).
2. Suburban (two sites were sampled: Pastita (14Q266352-2324963), and Music School (14Q 267277-2324000), and
3. Rural (one site were sampled: la Bufa-14Q 266565-2323525), (Figure 1).

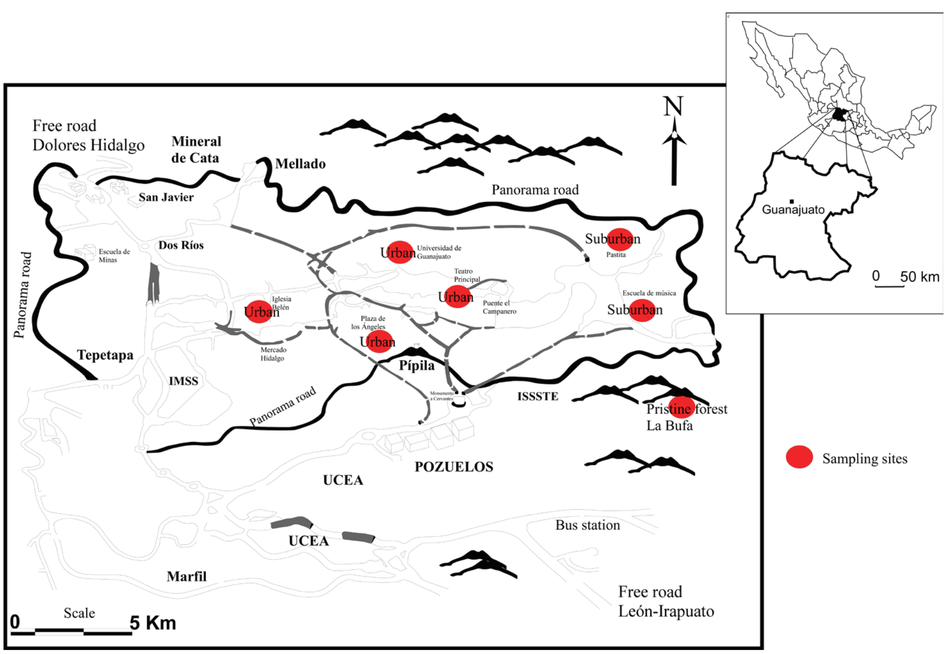

Figure 1. General map of Guanajuato city, showing the locations of the studied sites

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Sampling and sample treatment

Lichen specimens were sampled at the same time during October and November 2012, April, July, and October 2013 and January 2014 in three zones (Figure 1): rural (pristine forest 'La Bufa'), suburban (influenced by mining and stone crushers), and urban (influenced by mining and intense vehicular flow). Collections of the lichens, together with their substrates, were carefully sampled directly from uncontaminated rocks in the rural zone (named here standard reference material or SRM) and the other samples were taken from rocks influenced by human activities in suburban and urban zones (termed here as influenced by human activities or IHA). A minimum of three samples for each species were collected in selected sites with a steel knife and approximately 3-4 g of the lichen thallus were taken for each species. The specimens were stored in perforated plastic bags, maintained at 4°C during the transport to the laboratory and refrigerated at -4°C before use for the analysis of ICP-MS. The lichen specimens were reviewed taxonomically using specialized keys (Nash *et al*., 2004, 2007), taking into account their vegetative and reproductive characteristics (observed in the Olympus BX41 optical microscope); and chemical (lichen acids present), based on the reactions of the reagents: potassium hydroxide 10% (K) and saturated calcium hypochlorite solution (C), as well as combinations of both (KC).

Geology

The studied lichen grew in sandstones of the Losero Formation located in the pristine forest of 'La Bufa' (Figure 2). The sandstone Losero Formation shows great diversity in grain sizes, from coarse to fine sand. The grains generally are subrounded to angular and show a poor selection with respect to grain size. In regards to composition, these sandstones are immature, with high contents of rock fragments in size ranging from some micrometers up to several millimeters. Optical microscopy analyses show that all the lithofacies contain quartz, feldspars, biotite, volcanic lithics, metamorphic lithics and iron oxides in small quantities (Figure 3).

Geochemical analysis of the sandstones of the Losero formation

The stone material used for the geochemical analyses is crushed to a size smaller than 75u (200 mesh), and the concentration of major elements and trace elements from the powdered samples were determined using mass spectrometry-Inductively Coupled Plasma (ICP-MS) (Table 1).

Figure 2. a, b, c) Forest La Bufa; d, e) lichen species in Losero Formation; f) Sandstone of Losero Formation

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sandstone Composition	%
Quartz	32
Plagioclase	25
Biotite	7
Rock fragments volcanic	13
Rock fragments metamorphic	19
Iron Oxides	4
Total	100

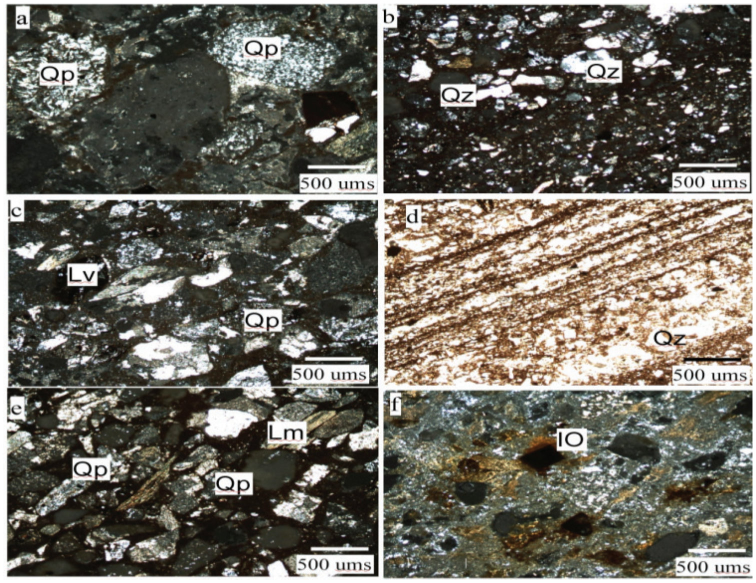

Figure 3. Mineralogical composition of sandstones of the Losero Formation, a) photomicrograph showing quartz grains consisting mainly of polycrystalline quartz grains, b) quartz grains consisting mainly of monocrystalline grains, c) volcanic fragments, d) monocrystalline quartz grains and plane parallel laminae, e) contact grains, f) iron oxides

