Diagnosing the traffic impact on roadside soils through a multianalytical data analysis of the concentration profiles of traffic-related elements

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Abstract

The road traffic has become one of the most serious environmental problems in many cities and the main source of pollution of urban soils. To diagnose properly the magnitude of such impacts on roadside soils, eight urban and metropolitan soils were selected as a function of traffic density, distance to the road and years of operation, for which the concentration of 60 elements (major, minor and trace elements) were measured by semi-quantitative ICP-MS after acid digestion, as a first step in assessing the traffic impact. With this information, a comprehensive study was carried out focusing on the quantitative analysis of the concentration of 46 elements from the 8 sampling areas, analysing the vertical and horizontal distribution of the metals in the roadside soils. The chemometric analysis showed that only the traffic-related elements accumulate in topsoil and present a high decreasing profile with depth and the distance to the road; however, this clear behaviour takes places only in old roads that have undergone the traffic impact for a long time, but not in new roads or roads with low traffic density. Finally, the geoaccumulation indexes are suggested to be used instead of the local guidelines to assess the pollution state of the roadside soils, especially for the emerging trace elements like Antimony.

Keywords

Roadside soil, ICP-MS, Traffic impact, Traffic-related elements, PCA

1. Introduction

With the rapid development of road communication networks in the last century, the road traffic has become one of the most serious environmental problems in many cities and the main source of pollution of urban soils. Moreover, the contribution of road traffic to global emissions of atmospheric pollutants is increasing every year (Amato et al., 2011; Hjortenkrans et al., 2007). The dispersion of these contaminants is determined by weather conditions and can be deposited in surrounding areas such as urban and agricultural soils as well as waters. Among all the possible pollutants coming from the road traffic, metals and polycyclic aromatic hydrocarbons (PAHs) are the most dangerous (Aatmeeyata and Sharma, 2011; Amato et al., 2011; Lough et al., 2005). Whereas organic compounds can be transformed or degraded by means of the microbial action of the soil in others innocuous compounds such as water and CO_2 (Wu et al., 2008) metals can remain in the media for a long time since they do not undergo decay (Chen et al., 2010).

Roadside soils have become an important sampling point to assess the anthropogenic concentrations of metals. Several studies have been carried out since years ago by different authors showing the pollution of roadside soils due to the traffic and it has been observed that the roadside soils have a high content of metals (Apeagyei et al., 2011; Bretzel and Calderisi, 2006; Chen et al., 2010; Wei and Yang, 2010). Most of them have focused on well-known traffic pollutants as Pb, Cd, or Zn (Garcia and Millán, 1998; Gratani et al., 1992; Lagerwerff and Specht, 1970; Viard et al., 2004). Other authors have extended the study to the analysis of metals in plants and urban trees (Li et al., 2007; Massadeh et al., 2009; Olowoyo et al., 2010) or to airborne particulate matter (Oliva and Espinosa, 2007).

The road traffic involves several potential sources of metals, such as exhaust fumes, tire and brake wear, oil spill, road pavement, building materials for traffic safety or resuspension of soil and road dust (McKenzie et al., 2009; Thorpe and Harrison, 2008; Wei and Yang, 2010). It has been observed that the roadside soils have a high content of metals, especially Pb, Ba, Zn, Cd and Cu. A study carried out in Sweden indicates that diffuse pollution generated by road traffic is the main source for the 90% of Cd, 40% of Cu and more than 99% of both Cr and Ni, 85% of Pb and 80% of Zn found in the roadside (Bergbaeck et al., 2001).

Before banning the use of leaded petrol, lead was discharged as organic or particulate lead in the exhaust fumes. Although there has been a significant reduction in the lead emissions from vehicles since it was banned in Europe (Directive, 1998) and other countries worldwide around 1998-2002, a major reservoir of lead in roadside soils still remains (MacKinnon et al., 2011). Besides lead, other metals such as Cd, Cr, Cu, Ni and V are also issued in the combustion of fossil fuels, such as petrol (de Miguel et al., 1997). Zinc is used in the process of vulcanization of tires as zinc oxide (Adachi and Tainosho, 2004), and as antioxidant in the engine oil. As a result of the tire wear and/or leaks of engine oil and emission of the exhaust fumes, zinc is deposited on the roadside soils (Councell et al., 2004). In addition, the tires have trace amounts of other metals such as Cd, Co, Cr, Cu, Hg, Mn, Mo, W, Ni and Pb (Apeagyei et al., 2011; Hjortenkrans et al., 2007). Other authors associate it to the emission of other metals such as, Sn, Cd, Cr, Ni, Pb, Zn, Zr and Mo (Apeagyei et al., 2011; Dongarra et al., 2009; Hjortenkrans et al., 2007; Johansson et al., 2009) in smaller amounts. Chromium is mainly derived from the erosion or abrasion processes, including metal plating and bodywork.

Traffic pollutants could show a different vertical and horizontal distribution pattern depending on their own nature, their main form of diffusion or their primary source. There is a general agreement that these metals decrease in concentration with depth and with distance from the roadway (Liu et al., 2009). Polluted roadside soils may pose a risk to health if the metals are transferred to other reservoirs. Some studies have demonstrated that Cu, Pb and Zn show a significant anthropic enrichment and can be transported into rivers, lakes, near shore seawater or sediment (Meland et al., 2010; Sutherland et al., 2000). On the soil, these pollutants can be transported to the aerial parts of vegetation, bioaccumulating in them (Veschambre et al., 2003; Wiseman et al., 2013). Therefore, humans and animals can ingest metals directly through inhalation of soil dust (Amato et al., 2011) or the metals can enter the food chain as a result of the ingestion of edible plants (Wei and Yang, 2010).

Soil is considered polluted when chemicals are present or other alterations have been made to its natural environment. In this sense, traffic emissions involve an anthropogenic input of metals to surrounding soils, altering their natural composition. There are different methods to estimate the metallic pollution level of an altered soil. The geoaccumulation index, I_{geo}, is a simple method for

assessing soil quality, providing a simple way of comparing the extent of metal pollution of the urban soils. It has been used since the late 1960s, and has been widely employed in European trace metal studies. Originally used for bottom sediments (Müller, 1969), it has been successfully applied to the measurement of soil pollution (Li et al., 2011). The I_{geo} enables the assessment of pollution by comparing current and background concentrations, although it is not always easy to reach background soil layers. It is calculated using the following equation: $I_{geo}=\log_2(C_n/1.5*B_n)$, where, C_n is the measured concentration of the element in soil and B_n is the geochemical background value. The constant 1.5 allows us to analyze natural fluctuations in the content of a given element in the environment and to detect very small anthropogenic influences. According to the geoaccumulation index, soils can be classified as non-polluted ($I_{geo} < 1$), very slightly polluted ($1 < I_{geo} < 2$), slightly polluted ($2 < I_{geo} < 3$), moderately polluted ($3 < I_{geo} < 4$), highly polluted ($4 < I_{geo} < 5$) and very highly polluted ($I_{geo} > 5$). However, metal background values are not enough to establish soil deterioration state and other methods are used as reference values within environmental protection policy framework to assess the risk for the ecosystems. This is the case of the Basque Indicative Values for Assessment (VIEs) (IHOBE, 1998), which are scientifically based on a generic assessment criterion to help evaluate long-term risks to human health and to the ecosystem due to chemical pollution in soils from the Basque Country (North of Spain).