Table 1. Geochemical analysis of the sandstones of the Losero Formation collected from rural (pristine forest "La Bufa") in the Guanajuato city. ----no detected

The major and trace elements	Sandstone of the Losero Formation
Na_2O (%)	---
Al_2O (%)	17.31
SiO_2 (%)	80.95
K_2O (%)	8.45
MgO (%)	---
CaO (%)	0.6
Fe_2O_3 (%)	0.43
Be ($\mu g\ g{-1}$)	3.41
Ni($\mu g\ g{-1}$)	7.39
Cu($\mu g\ g{-1}$)	9.12
Co($\mu g\ g{-1}$)	2.80
Sn($\mu g\ g{-1}$)	5.70
Sb($\mu g\ g{-1}$)	1.19
Zn($\mu g\ g{-1}$)	37.88
Pb($\mu g\ g{-1}$)	6.14
Cr($\mu g\ g{-1}$)	17.71
V($\mu g\ g{-1}$)	43.55
Th($\mu g\ g{-1}$)	0.23

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Analyses of trace elements and heavy metals were performed by ICP-MS using a Thermo Series XII instrument at 'Centro de Geociencias-UNAM' (Querétaro, México). Lichen samples were previously crushed to a size of 75μ. For sample preparation was used the methodology of Mori *et al.* (2009).

Statistical analysis

A one-way analysis of mean concentrations, standard deviations, median, minimum, maximum, correlation and cluster analysis were carried out using the NCSS2007 software.

Pollution indices

The air pollution status of the studied area was quantified using the CFs by Nyarko *et al*. (2004) and (PLI) Tomlinson *et al*. (1980), to assess the metal contents in the lichens. The CFs and PLI were computed using Microsoft Excel 2007.

CFs

The CFs is the ratio obtained by dividing the average concentration of elements in the samples and the average concentration of elements in the standard or an unpolluted area (i.e. CFs = Cs/Cc; where Cs= average concentration of element in the sample, Cc= average concentration of element in the standard). According to Bhuiyan *et al*. (2010) and Harikumar *et al*. (2010), the contamination levels may be classified based on their grades and intensities (< 1.2: grade I, Intensity unpolluted area; 1.2-2 grade II, Intensity Lightly polluted area; 2-3grade III, Intensity Medium polluted area; > 3grade IV, Intensity Heavily polluted area).

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PLI

Tomlinson *et al*. (1980) proposed the use of PLI as an empirical index which provides a simple method for assessing the levels of heavy metal pollution: PLI= $(CF1 \times CF2 \times CF3 \times \ldots CFn)^{1/n}$ (where CF= Contamination Factor, n= number of metals). PLI values > 1 correspond to polluted stages and values < 1 indicate unpolluted stages (Harikumar *et al*., 2009), whereas values equaling to 1 imply that only baseline levels of pollutants are present (Tomlinson *et al*., 1980).

Results and Discussion

Recognition of lichen species

The lichen specimens were reviewed taxonomically using specialized keys (Nash *et al*., 2004, 2007), taking into account their vegetative and reproductive characteristics (observed with an Olympus BX41 optical microscope); as well as chemical (lichen acids present), based on the reactions of the reagents: potassium hydroxide 10% (K) and saturated calcium hypochlorite solution (C). Microscopic observations and chemical tests allowed the identification of five species of saxicolous lichens, two of them foliose: *Xanthoparmelia mexicana (Gyeln.) Hale*, and *Xanthoparmelia tasmanica (Hook. f. & Taylor) Hale*, and three crustose: *Caloplaca aff. brouardii (B.deLesd.) Zahlbr*, *Caloplaca aff. ludificans Arup*, and *Aspicilia sp* (Figure 4). *Xanthoparmelia mexicana (Gyeln) Hale*, which belongs to the family Parmeliaceae, presents a rosette-like foliose thallus and its photobiont is a green algae; the upper surface of the thallus has a yellowish green color, without imbricated lobes, 4 mm wide, the bone is white and the underside has a pale brown color moderate to densely rizinada, the rizinas are pale brown; slightly adhered to the substrate. The specimen, with no apothecia or pycnidia, has isidia (asexual reproductive structures) plentifully subglobose. Reactions are presenting K, C, KC on the upper surface and spinal K + yellow to dark red shifting and C, KC. *Xanthoparmelia tasmanica (Hook f & Taylor) Hale*, belongs to the family Parmeliaceae, presents a foliose thallus grows as a rosette and its photobiont a green algae; the upper surface of the thallus is yellowish green, with small lobes 2-3 mm wide, and overlapping. Bone is white and the lower surface is black with little rizinas in black; slightly adhered to the substrate. Shows apothecia with brown disc 2 to 25 mm; presents pycnidia (asexual reproductive structures). Reactions are presenting K, C, KC, in the upper crust; while the bone is K + yellow changing to dark red and C-KC. *Caloplaca aff. brouardii (.B.deLesd) Zahlbr* corresponds to the Teloschistaceae family, has a crusty thallus, its photobiont a green alga; talus is areolado (forming plaques) to the center and form elongated lobes to the margins of 0.3 to 0.5 mm wide. The upper surface is orange, no bottom surface and is tightly bound to the substrate. Presents flat circular apothecium, with the disc and the margin of the same color of the thallus, with a diameter of 0.2 to 0.8 mm; in the specimen, the immature apothecium was presented and it was not possible to observe spores. The central portion of the stalk shows isidia (asexual reproductive structures) as buds. The reactions are presented C and K + purple in the top surface and the margin of apothecium. *Caloplaca aff. ludificans Arup*, the Teloschistaceae family, has a crusty thallus underdeveloped, areolado (forming plates) over its entire surface without forming elongated lobes, its photobiont a green alga. The upper surface is orange-yellow; no bottom surface and is tightly bound to the substrate. Features, as well, numerous orange disc-shaped apothecia ranging from 0.4 to 0.8 mm in diameter, spores are polariloculares (two cores) 9-11 x 5-6 microns eight per ascus are presented. No asexual reproduction structures were observed. The reactions presented C and K + purple in the top surface and the margin of apothecium. *Aspicilia* sp., the Megasporace family, is a crusty lichen, (forming plaques) in the center, form rounded lobes marginally. The upper surface is gray, somewhat greenish, bone is white and its lower part is not visible. The photobiont is green algae. The analyzed sample is very small, with a diameter of 2 mm, and immature, no structure of either sexual or asexual reproduction was observed. Reactions to K, C and KC, are negative.