The established methods to diagnose the traffic impact on roadside soils may not be the most adequate due to the possible simultaneous presence of several sources of pollution. The aim of this study was to identify the current traffic-related elements (TREs) and to establish its concentration profiles in both, horizontal and vertical distribution, in order to monitor the contribution of traffic to environmental pollution and risk and to assess their level of pollution. To attain those objectives, selected soils with different levels of impacts (proximity to the roads and time exposed to traffic) were screened, in a first step, by semiquantitative ICP-MS analysis (Laborda et al., 2001) to search for all constituents of significance. In a second step, only those elements with a significant concentration were quantitatively determined as a function of the horizontal profile and vertical depth. Finally, chemometric analysis of the data, as well as, the mentioned methods for assessing the quality of soils were applied to decide the most simple and relevant method to diagnose properly the impact of traffic-related elements.

2. Material and methods

2.1. Sampling design

Four different sampling areas were selected according to their different exposure times to traffic impact. The first study area is an old secondary road located in the Mungia-Bilbao road (43º19´35.53´´N, 2º52´20.39´´W, Biscay, north of Spain), near the city of Bilbao, that has been in service for more than 60 years and exposed to high traffic impact for a long time till the construction of a new highway two decades ago. Even today this secondary road suffers a medium traffic density about 1800 vehicles per day and 5.9% of them are of high tonnage (BFA/DFB, 2004). The second study area is a modern highway with more than 20 years of service, designed in parallel to the old road but separated by a stream that ensures the non translation of anthropic elements by runoff from one soil to the other; it bears most of the traffic in the area and has a traffic density of about 28.200 vehicles per day from the year 2004 until now, being 5.7% of them of high tonnage (BFA/DFB, 2004).

The other two locations are two roundabouts in Berango (43º21´46´´N 3º00´12´´O) and Sopelana (43º22´45´´N 2º59´56´´O), both in the metropolitan Bilbao. In Berango the roundabout was built 5 years ago, whereas the one from Sopelana was only one year old when the sampling was done and therefore it had scarcely been exposed to traffic impact. The Fig. S1 shows a picture of the above described sampling zones together with a map locating the metropolitan area of Bilbao, in the north of Spain.

In a first stage, a preliminary study was conducted collecting roadside soil samples from the upper 0-10 cm at different sampling points in the secondary road and the highway. Sampling in the highway was carried out at a distance of 0.5, 3, 6 and 9 m from the highway (H 0.5, H 3, H 6 and H 9 sample codes). In the secondary road, soil samples were collected at both roadsides (SR L and SR R sample codes) but the sampling was only completed at 0.5 m in the west roadside and at 3 m in the east roadside because of the existence of a road cut and a stream that precluded sampling at a greater distance. Control soils were sampled 700 m away from both traffic roads in the north-west direction. In

a second stage, and in order to study the vertical and horizontal distribution of metals, soil sample transects of 20 cm in depth were also collected at different distances from the highway at 0 meters (S0m) just immediately after the road, and at 1 and 3 meters of distance (S1m and S3m). In this area there is no channel and thus, runoff waters from the road arrive directly to the soil. Samples were divided in subsamples of 2-3 cm of depth (S1m A - S1m H and S3m A - S3m F). The same procedure was carried out in roundabouts from Berango and Sopelana, where sampling was done at 0 m and 1 m of distance to the road (BE 0A – BE 0D, BE 1A – BE 1D, SO 0A – SO 0E and SO 1A – SO 1D). Samples were mainly clay soils, as this is the typical soil composition of the Bilbao metropolitan area.

2.2. Analytical procedure

All plastic and glassware material in contact with samples or ICP-MS solutions were soaked in a 10% HNO_3 bath for at least 24 h, then rinsed twice with Elix (Millipore, USA) quality water and finally rinsed with Milli-Q water (18.2 MΩ cm, Millipore, USA). After drying the material in a laminar airflow hood inside a class 100 clean room, it was stored in clean plastic bags until use. Nitric acid (69%) and hydrochloric acid (36%) used for microwave digestion and ICP-MS analysis were of Tracepur grade and supplied by Merck (Darmstadt, Germany).

Soil samples were air dried in a fume hood during 24 h, ground in a planetary ball mill Pulverisette 6 (Fritsch, Germany) for their homogenization and sieved to particle size under 2 mm removing small stones and vegetation remains. Acid digestion of the soils was conducted according to the US Environmental Pollution Agency (USEPA) 3051A method (EPA, 2007) in a microwave oven Multiwave 3000 (Anton Paar, Graz, Austria) equipped with a rotor 8XF100 with PTFE vessels of 100 mL. 0.5 g of samples were accurately weighed in each Teflon vessel, 9 mL of nitric acid and 3 mL of hydrochloric acid were added and allowed to react for a few seconds before closing the vessels. The extracts were filtered with 0.45 µm pore size filters (Millipore Millex-HV) and were kept in the refrigerator until their analysis.

Elemental analysis was carried out using a Perkin Elmer SCIEX 9000 ICP-MS (Toronto, Canada) inside a class 100 clean room. Sample solutions were diluted to 1% HNO_3 concentration prior to

analysis. The performance of an ICP-MS instrument strongly depends on the operating conditions and therefore, the plasma operating conditions such as the nebulizer flow rate, the position of the torch and the ion lens voltages of the instrument were optimized everyday prior to any experiment with a 10 ng/mL standard solution of Mg, Rh, In, Ba, Pb and U. The nebulizer gas-flow rate was optimized to obtain a good compromise between high sensitivity and low oxide levels (lower than 3% for CeO/Ce). Two different methods were used for data acquisition, a semi-quantitative one for the first preliminary study and a quantitative one for the subsequent analyses. Sample acquisition and experimental conditions for the semi-quantitative method are published in a previous work (Carrero et al., 2010). Experimental conditions for the quantitative analysis are summarised in Table S1.

In a first approach, soil samples from the secondary road and the highway were screened for 60 elements by means of multi-element semiquantitative analysis using the Perkin Elmer TotalQuant III software (Laborda et al., 2001; Soldevila et al., 1998). Common isobaric interferences are pre-programmed and corrections are automatically applied. The software has stored pre-calibrated intensities per concentration unit covering the required m/z range. In order to increase the accuracy, these values are updated by running samples spiked with a few selected elements with known concentration (Ag, Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Sb, Se, Sn, V and Zn at 20 ng/g) and using Rhenium (Re) as internal standard. The aim of this multi-elemental semi-quantitative analysis was to obtain a first list of the traffic-related elements at the same time that the study area is limited to those sites more impacted by the traffic impact.

After the screening of the soils, a quantitative method using external calibration was applied in order to conduct vertical and horizontal metal distribution analysis. In addition to the secondary road and the highway, soil samples from the roundabouts from Berango and Sopelana were also included in this study. 46 metals, including alkaline, transition metals and rare earth elements (REE) were determined in the samples of the different sampling areas measuring the following isotopes: ^{7}Li, ^{23}Na, ^{24}Mg, ^{27}Al, ^{39}K, ^{43}Ca, ^{47}Ti, ^{51}V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{68}Zn, ^{75}As, ^{82}Se, ^{88}Sr, ^{93}Nb, ^{98}Mo, ^{107}Ag, ^{114}Cd, ^{120}Sn, ^{123}Sb, ^{138}Ba, ^{184}W, ^{202}Hg, ^{205}Tl, ^{89}Y, ^{208}Pb, ^{139}La, ^{140}Ce, ^{141}Pr, ^{142}Nd, ^{152}Sm, ^{153}Eu, ^{158}Gd, ^{159}Tb, ^{164}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{174}Yb, ^{175}Lu, ^{232}Th, ^{238}U. ^{45}Sc, ^{74}Ge, ^{115}In, ^{187}Re and ^{209}Bi were used as internal standards. All solutions were prepared using Milli-Q water. ICP-MS standard solutions were

prepared from Alfa Aesar (Specpure®, Plasma standard solution, Germany) stock solutions. For quality assurance purposes soil certified reference materials (SRM 2711, total content; and BCR 142R, *aqua regia* soluble content) and a freshwater containing trace elements (SRM 1640) were routinely analyzed in each sample batch.

2.3. Physicochemical properties

2.3.1. pH, pE and Conductivity

The pH and the conductivity of the soil were measured after shaking 5 grams of soil during 1 hour in 25 ml of water. The redox potential was determined after 30 minute shaking.

2.3.2. Determination of the Organic Matter

Organic matter content was estimated by means of the total organic carbon (TOC) according to the classic method of Walkley-Black (Walkley and Black, 1934). This method involves the oxidation of the soil organic matter with an excess of potassium dichromate (equation 1) and titration the excess with Mohr's salt ($Fe(NH_4)_2(SO_4)_2$) (equation 2).

$$2\,Cr_2O_7^{2-} + 3\,C + 16\,H^+ \rightarrow 4\,Cr^{3+} + 3\,CO_2 + 8\,H_2O \qquad 1$$

$$6\,Fe^{2+} + Cr_2O_7^{2-} + 14\,H^+ \rightarrow 2\,Cr^{3+} + 6\,Fe^{3+} + 7\,H_2O \qquad 2$$

In this way, the amount of readily oxidizable organic matter (W_{ROOM}) is obtained. It is assumed that organic matter contains 58% of C and that 77% of the organic matter is oxidized by this method. Thus, a correction factor of 1.33 and 0.58 is applied to obtain the total amount of organic matter according to the equation $TOC\% = (W_{ROOM} \cdot 1.33)/(m_{soil} \cdot 0.58)$, where W_{ROOM} is the amount of readily oxidable organic matter calculated by titration and m_{soi} is the amount of soil weighed for the titration.

3. Results and discussion

3.1. Physicochemical parameters

All the values of some physicochemical properties were among normal ranges of typical clay soils. The variable that changed the most among different soils was the conductivity. Soils from the left side of the secondary road showed the higher values (200-250 $\mu S.cm^{-1}$), whereas the lowest ones were found in the soil samples from the right side of the same road (50-100 $\mu S.cm^{-1}$). Soil samples from the highway present conductivity values in the range 100-150 $\mu S.cm^{-1}$. Conductivity is an indicator of the soluble salts, therefore it seems that a different behaviour exists among soils from different locations.

The pH value was in the range 7.4-7.8 as is expected in clay soils with low carbonate presence and the pE was around 200-250 mV indicating aerobic conditions. Soil samples were poor in organic matter as is deduced from the percentage of the TOC values, less than 5% except in samples from the left side in the secondary road where the amount of organic matter is a bit higher (4-7%). This left side showed the highest conductivity values, maybe related to the ionic content of the organic matter.

3.2. Chemometric analysis of the metal concentration

In a first approach, roadside soils from the secondary road and the highway were screened in order to establish TREs and the impacted areas. 50 of the 60 tested elements (Ag, As, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, In, K, La, Li, Lu, Mg, Mo, Na, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Se, Sm, Sn, Sr, Tb, Te, Th, Tl, Tm, U, V, Y, Yb, Zn, Zr) were determined above the detection limit in the soil extracts. These results were statistically treated with “The Unscrambler 9.2” software. After centring and autoscaling the data, principal component analysis (PCA) revealed two main components accounting for 68% of the total variance (PC1, 51%; PC2, 17%). The projection of the scores and loadings on the bi-dimensional space, defined by these two principal components, is shown in Fig. 1. Samples can be grouped according to sampling point in three groups. Samples from the west (left) roadside of the secondary road (SR L) clearly differentiate from the rest, and are gathered in the right side of the x axis (PC1). Samples from the highway (H 0.5, H 3 and H 6) form another group in the lower side of the graphic. Finally, samples from the east roadside (right) of the secondary road (SR R), further samples from the highway (H 9) and control soils are together on the left side of the x-axis (PC1).

When the scores and loading plots are overlapped, the concentrations of Cd, Cr, Cu, Hf, Mo, Nb, Ni, Pb, Sb, Sn, Sr, Zn and Zr are clearly the variables that explain most of the variance of the SR L sampling point. In fact, the concentration of these metals was considerably higher in these soil samples as can be seen in Fig. 2, where average concentration of some of these metals has been represented by sampling area: samples from the west and east roadside of the secondary road (SR L and SR R), samples from the highway (HG) and control soils (C).The rest of the above mentioned metals (data not shown) have the same behaviour. Therefore, soil samples are grouped according to their TREs concentration in samples heavily impacted by the traffic (west roadside at the secondary road, SR L), samples moderately impacted by the traffic (samples from the highway, H 0.5, H 3 and H 6) and samples not impacted by the traffic (east roadside at the secondary road, further samples at the highway and control soils, SR R, H 9 and C).

The high metal concentration in samples from the west roadside of the secondary road suggests an accumulation of TREs for a long time since it is a very old road and has borne all the traffic of the area in the past, a time were the exhausted fumes from cars were not under strict environmental control. This can be seen also in the extremely high Pb concentration because of the use of leaded gasoline for many years. Although the consumption of leaded gasoline in Spain has been banned since August 2001 (Law, 2001), a high Pb concentration in roadside still remains. It must be also beard in mind that the dominant wind direction in this area is from NW and the existing road cut protect this roadside from the wind and also from the rain. Therefore, there is not dispersion and exhaust fumes from vehicles impact directly the soil and are not washed by the rain.