Geochemical analysis of major and trace elements

The major and trace elements in the sandstone of the Losero Formation and lichens in the pristine forest 'La Bufa', are shown in Table 2. A high concentration of Si (80.95%), and Al_2O (17.31 $\mu g\ g^{-1}$), in the sandstone of the Losero Formation can be observed. In response to lichens (*Xanthoparmelia mexicana (Gyeln.) Hale, Xanthoparmelia tasmanica (Hook. f. & Taylor) Hale, Caloplaca aff. brouardii (.B.deLesd) Zahlbr, Caloplaca aff. ludificans Arup,* and *Aspicilia* sp.) these show high values of major and trace elements when compared with the values of sandstones. In the *Xanthoparmelia* species the resulting values correspond to CaO (27.9%), Fe_2O_3 (13.32%), Cu (21.71 $\mu g\ g^{-1}$), Zn (95.10 $\mu g\ g^{-1}$), and Pb (21.40 $\mu g\ g^{-1}$), respectively (Table 2). For Caloplaca species, the values are CaO (5.88%), Fe_2O_3 (22.35%), Cu (18.09 $\mu g\ g^{-1}$), Zn (172.97 $\mu g\ g^{-1}$), and Pb (26.42 $\mu g\ g^{-1}$), respectively (Table 2), while the Aspici-

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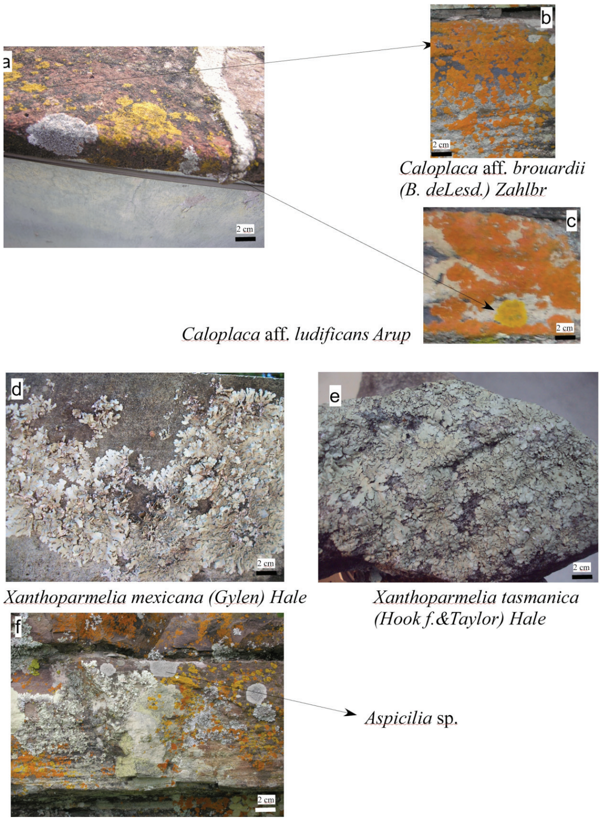

Figure 4. The lichen species, a) Caloplaca sp, b) *Caloplaca* aff. *brouardii*, c) *Caloplaca* aff. *Ludificans*, d) *Xanthoparmelia mexicana,* e) *Xanthoparmelia tasmanica*, f) *Aspicilia* sp

lia, sp. Shows the following values in CaO (8.2%), Fe_2O_3 (17.7%), Cu (17.89 μg g^{-1}), Co (4.64 μg g^{-1}), Zn (57.09 μg g^{-1}), and Pb (20.06 μg g^{-1}), (Table 2).