3.3. Traffic-related elements profile on roadside soils

After screening of the top soils and establishment of a first list of TREs, the horizontal and vertical distribution of the TREs was investigated. To perform this study the west roadside soil of the old road was excluded due to the high concentrations of the trapped TREs (near saturation) that probably mask the vertical and horizontal trends. As it could be expected after the chemometric treatment of the metal concentration data in soil samples from the secondary road and the highway, the different exposure time to the traffic impact and, therefore, the age of the road, could appear to be an important factor to

take into account when investigating the accumulation of TREs in roadside soils. Thus, the study was extended including the other two sampling sites from roundabouts at Berango and Sopelana with only 5 and 1 years old in service, respectively.

High concentrations of some metals were found in upper soils close to the highway (S0m and S1m) compared with those values obtained in deeper soils and at 3 meters of horizontal distance to the highway (S3m). Furthermore, concentrations show a severe decreasing profile with depth and distance to the highway, reaching a constant value in the deepest samples. The fact that element concentrations in depth reach a plateau and that it was similar to the concentration of soils at 3 meters of distance, suggests that those values could correspond to the natural values of the elements in these soils. Besides, these values are in agreement with those given by IHOBE, the Basque Environmental Public Corporation, for some metals as background levels in The Basque Country soils (Table 1).

Three different types of metal profiles were found in the roadside soil samples from the highway. Some elements show a steep decreasing profile between upper and deeper soils. That is the case of Ti, Cu, Zn, Mo, Cd, Sn, Sb, W, Hg, Nb and Pb, whereas others like Na, Mg, Ca, V, Cr, Mn, Co, Ni, Sr, Ag or Ba have a less sharper profile. All of these elements have a traffic-related emission source (Hjortenkrans et al., 2006; Wei and Yang, 2010) and most of these elements were already related to traffic emissions in the preliminary screening but in this study other elements such as Na, Mg, Ca, Ti, V, Mn, Co, Ag, Ba, W and Hg also appear. The last group of elements is formed by Li, K, Al, Fe, As, Tl, and REE, and their concentrations in soil keep nearly constant, without a significant trend. Therefore, there is a clear input of some of these elements from the road traffic to the roadside soil in the highway. The effect of traffic on the soils is more important in those samples closest to the highway. In fact, the metal concentrations in soils at 3 meters of distance to the highway were similar to the background values, except in the upper 2 cm (S3m A), where values were slightly higher. Fig. 3 is a 3D representation of the concentration of the Zn metal, showing the above-mentioned decreasing behaviour with depth and distance and the metal accumulation in topsoil. Other TREs, like Cd, Pb and Mo, present the same behaviour, whereas Fe, Al, Dy and Y show the normal behaviour of soil natural elements not affected by traffic emissions.

The same study was carried out in soils from the less impacted roads in Berango (BE) and Sopelana (SO). These soils have been subjected to the traffic impact for a shorter time since they are new roads and therefore the accumulation of metals is lower than in the highway. In fact, there is no trend with the depth and the distance to the road as occurs in soils taken in the highway and the concentration of the represented TREs keeps constant or without a clear trend. Furthermore, metal concentration ranges at these both sites are quite lower than the concentrations found in the highway.

Finally, a chemometric analysis of the soil transects from the three different sampling sites was done. The concentration of the 46 measured elements was included in the analysis. In Fig. 4 the bi-plot with the scores and loadings of the obtained PCA is shown. The first two PCs account for the 80% of the total variance (PC1 51%, PC2 29%). PC1 can be associated to REE concentration and therefore, to the origin of the soil. On the other hand, PC2 is related with the depth of the soil samples. Topsoil samples closest to the highway appear together in the upper-left side of the PCA, whereas deeper ones are in the bottom together with further samples from the highway. Middle-depth samples are found between topsoil and deep soils. This fact shows the existing metal gradient concentration in soils close to the highway as has been previously shown. Moreover, metals having a gradient profile can be ascertained as they appear together differentiating topsoil from deep soils. Soil samples from Berango and Sopelana appear in the right side and there is no difference among samples from different depth or distance to the road. They appear mixed between them and without any depth order, unlike the samples from the highway.

3.4. Assessment of the traffic impact on roadside soils

The assessment of the traffic impact on the studied areas was carried out with the aim of ascertaining the pollution state of soils from the different places. Geoaccumulation indexes were calculated using the background values obtained from deeper soils, since metal concentrations reach a plateau and these values agree with those given by IHOBE, the Baque Environmental Public Corporation, for some metals listed in Table 1 as has been previously stated.

In the Fig. 5 the pollution state of all the soils analyzed in this work has been summarised. Geoaccumulation indexes of the most important TREs has been represented: Cd, Cu, Ni, Pb, Sb, Sn and Zn. The most impacted soils correspond to those in the west roadside of the secondary road (SR L) and in the highway at 1 metre distance since these soils have the highest I_{geo} values. As can be seen in the Fig. 5 roadside soils from the secondary road appear to be polluted ($I_{geo} > 1$) in Cd, Pb, Sb and Zn, whereas those from the highway are polluted in Cd, Cu, Pb, Sb, Sn and Zn but also in Hg, Mo, Nb, Ti and W (data not shown).

The worst case, as has been previously stated, is the high pollution of Pb ($I_{geo} > 4$) in soils from the west roadside of the secondary road due to the past use of leaded gasoline. On the contrary, the east roadside from the secondary road (SR R) and soil samples at 3 metre distance to the highway appear to be non-polluted in all the studied elements, $I_{geo} < 1$. Soils from Berango and Sopelana appear to be not polluted for most of the TREs ($I_{geo} < 1$). Only Sb has a I_{geo} value of 2 in samples from Sopelana classifying them as slightly polluted soils. Other significant metal that presents certain pollution level was Cd with a $I_{geo} = 2$ in topsoil at 1 metre distance from the road and values between 1-2 at 0 m (very slightly polluted). These soils are also very slightly polluted in Cu ($1 > I_{geo} < 2$) both at 0 and 1 metre of distance, and in the case of Berango, also in Pb. The rest of elements have values of geoaccumulation index below 1.

The elevated concentration values of Sb must be highlighted. In particular, Sb is the only TRE found in the Sopelana sampling site, a new road with very low traffic density but which is located in the surroundings of the beach and during the summer, many cars park in the roadside. This is in agreement with a recent work that studied the Sb speciation in different fractions of urban dust in Buenos Aires, Argentina (Fujiwara et al., 2011), highlighting its presence as a TRE together with Cu and Pb, like we have detected in these new soils. Besides, it is known that Sb is used in brake linings (Hjortenkrans et al., 2007; Thorpe and Harrison, 2008) and could be released to roadside soils in the dust originated by the brake wear when cars park in the roadside.