Heavy metal contents in lichen species

Heavy metal concentrations (Be, Ni, Cu, Co, Sn, Sb, Zn, Pb, Cr, V, and Th (μg g^{-1}) in the nine analyzed lichens from SRM (rural zone) and IHA (suburban and urban zone) are shown in Table 3. Heavy metal concentrations from the rural, suburban and urban zone display a wide range of values. Among the analyzed metals, Pb, Zn, Cr, Cu, V, and Ni show a higher range of variability, while Be, Co, Sb and Th are the least variable. The selectivity sequence of metals in the three studied areas were Pb>Zn>Cr>Cu>V>Ni>Sn>Th>Co>Be>Sb. Two groups of metals could be clustered (Figure 5), according to their maximum values from the uncontaminated and contaminated zones: group 1 is formed by Be, Ni, Co, Sn, Zn, Cr, V, and Th with the highest contents in the rural zone and group 2 includes Cu, and Pb with the highest concentrations in the suburban and urban zone, and Sb in suburban zone. In group 1, the selectivity sequence of elements were Zn>Cr>V>Ni>Sn>Pb>Cu>Th>Co>Be>Sb, varying Zn from 57.09 to 172.97 μg g^{-1} and Sb from 1.31 to 1.68 μg g^{-1} (Table 2). Conversely, in group 2 the selectivity sequence of metals were Pb>Cu>Zn>V>Sb>Cr>Sn >Th>Ni>Co>Be, ranging Pb between 92.23 - 612.91 μg g^{-1} and Cu between 15.73 - 91.23 μg g^{-1} (Table 2). According to these results, metals clustered in group 1 (Be, Ni, Co, Sn, Sb, Zn, Cr, V and Th) with the highest concentrations in the rural zone could suggest that a natural source, the rock, is controlling the geochemical signals in the lichens. Conversely, metals conforming group 2 (Cu and Pb) undoubtedly indicate that metals deposited on lichens come from an anthropogenic source in the suburban and urban zone. Furthermore, a selective deposition of metals is observed in the lichen specimens. *Xanthoparmelia* species best accumulate Cr, V, Ni and Co and with the highest values in the rural zone: 105.15, 58.40, 48.93 and 7.00 μg g^{-1}, respectively. *Caloplaca* species, however, show maximum levels of Zn, V, Sn, Th, and Sb for the rural zone and Cu for the urban zone: 172.97, 53.51, 27.56, 13.13, 1.68 and 91.23 μg g^{-1}, respectively. Finally, *Aspicilia* sp has the highest concentration of Pb (612.91-600.92 μg g^{-1}) in both the suburban and urban zone, respectively. It should be noted that although all lichen samples are clearly Pb enriched in polluted zones (IHA: 92.23-600.92 μg g^{-1}) with respect to SRM (20.06 μg g^{-1}). According to Nieboer *et al*. (1978), threshold values for Pb in lichens range from 5 to 100 μg g^{-1}, reaching enhanced levels above 100 μg g^{-1}, whereas the threshold values of Cu for lichens are 1-50 μg g^{-1}. The same authors found in their study extreme values for Zn in lichen species reaching levels up to 500 μg g^{-1}. Pb and Cu contents determined in the present study show that the study area is clearly polluted by Pb, and Cu. These results reveal that high concentrations of Pb and Cu accumulated by lichens in the suburban and urban zone may be explained by the heavy traffic flow, as well as industrial and mining emissions in the most populated area of Guanajuato. In the case of Zn, it accumulated with a maximum value of 172.97 μg g^{-1}in the pristine area (*Caloplaca* species), exceeding widely the common levels documented in lichens for this metal. In particular, enriched contents of Zn in *Xanthoparmelia* and *Caloplaca* communities may be contributed by natural sources and amplified by metabolic interactions in the lichens. Brunialti and Frati (2007) have recorded that Cu and Zn are essential elements for lichen metabolisms. Zn contents in *Caloplaca* species are lower in anthropogenic areas (IHA, maximum value: 77.11 μg g^{-1}) in comparison with the rural zone (172.97 μg g^{-1}).

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Table 2. Chemical compositions of lichen and sandstone samples collected from rural (pristine forest "La Bufa") in the Guanajuato city. --- no detected

The major and trace elements	Sandstone of the Losero Formation	Xanthoparmelia species lichen	Caloplaca species lichen	Aspicilia sp	Mean lichen
Na_2O **(%)**	---	---	---	---	---
Al_2O **(%)**	**17.31**	12.82	11.13	15.13	13.0266
SiO_2 **(%)**	**80.95**	32.42	54.28	38.13	41.61
K_2O **(%)**	8.45	13.52	5.68	5.03	8.07666
MgO **(%)**	---	---	1.85	1.9	1.25
CaO **(%)**	0.6	27.9	5.88	8.2	13.9933
Fe_2O_3 **(%)**	0.43	13.32	22.35	17.7	17.79
Be ($\mu g\ g{-1}$)	3.41	3.1021	3.1064	14.8402	7.0162
Ni($\mu g\ g{-1}$)	7.39	**48.9306**	6.4322	14.0175	23.1267
Cu($\mu g\ g{-1}$)	9.12	21.7104	18.0997	17.8997	19.2366
Co($\mu g\ g{-1}$)	2.80	7.0012	3.9307	4.641	5.1909
Sn($\mu g\ g{-1}$)	5.70	5.7003	27.5609	6.224	13.1617
Sb($\mu g\ g{-1}$)	1.19	1.4497	1.6869	1.3181	1.4849
Zn($\mu g\ g{-1}$)	37.88	**95.1035**	**172.971**	**57.0977**	108.3907
Pb($\mu g\ g{-1}$)	6.14	21.4031	26.4245	20.0676	22.6317
Cr($\mu g\ g{-1}$)	17.71	**105.1565**	29.3347	15.1433	49.8781
V($\mu g\ g{-1}$)	43.55	**58.4043**	**53.5166**	**56.2548**	56.0585
Th($\mu g\ g{-1}$)	0.23	5.1625	13.1387	5.1917	7.8309

Statistical analysis

Mean, standard deviation and correlation

The statistical analyses performed in heavy metal accumulations on lichens are presented in Table 4. Mean, standard deviation, Min, Max, Med for each of the eleven metals analyzed in lichen thallus from rural, suburban and urban zones resulted significant at < 0.05. According to statistical tests, the selectivity sequence of metals resulted as follows: Suburban (zone 1):

mean
Pb>Zn>Cu>V>Cr>Ni>Sb>Sn>Th>Co>Be;
standard deviation show the selectivity series:
Pb>Cu>Zn>V>Sb>Th>Sn>Be>Cr>Co>Ni.
Urban (Zone 2): mean
Pb>Zn>Cu>V>Cr>Ni>Sn>Th>Be>Co>Sb;
standard deviation, Pb>Cu>Zn>V>Sn>Th>Co>Be>Cr>Ni>Sb.
Rural (Zone 3): mean
Zn>V>Cr>Ni>Pb>Cu>Sn>Th>Be>Co>Sb;
standard deviation, Zn>Cr>Ni>Sn>Be>Th>Pb>V>Cu>Co>Sb.

In summary, the group of metals conforming by Pb, Zn, Cr, V and Cu present the highest values for means, while the group of elements constituted of Co, Sn, Be, Th and Sb show the lowest values. Standard deviation has a wide range of variation for the first mentioned group with an extreme value for Pb. For the second group, however, fluctuations in values maintain within a minor range of variation. The statistical significance of correlations between Co–V; Ni–Cr; Ni-Co; Sn-Zn; Co-Cr; Zn-Th, and Sn–Th concentrations (Table 5) confirm anthropogenic sources mainly due to emissions from vehicular traffic, fossil fuel combustion, solid waste disposal and other local anthropogenic activities. Suburban and urban areas show a high correlation with *Xanthoparmelia-Aspicilia* species (0.9276), (0.9393) respectively. The correlation between these two areas is very good (0.9998). While in the rural area the correlation is good with *Caloplaca-Aspicilia* sp species (Table 4).

Cluster analysis

Cluster analysis in R-mode was performed on the lichen data set for all the examined elements. Three clusters were revealed and are shown in Figures 4 and 5. The lichen sample site shows three statistically significant clusters. Group 1 consists of the rural zone (samples 8 and 7) which is not influenced by vehicular emissions activity. Group 2 consists of suburban and

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Table 3. Concentrations (μg g−1) of the heavy metals detected in lichens collected in the three sampling sites (urban, suburban and rural) in Guanajuato city

URBAN (IHA)	*Xanthoparmelia species*	*Caloplaca species*	*Aspicilia.* sp
Be	4.241	4.1234	1.3245
Ni	4.1254	5.6214	3.6721
Cu	15.7321	**91.2346**	**17.9876**
Co	1.324	4.6389	1.8234
Sn	1.4672	8.3297	2.9314
Sb	0.7271	1.3425	0.8976
Zn	**45.624**	**77.0293**	**71.2394**
Pb	**96.21**	**92.234**	**600.9243**
Cr	8.9774	8.6234	5.9874
V	12.9876	**27.4325**	17.5289
Th	0.5432	7.3214	2.431

SUBURBAN (IHA)	*Xanthoparmelia species*	*Caloplaca species*	*Aspicilia.* sp
Be	0.3633	4.241	1.4687
Ni	4.2671	5.7025	3.4326
Cu	17.8363	**90.5964**	**18.242**
Co	1.4692	4.7287	1.9826
Sn	1.5219	6.224	3.0926
Sb	10.7066	1.3558	0.9161
Zn	**47.838**	**77.1148**	**72.2406**
Pb	**95.1006**	**92.4253**	**612.9113**
Cr	9.44	8.967	6.0574
V	13.4938	**27.6598**	17.3029
Th	0.5686	7.232	2.3781

RURAL (SRM)	*Xanthoparmelia species*	*Caloplaca species*	*Aspicilia.* sp
Be	3.1021	3.1064	**14.8402**
Ni	**48.9306**	6.4322	14.0175
Cu	**21.7104**	18.0997	**17.8997**
Co	**7.0012**	3.9307	4.641
Sn	5.7003	**27.5609**	6.224
Sb	1.4497	1.6869	1.3181
Zn	**95.1035**	**172.971**	**57.0977**
Pb	21.4031	**26.4245**	20.0676
Cr	**105.1565**	29.3347	15.1433
V	**58.4043**	**53.5166**	**56.2548**
Th	5.1625	**13.1387**	5.1917

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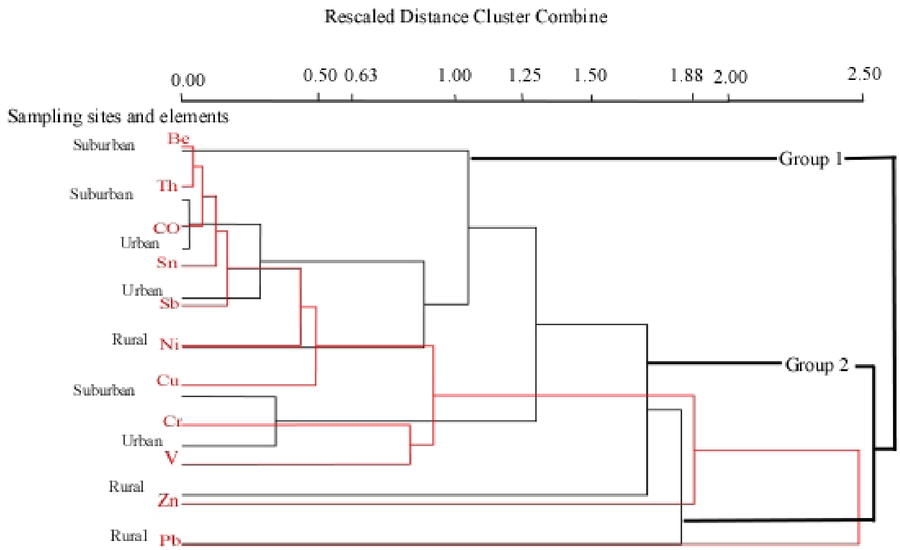