On the other hand, the Indicative Values for Assessment (VIE) are guideline values to establish the risk acceptance limits for the different uses of a soil in the Basque Country. There are three levels of

acceptance. VIE-A is a reference level and below it, it is possible to state that the soil is not affected and there is no risk for the human health. VIE-B marks the lower limit of acceptability of the risk. Values lower than this but higher than VIE-A involve acceptable risk, whereas values higher than VIE-B suggest an unacceptable risk and a more detailed study of the zone must be carried out. VIE-C represents the upper limit of acceptability of the risk and when exceeded, implies a serious risk to the ecosystem and soil recovery measurements are required.

The average concentration of metals in some of the sampling locations have been plotted in Fig. 6 against the VIE-B and VIE-C values. As can be seen, the concentration of some elements is higher than the VIE-B, even the VIE-C, in roadside samples from the highway and from the west roadside of the secondary road. In the case of roadside soils at 1 meter of distance to the highway, the concentration of Mo, Cd, Ni, Cu and Pb is higher than the VIE-B value, whereas Hg and Zn exceed the VIE-C value. The concentration of Cd, Cu and Zn in soils from the west roadside in the secondary road was also above the VIE-B, whereas Pb concentration surpassed the VIE-C. Although Berango and Sopelana do not have high values for most of the TREs, the concentration of Cu is above the VIE-B in both sites and Pb and Zn levels are higher than VIE-B in Berango and Sopelana respectively. There were no more limit cases in the rest of the sites. The concentration of As and Co, the other two metals for which the Basque Government regulates its concentration in soil, are lower than the VIE-B and do not suppose a risk for the environment in any of the studied areas.

Metals such as, Pb, Zn and Hg, have been measured recently at unexpected moderate concentrations in the sediments of the Bilbao estuary after removing the industrial sources of pollution (Fdez-Ortiz de Vallejuelo et al., 2010; Fernández et al., 2008) as well as in the Urdaibai estuary (Bartolome et al., 2006) indicating that traffic could be the source for them (probably through a run-off process from soils behind the roads circumvolving both estuaries).

4. Conclusions

This work showed the traffic impact that happens in roadside soils from roads with a high traffic density, leading to a high traffic-related element concentration in them. ICP-MS semi-quantitative

analysis of the acid extracted soils allows the fast determination of most soil elements as a first tool for evaluating the candidate sites to suffer the traffic impact. The studied area could be easily fenced in the most impacted sampling points after a first screening of the concentration of 60 elements in soils. Cd, Cr, Cu, Hf, Mo, Nb, Ni, Pb, Sb, Sn, Sr, Zn and Zr were identified as traffic-related elements (TREs) after chemometric treatment of the obtained results. The concentration of these metals in the west roadside of the old secondary road studied appears at higher concentrations than the rest of sampling areas, including the control soils. This high metal concentration values in that secondary road can be explained due to a long-term accumulation of metals from the past decades.

The quantitative analysis of the vertical and horizontal profile of concentration of metals reveals that there is an accumulation of TREs on topsoil of roadsides affected by high traffic impact during long time. For this reason, a high decreasing profile with depth and distance to the road/highway in the concentration of the above mentioned elements was detected in roadside soils from the studied highway (more than 15 years in service), but not in the roundabouts from Berango and Sopelana (less than 5 years in service). Here, the concentration of TREs keeps constant with depth and distance to the road since they are new roads and they have not been exposed to the traffic impact enough time to accumulate the metals in topsoil.

The use of the geoaccumulation index to assess the impact and the contamination degree of the roadside soils concluded that the secondary road and the highway are much more polluted by the traffic emissions than the other studied roads. Pollution of the soil decreases rapidly with distance to the highway and soils are classified as non-polluted at 3 meters of distance. In the newer roads the geoaccumulation indexes suggest that a slight pollution of Sb, Cd, Pb and Cu, has started in a site with less than 5 years at service. In particular, Sb seems to be the most important TRE impacting the soil. Regarding the indicative values for assessment (VIE) that the Basque Environmental Public Corporation (IHOBE) sets up for some toxic metal concentration in soils, some of them were detected above the values established for the acceptability of the risk. In the case of the concentration of Pb in roadside soils from the secondary road, and Hg and Zn in the highway, the upper limit of acceptability of the risk (VIE-C) is surpassed.

To sum up, the obtained results illustrate the accumulation of metals that occurs in roadside soils due to the traffic emissions. This accumulation is higher in roads with more years in service and more traffic density, reaching in some cases metal concentrations on topsoil above the target values regulated by the local administration. The use of the geoaccumulation indexes is a good approach to establish the range and pollution degree of soils impacted by the traffic emissions. Although leaded petrol was banned more than ten years ago, Pb continues being a problem for the environment as high concentrations still remains in roadside soils. Apart from this well-known TRE other metals, such as Sb, are starting to accumulate in newer roads as a result of its presence in nowadays brakes. Further actions should be adopted to avoid spreading the pollution from topsoil near the roads to other areas since elevated concentrations of some TREs are being detected in the sediments of the Bilbao estuary as a consequence of, probably, the metal run-off originated by the rain.

Acknowledgments

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Tables

Table 1. Background levels of some metals (mg/Kg) in soils from the Basque Country (IHOBE, 1998).

	Cd	Cr	Cu	Ni	Pb	Zn
This study	0.1	38	15	21	22	60
IHOBE	0.2	30	14	19	22	65

Figure captions

Fig. S1. Pictures of the sampling sites: a) the secondary road; b) the highway; c) the roundabout from Berango; and d) the roundabout from Sopelana.

Fig. 1. Scores and loadings plot for the first two PCs resulting from the PCA of all elements determined in roadside soils from the secondary road and the highway. C: control; SR L: west roadside of the secondary road; SR R: east roadside of the secondary road; H 0.5, H 3, H 6 and H 9: highway soil samples at 0.5, 3, 6 and 9 m distance from highway.

Fig. 2. Average value of some metal concentration in SR L and SR R: west and east roadside of the secondary road; HG: highway; and C: control.

Fig. 3. 3D representation of the variation of Zn concentration (mg/Kg) with the depth and distance to the highway in roadside soil samples from the highway.

Fig. 4. PCA of the soil transects from the 3 different sampling sites at the highway, Berango and Sopelana.

Fig. 5. Geoaccumulation indexes for some TREs in the different studied areas.

Fig. 6. Concentration of some metals and their regulated values for the Basque Country, given by IHOBE (Basque Environmetal Public Corporation).