Figure 5. A dendrogram showing clustering of analyzed lichen sample sites from the study area

urban zones (samples 2 and 5), and group 3 consists of suburban, urban, and rural zones (samples 9, 4, 6, 3, 1). These results confirmed that Zn, Pb, and Cu derive from vehicular traffic, while Co, and V have a main common source in the metallurgical industry emissions. The groups of metals in clusters 1 and 2 might indicate a geological origin, taking into account that elevated levels of these heavy metals were found in pristine area lichen samples (*Xanthoparmelia* and *Caloplaca* species). Conversely, cluster 3 suggests that both metals could derive from a common cultural source, contributing to the high pollutant contents on lichens (*Caloplaca* species and *Aspicilia* sp.). Hawksworth *et al*. (2005) and Conti *et al*. (2008) reported that fossil fuel combustion was an important anthropogenic source for Pb and Cu. In the case of Cu, important pollution sources include industrial emissions and fossil fuel combustion processes (Bernasconi *et al*., 2000; Cuni *et al*., 2004). Particularly, Guanajuato is a mining district well known all over the world for strip mining different types of metals, especially Ag and Au associated to sulphide veins. Currently, there is no record of the emissions released to the environment by the mineral industry, but it is known that the particular amount of Pb per year is 6.4 $\mu g\ g^{-1}$. This activity, combined with an increase in human population and the related heavy vehicular traffic could act as the primary sources of Pb and Cu emissions. Although Zn is a metal commonly considered to be emitted from anthropogenic sources (traffic, metallurgy, waste incineration), this study shows much higher concentrations in pristine zones. However, *Aspicilia* sp. accumulates this metal in higher contents in suburban and urban zones and it is possible that part of the released Zn in this area may be derived from mining and vehicular emissions.

Estimating Pollution impacts

The levels of heavy metals in lichens

In general, high levels of the heavy metals were observed in all studied lichen samples (Tables 2 and 3). These lichens have the ability to accumulate Pb, Cu, Co, Zn, and V. The *Xanthoparmelia* species has the ability to accumulate Pb, Zn, and Cu, whilst *Caloplaca* species and *Aspicilia* sp., have accumulated Pb, Cu, Co, Zn, and V, respectively. It is well known that the deposition of Pb is mainly incorporated from street dust, by vehicular emissions and fuel combustion from circulating trucks and cars (Hawksworth *et al*., 2005; Conti *et al*., 2008). The Zn and Cu in *Caloplaca* species indicate that lichen concentrated these elements. Zn and Cu concentrations are due to industrial emissions of steel or regular wear of engines of automobiles, abrasion and burning of tires (Bernasconi *et al*., 2000). The Co and V concentrations in the *Aspicilia* sp. lichen show that the above element comes from metallurgical industry emissions (Bernasconi *et al*. 2000). According to Bennett & Wetmore (1999), the corticolous species would accumulate a higher concentration of atmospheric elements because they are more exposed to a mixed atmosphere than the saxicolous species. However, higher concentrations of heavy metals were found in saxicolous species (*Xanthoparmelia, Caloplaca* and *Aspicilia* sp).

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Table 4. Statistical summary of Heavy Metals concentrations ($\mu g\ g^{-1}$) in lichens collected at 7 sampling sites. SD, standard deviation; Min, minimum; Max, maximum; Med, median; N, number of samples over detection limits. Mean, standard deviations, minimums, maximums and medians were calculated using zero for under detection limit values

URBAN Zone 2	*Xanthoparmelia species*	*Caloplaca species*	*Aspicilia.* sp	*Mean*	*SD*	*Min*	*Max*	*Median*	*N*
Be	4.241	4.1234	1.3245	3.2296	1.3479	1.3245	4.241	4.1234	7
Ni	4.1254	5.6214	3.6721	4.4729	0.8328	3.6721	5.6214	4.1254	7
Cu	15.7321	91.2346	17.9876	41.6514	35.0726	15.7321	91.2346	17.9876	7
Co	1.324	4.6389	1.8234	2.5954	1.4592	1.324	4.6389	1.8234	7
Sn	1.4672	8.3297	2.9314	4.2427	2.9510	1.4672	8.3297	2.9314	7
Sb	0.7271	1.3425	0.8976	0.9890	0.2594	0.7271	1.3425	0.8976	7
Zn	45.624	77.0293	71.2394	64.6309	13.6461	45.624	77.0293	71.2394	7
Pb	96.21	92.234	600.9243	263.1227	238.8672	92.234	600.9243	96.21	7
Cr	8.9774	8.6234	5.9874	7.8627	1.3339	5.9874	8.9774	8.6234	7
V	12.9876	27.4325	17.5289	19.3163	6.0310	12.9876	27.4325	17.5289	7
Th	0.5432	7.3214	2.431	3.4318	2.8562	0.5432	7.3214	2.431	7

RURAL Zone 3	*Xanthoparmelia species*	*Caloplaca species*	*Aspicilia.* **sp**	*Mean*	*SD*	*Min*	*Max*	*Median*	*N*
Be	3.1021	3.1064	14.8402	7.0162	5.5323	3.1021	14.8402	3.1064	7
Ni	48.9306	6.4322	14.0175	23.1267	18.5069	6.4322	48.9306	14.0175	7
Cu	21.7104	18.0997	17.8997	19.2366	1.7511	17.8997	21.7104	18.0997	7
Co	7.0012	3.9307	4.641	5.1909	1.3124	3.9307	7.0012	4.641	7
Sn	5.7003	27.5609	6.224	13.1617	10.1839	5.7003	27.5609	6.224	7
Sb	1.4497	1.6869	1.3181	1.4849	0.1526	1.3181	1.6869	1.4497	7
Zn	95.1035	172.971	57.0977	108.3907	48.2290	57.0977	172.971	95.1035	7
Pb	21.4031	26.4245	20.0676	22.6317	2.7367	20.0676	26.4245	21.4031	7
Cr	105.1565	29.3347	15.1433	49.8781	39.5147	15.1433	105.1565	29.3347	7
V	58.4043	53.5166	56.2548	56.0585	2.0002	53.5166	58.4043	56.2548	7
Th	5.1625	13.1387	5.1917	7.8309	3.7531	5.1625	13.1387	5.1917	7

SUBURBAN Zone 1	*Xanthoparmelia species*	*Caloplaca species*	*Aspicilia.***sp**	*Mean*	*SD*	*Min*	*Max*	*Median*	*N*
Be	0.3633	4.241	1.4687	2.0243	1.6310	0.3633	4.241	1.4687	7
Ni	4.2671	5.7025	3.4326	4.4674	0.9374	3.4326	5.7025	4.2671	7
Cu	17.8363	90.5964	18.242	42.2249	34.2042	17.8363	90.5964	18.242	7
Co	1.4692	4.7287	1.9826	2.7268	1.4309	1.4692	4.7287	1.9826	7
Sn	1.5219	6.224	3.0926	3.6128	1.9545	1.5219	6.224	3.0926	7
Sb	10.7066	1.3558	0.9161	4.3261	4.5152	0.9161	10.7066	1.3558	7
Zn	47.838	77.1148	72.2406	65.7311	12.8078	47.838	77.1148	72.2406	7
Pb	95.1006	92.4253	612.9113	266.8124	244.7313	92.4253	612.9113	95.1006	7
Cr	9.44	8.967	6.0574	8.1548	1.4956	6.0574	9.44	8.967	7
V	13.4938	27.6598	17.3029	19.4855	5.9856	13.4938	27.6598	17.3029	7
Th	0.5686	7.232	2.3781	3.3929	2.8133	0.5686	7.232	2.3781	7

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Table 5. Values of correlation coefficient (P<0.01) between sampling sites (suburban, urban and Rural) and the amounts of heavy metals found in saxicolous lichen

	Be	Ni	Cu	Co	Sn	Sb	Zn	Pb	Cr	V	*Th*
Be	1	0.1247	0.0074	**0.3664**	0.0498	-0.3069	-0.1479	-0.4139	-0.0315	**0.5476**	0.1754
Ni		1	-0.1530	**0.7577**	-0.0150	-0.1267	0.1519	-0.3536	**0.9701**	**0.6661**	0.0931
Cu			1	**0.3784**	0.0241	-0.1653	-0.0220	-0.2203	-0.1925	-0.0924	**0.3490**
Co				1	**0.3167**	-0.3181	**0.3778**	-0.5341	**0.7196**	**0.8191**	**0.5831**
Sn					1	-0.1829	**0.9463**	-0.3429	0.1494	**0.5761**	**0.9170**
Sb						1	-0.2410	-0.1977	-0.1030	-0.2803	-0.3193
Zn							1	-0.1874	**0.3346**	**0.5732**	**0.8745**
Pb								1	-0.3611	-0.5375	-0.4067
Cr									1	**0.6646**	0.2021
V										1	**0.6603**
Th											1

SAMPLING ZONE	SUBURBAN	URBAN	RURAL
SUBURBAN	1		
URBAN	**0.9998**	1	
RURAL	0.1445	0.1458	1

SAMPLING ZONE	LICHENS	CORRELATION COEFFICIENT
SUBURBAN	*Xanthoparmelia /Caloplaca*	0.7959
	Xanthoparmelia/Aspicilia	**0.9276**
	Caloplaca /Aspicilia	0.6232
URBAN	*Xanthoparmelia /Caloplaca*	0.7868
	Xanthoparmelia/Aspicilia	**0.9393**
	Caloplaca /Aspicilia	0.6208
RURAL	*Xanthoparmelia /Caloplaca*	0.6521
	Xanthoparmelia/Aspicilia	0.6455
	Caloplaca /Aspicilia	**0.8065**

CFs

The contamination Factor is defined by Tomlinson *et al*. (1980) as the metal concentration in sediment divided by some background base value for each element. The background value corresponds in these work to data obtained from the rural (pristine forest “La Bufa”), (Table 2). The ranges used to describe the contamination factor are: CF<1 is considered as low contaminated; 1<CF<3 is moderate contamination; 3<CF<6 is considerable contamination and CF> 6 is high contaminations. The CF values for the various metals are shown in table 6. The metal CF levels at all sample in urban site is present in the following order *Xanthoparmelia* species: Pb>Be>Cu>Sb>Zn>Sn>V>Co>Th>Cr>Ni; *Caloplaca* species: Cu>Zn>Cu>Sb>Sn>Th>Cr>Co>V>Ni>Be;
Aspicilia sp: Pb>Zn>Cu>Sb>Sn>Th>Cr>Co>V>Ni>Be.

In suburban site the following order is *Xanthoparmelia* species: Sb>Pb>Cu>Zn>Sn>Co>V>Be>Th>Cr>Ni; *Caloplaca* species: Cu>Pb>Th>Be>Co>Ni>Sb>V>Zn>Cr>Sn; *Aspicilia* sp: Pb>Zn>Cu>Sb>Sn>Th>Co>Cr>V>Ni>Be.

Lead concentrations are very high in the study area, the CF ranged between 3.49-30.54 suggesting high contamination in all sites (urban and suburban). Copper concentration is relatively high in the study area, the CF ranged between 0.72-5.04 suggesting moderate contamination. Antimony concentration is present high in suburban area, the CF is 7.38 suggesting high concentration. Low concentration factor was observed for Be, Ni, Co, Sn, Zn, Cr, V, Th at all sites.

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PLI

We calculated the Pollution loading Index (PLI) using the following equation

$$PLI= (CF_1 \times CF_2 \times CF_3 \times CF_4 \times CF_5 \times \ldots\ldots CF_n)^{1/n}$$

where

PLI= pollution loading index
CF= contamination factor
n= number of metals investigated

The PLI was calculated for the two areas under investigation using the eleven investigated metals (Be, Ni, Cu, Co, Sn, Sb, Zn, Pb, Cr, V and Th). It was observed that the highest PLI was found at Suburban area (0.037), while the lowest was calculated for Urban (0.024), the calculated PLI were found in the following sequences: Suburban >Urban (Table 6).