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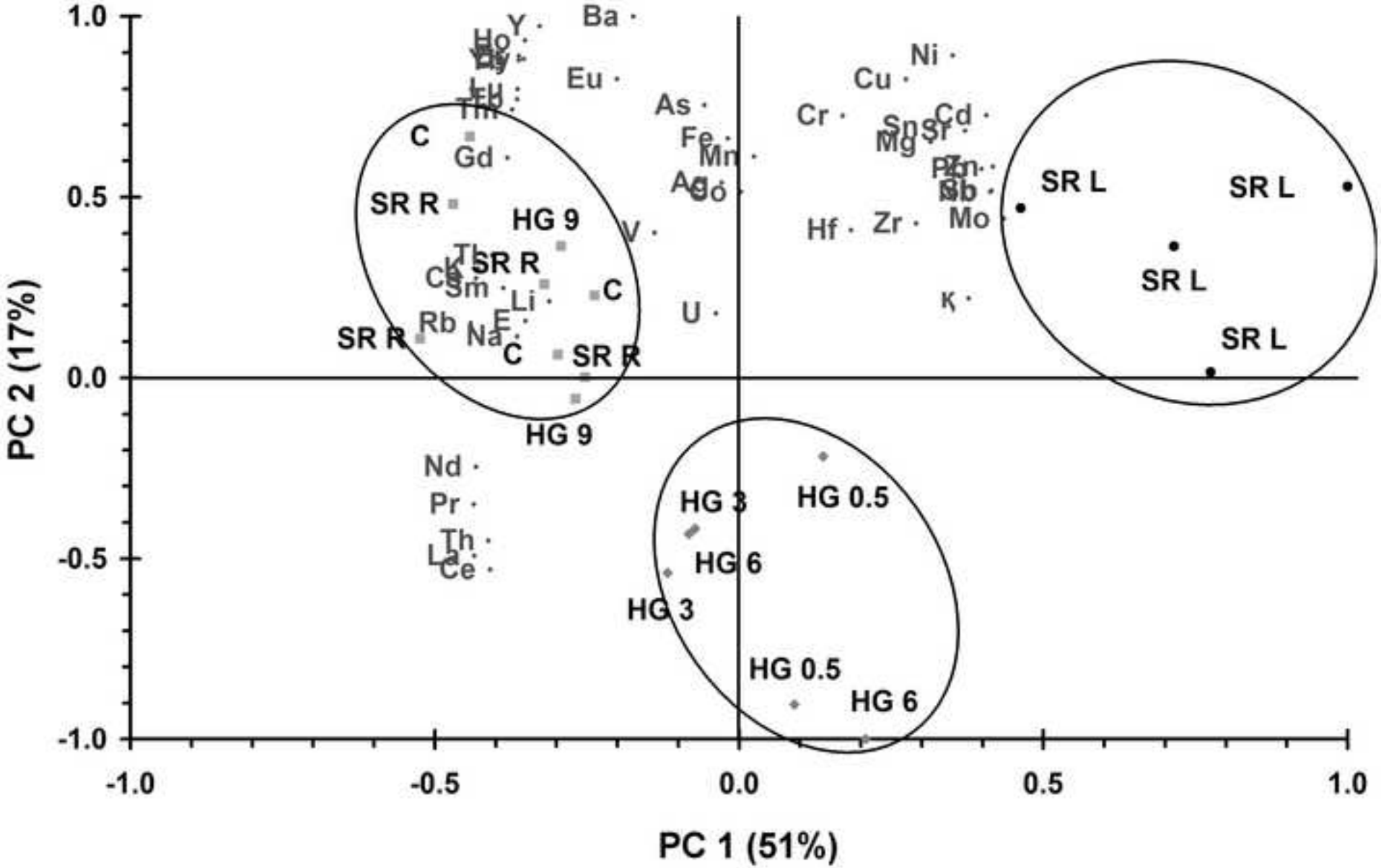

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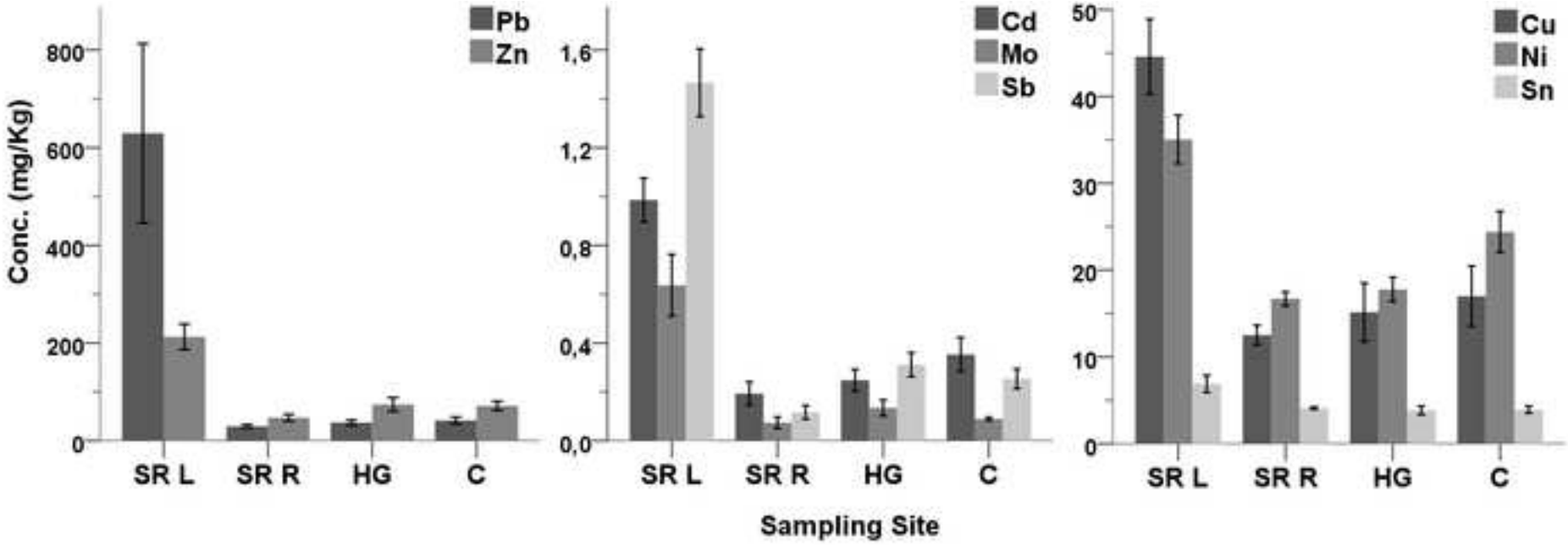

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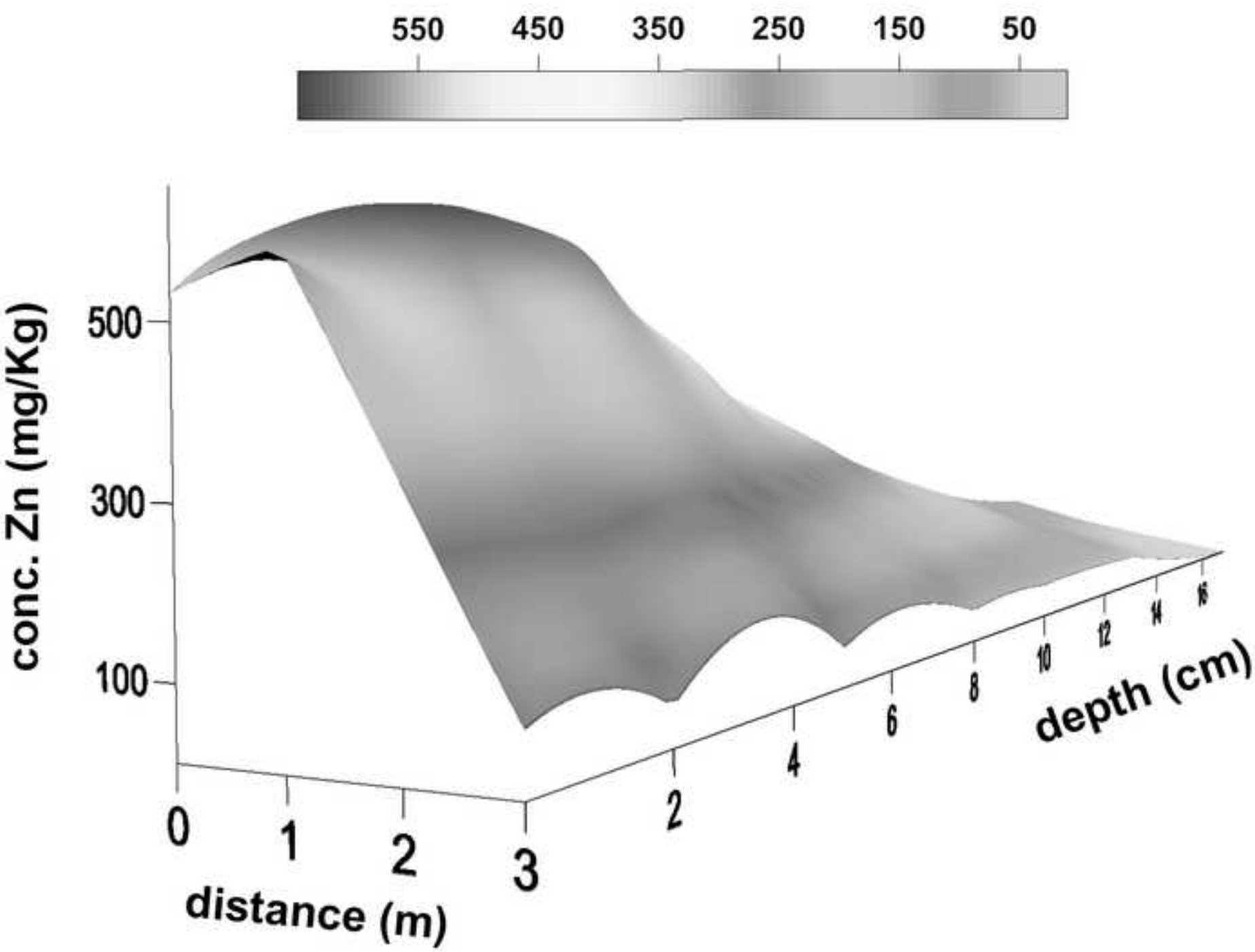

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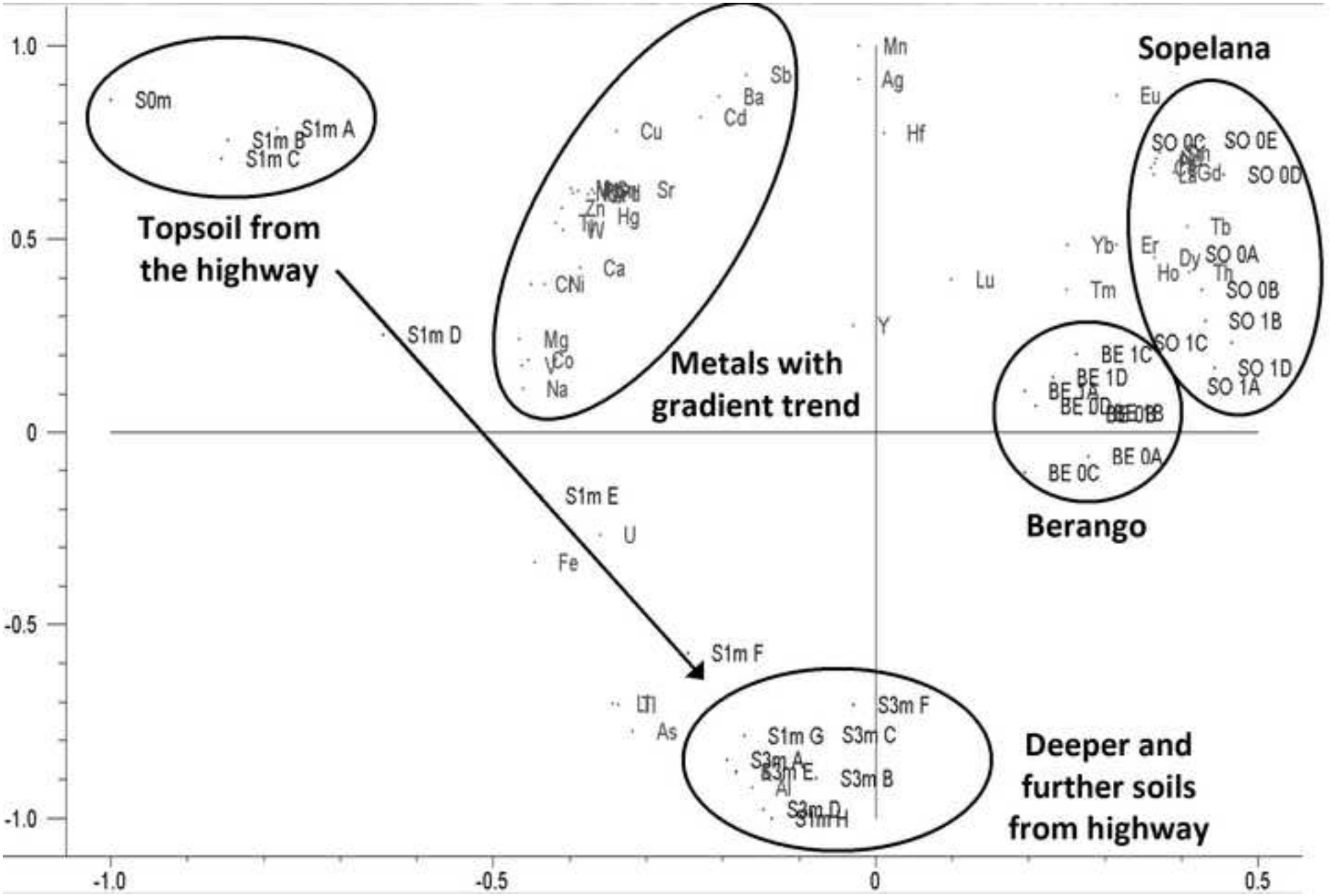