Table 6. Lichens and their pollution index factors (PIF): contamination factors (CFs) and pollution load indices (PLI)

URBAN (IHA)	Xanthoparmelia species	CFs	PLI	Caloplaca species	CFs	PLI	Aspicilia sp	CFs	PLI
Be	**4.241**	**1.3671**	**O.0000**	**4.1234**	**1.3273**	**0.0196**	**1.3245**	**0.0892**	**0.0053**
Ni	**4.1254**	**0.0843**		5.6214	0.8739		3.6721	0.2619	
Cu	15.7321	0.7246		91.2346	5.0406		17.9876	1.0049	
Co	**1.324**	**0.1891**		4.6389	1.180		1.8234	0.3928	
Sn	1.4672	0.2573		8.3297	0.3022		2.9314	0.4709	
Sb	**0.7271**	**0.5015**		1.3425	0.7958		0.8976	0.6809	
Zn	45.624	0.4797		77.0293	0.4453		71.2394	1.2476	
Pb	**96.21**	**4.4957**		92.234	3.4904		600.9243	29.945	
Cr	8.9774	0.0853		8.6234	0.2939		5.9874	0.3953	
V	**12.9876**	**0.2223**		27.4325	0.5125		17.5289	0.3115	
Th	0.5432	0.1052		7.3214	0.5572		2.431	0.4682	
SUBURBAN (IHA)	Xanthoparmelia species	CFs	PLI	Caloplaca species	CFs	PLI	Aspicilia sp	CFs	PLI
Be	**0.3633**	**0.1171**	**0.0000**	**4.241**	**1.3652**	**0.037**	**1.4687**	**0.0989**	0.0005
Ni	**4.2671**	**0.0872**		5.7025	0.8865		3.4326	0.2448	
Cu	**17.8363**	**0.8215**		90.5964	5.0054		18.242	1.0191	
Co	**1.4692**	**0.2098**		4.7287	1.2030		1.9826	0.4271	
Sn	**1.5219**	**0.2669**		6.224	0.2258		3.0926	0.4968	
Sb	**10.7066**	**7.385**		1.3558	0.8037		0.9161	0.6950	
Zn	**47.838**	**0.5030**		77.1148	0.4458		72.2406	1.2652	
Pb	**95.1006**	**4.4433**		92.4253	3.4977		612.9113	30.5423	
Cr	**9.44**	**0.0897**		8.967	0.3056		6.0574	0.4000	
V	**13.4938**	**0.2310**		27.6598	0.5168		17.3029	0.3075	
Th	**0.5686**	**0.1101**		7.232	1.3929		2.3781	0.4580	

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Conclusions

Our results represent the first study of heavy metals in saxicolous lichens from the Guanajuato city. The elemental concentrations of heavy metals in saxicolous lichens (*Xanthoparmelia mexicana (Gyeln.) Hale, Xanthoparmelia tasmanica (Hook. f. & Taylor) Hale, Caloplaca aff. brouardii (B.deLesd.)Zahlbr, Caloplaca aff. ludificans Arup, and Aspicilia* sp.*)* were obtained from the distribution of heavy metals in the suburban, urban, and rural zones of the Guanajuato city and identify places with higher levels of heavy metal concentration. The concentration of these metals was observed to be in higher range as maximum values of Pb, Zn, Cu and V, were reported from the lichen samples from the suburban and urban zone in the Guanajuato city. However, the accumulations of Ni, Co, and Th from both zones are more or less similar in concentration. Metals such as, Zn, Cr, V exhibits the highest concentrations in rural lichen samples, whereas Cu and Pb show the maximum contents in suburban and urban lichen samples. These results suggest that a natural source (rock) could be the main controlling source of concentrations in the studied lichens within the pristine area. Elevated Pb, Cu, Zn and V levels measured in the urban and suburban sampling sites point out sources of anthropogenic origin. In Guanajuato city, fossil fuel combustion due to heavy traffic and mining activities are suggested to be important anthropogenic emission sources for Pb and Cu. A selective bioaccumulation potential could be recognized among the studied lichen communities for certain elements. *Xanthoparmelia* species show in urban and suburban area the highest accumulation capacity for Zn and Pb, whilst *Caloplaca* species best accumulate Zn, Pb, V and Cu. *Aspicilia* sp. has the highest Pb, Cu and Zn accumulation ability, with extreme values reaching 612.91$\mu g\ g^{-1}$.These results indicate that *Xanthoparmelia* species could be a useful species for biomonitoring elevated levels of Zn and Pb and *Caloplaca* for Zn, Pb, V and Cu. *Aspicilia* sp. tolerates large and toxic amounts of Pb, making us consider this particular species as a good bioindicators of Pb air pollution. Correlation analyses showed a high affinity among Co-V; Ni-Cr; Ni-Co; Sn-Zn; Co-Cr; Zn-Th; and Sn-Th. The results of the first cluster suggest that geology mainly contributes with metal contents in lichen samples. The second cluster also indicates a natural source controlling metal concentrations in lichens with the exception of Zn, which could be partly supplied by vehicular emissions. The associations of Pb and Cu indicate that emissions from heavy traffic, industrial and mining activities control the metal levels in lichen samples.

Pollution evaluation using the PLI index indicates *Caloplaca* and *Aspicilia* have higher CFs in Be, Cu, Co, Pb, Zn and Th, when compared with *Xanthoparmelia* (Be, Pb and Sb). These results show a higher bioaccumulation potential for the *Caloplaca* and *Aspicilia* species and a lower bioaccumulation capacity for the *Xanthoparmelia* species. The studied species in this work are proposed for biomonitoring in the Guanajuato city, specifically in respect to Pb, Sb and Cu, and to a minor degree, Co, Be, Th and Zn. The results of this study could be used as a baseline for know the effects of the pollution at the Miners sites.

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