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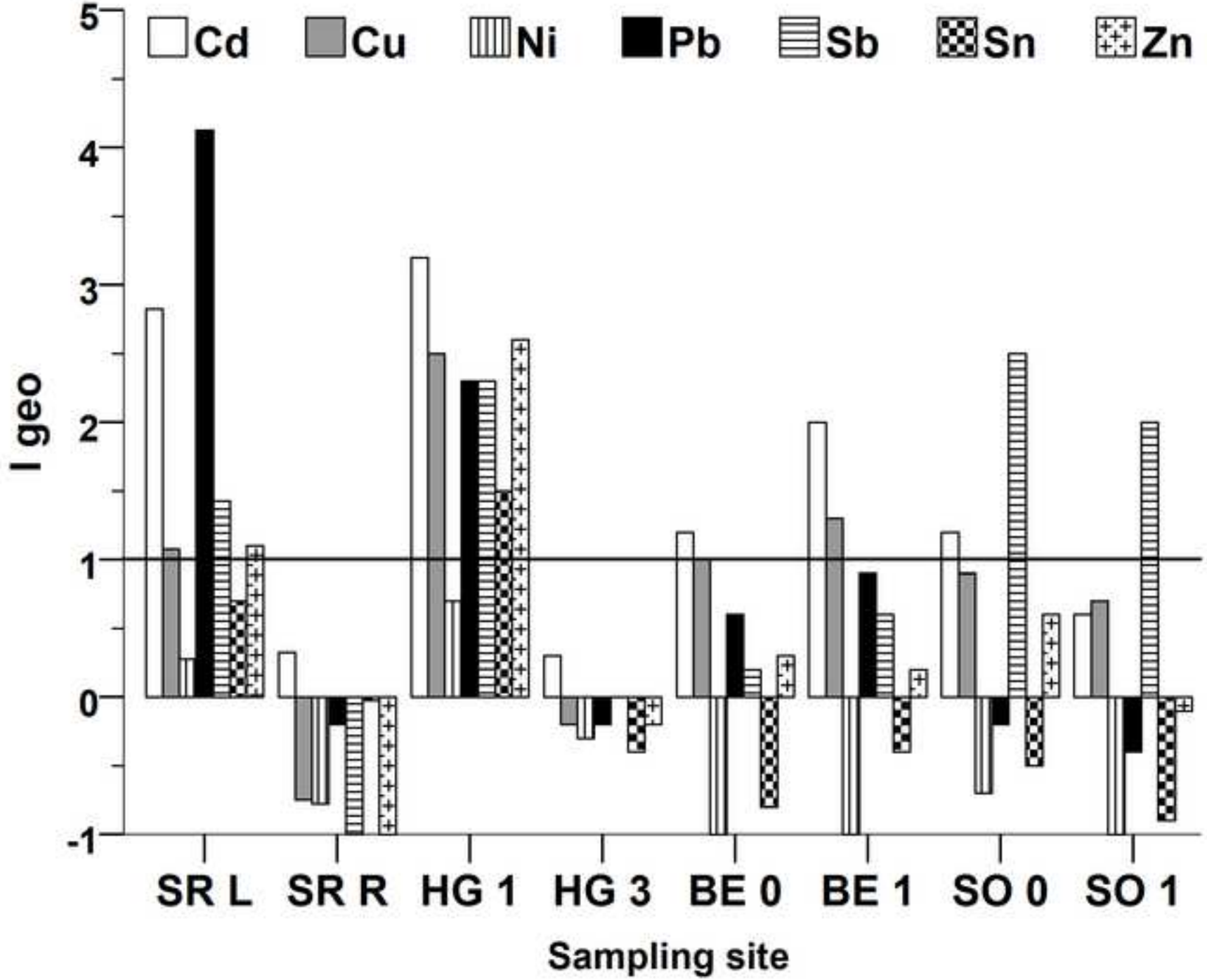

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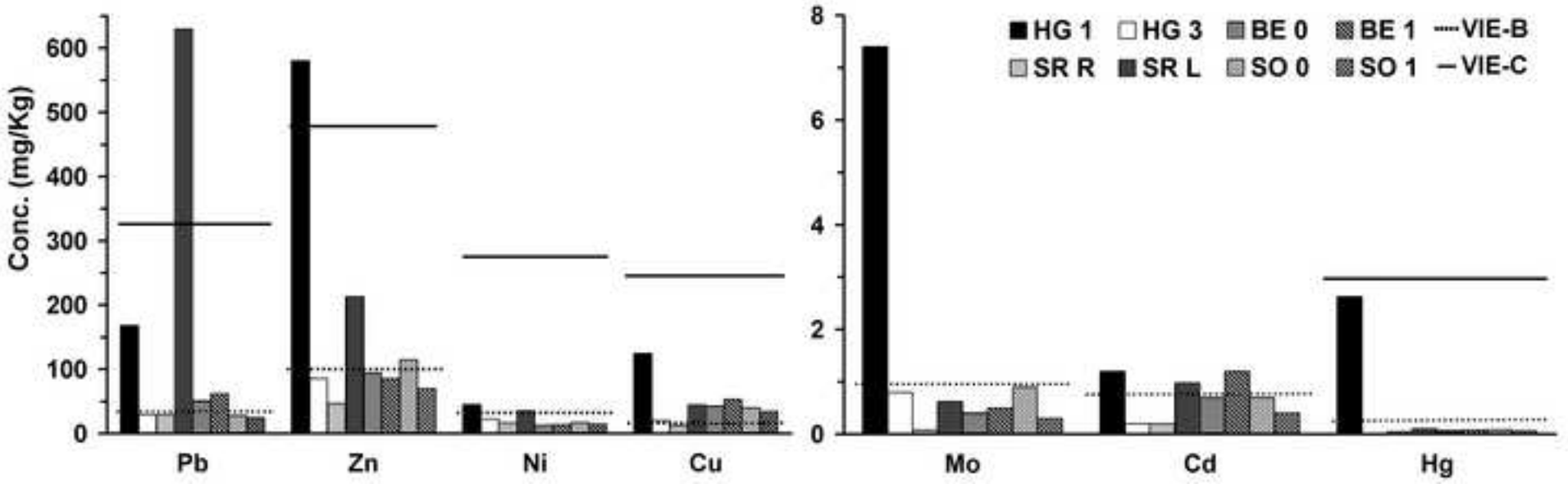

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