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Lead concentration in soil from an old mining town

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Abstract Lead concentration in soils has been measured in Vetagrande, an old mining town located at the state of Zacatecas in México. Eighty nine soils samples were analyzed using Energy Dispersive X-ray Fluorescence. The lead concentrations were treated with the Kriging method in order to estimate the lead concentration distribution in the studied area. Pb levels in soils were from 8 to 7730 μg kg^{-1}, where 28.1% of soil samples have less than 400 μg kg^{-1}, 71.9% is above 400 μg kg^{-1} which is the maximum level recommended by the EPA for residential use of soil. Lead concentration measured around public sites represent a risk of lead intake in the population.

Keywords Lead · EDXRF · Kriging method · GIS · Contamination · Soil

Introduction

After the discovery of the American continent the exploitation of mines reached a primitive industrial scale, with the consequent production of mine or mill tailings affecting adversely air, soil and water [1]. Tailings have elevated concentrations of metals such as lead, arsenic, cadmium, copper, manganese, iron and zinc [2]. Some industrial activities, like mining, lead to changes in the concentration of some minor and trace elements in the soil [3].

Natural and human activities are both important in determining the complex spatial variation of heavy metal concentrations in soil. The contamination of heavy metals is a current topic in the area of environmental sciences as well as in the area of public health. The impact of the heavy minerals of an anthropogenic origin in the environment, has been the object of study in several investigations, in particular, the Pb is recognized as one of the most important eco-toxicological contaminants [4].

Lead is a ubiquitous metal that has been used since prehistoric times. Over the years, its wide distribution and transport in the environment has resulted in increasing human exposure and uptake [5]. The most common sources of lead exposure include lead-containing paint, soil/dust, leaded gasoline, plumbing leachate (water), occupational exposure, and hobbies using lead-containing materials like the lead glazed items [6].

Lead glazed used for cooking and food storage is also a source of lead exposure, it has been reported lead glazed ceramics, sampled in 54 households in Mexico, have an average lead leached concentration of 2163.3 ppm [7]. In the USA, some pieces of glazed pottery manufactured in Italy and Mexico were found to leach large amounts of lead [8].

Concentrations of lead in air in Mexico have decreased over the past decade in response to regulatory control of emissions of leaded gasoline. However, some high dose lead sources remain including residual contamination of soil and dust by gasoline exhaust [9].

In the last 200 years, hand-made dinnerware, bottles, vessels, jugs and pots prepared from glazed terracotta were widely used for daily cooking and storage of food and beverages, frequently alcoholic drinks such as wine, in

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Hungary and in the area of the Carpathian basin [6]. Here it is popular and traditional to use terracotta pottery for household decoration and to store solid and liquid foods (e.g., sauerkraut). Most pottery is covered with glaze frequently containing high concentrations of Pb. EDXRF and ICP-AES were applied to investigate the dissolution of lead from the surface layer of glazed pottery vessels into different water media of different acidities. Lead extraction was found to depend on the acid type (citric and tartaric acid), the origin or manufacturer of the pottery, the pH of the liquid and time and temperature of dissolution [10].

Lead in soil, dust, and residential lead paint are the primary sources of environmental lead exposure [11], pollution due to lead rich soil causes a wide range of health and environmental problems [2]. Lead available in the environment is recognized as an important health problem, which makes intervention important in order to prevent the toxic effects; especially in infants and pregnant women and during the period of breastfeeding [12]. Mining zones should being considered as potentially dangerous zones that must be monitored, because the bio-availability of heavy metals is an intoxication risk of population [13].

Since the Prehispanic and the Colony eras up nowadays mining activity has played an important role in Mexico. In the region of Zacatecas city the abundance of silver-rich ores was the reason of the city foundation during the Colony period (1546–1548) becoming one of most important mining and economic centers of the New Spain. Currently, Zacatecas is worldwide the largest producer of silver; nationally Zacatecas is the main producer of Pb, and Zn [11]. Mining has generated a large amount of granular solid and semisolid residues, locally known as "*jales*" (*Nahuatl* voice derived from "*xalli*", that means "*sand*"). These tailings have been stored open-cast, contaminating the ecosystems and nearby population. Today, ground with mine tailings are urban and agricultural zones. Therefore, the evaluation of exposure to contaminants from mining activities is important especially in the old mining towns like Vetagrande where there are large areas affected by the presence of mine tailings.

The development of the geographic information systems, GIS, and the application of geo-statistics have given a boost to the analysis of the space distribution applied to the ecology and to the environmental sciences. Kriging techniques have been widely applied in soil science to analyze the spatial patterns and variability of concentrations of pollutants that enables its accurate monitoring [14]. In order to evaluate the environmental impact of contaminants, like the lead, their spatial distribution must be determined. This is important in an urban area due to the complex and heterogeneous nature of soil. The use of GIS provides a mean to estimate either the value of a soil attribute at locations between samples, or the probability that the contaminant concentration will exceed a given threshold at a particular location [15].

The purpose of this study was twofold, first the lead concentration was measured in soil samples using the Energy Dispersive X-ray Fluorescence, and then these values were utilized to obtain, using a geographic information system, a map of lead distribution around the town of Vetagrande, identifying risk areas to human health.

Materials and methods

This study was carried out in Vetagrande town located at 22°83′33″ latitude and −102°55′58″ longitude at the state of Zacatecas in Mexico. From this area 89 ground samples were taken in several sites including downtown, schools and public areas. The sample size was determined assuming that the number of possible samples was infinite were 50% has a lead concentration larger than 400 μg/g. It was assumed 99% of confidence level with a maximum error of 6%. The sampling sites were selected using an unrestricted random procedure in the aim that derived results will be representative of lead concentration of this area.

Soil samples were dried at 40 °C for 40 h and sieved (<325 μm), then were homogenized and weighed. Samples were 1.5 g of powdered soil. The total amount of lead on the soils was measured by spectrometry of energy dispersive X-ray fluorescence, EDXRF, using a MinPal PW4025 model [16]. This technique has been utilized to characterize the environmental pollution in complex urban environments [17, 18]. The X-ray spectra were analyzed with the MiniPal II software. The X-ray tube was feed with 30 kV with a current of 13 mA. The X-rays was filtered with Mo to reduce the amount of small energy X-rays. The spectrometer was calibrated with 12 standards, four of them belonging to the National Institute of Standards and Technology USA (NIST): Montana soil 2710 and NBS 1570, 1573, 1575, another 8 were prepared with soil which was added with different concentrations of lead acetate ranging from 10 to 8×10^4 ppm. Standards have the same geometry and shape as the unknown soil samples. Seven of these standards were measured independently using the Atomic absorption technique in order to verify the calibration curve obtained with EDXRF.

Each sample was measured five times and measurements were used to obtain an average value of lead concentration. The spectrometry was calibrated using the standard NIST-SRM2710 (Montana soil standard) from the US National Institute of Standards and Technology. Lead was determined measuring the K_β lines arising from transitions from M and N shells, with energies of 85 and 87 keV and those of K_α arising from transitions from the L shells, with energies of 72 and 75 keV.

The lead concentration mean values were input on a map through the ArcGIS 8.3 and Arc View 3.2[a] systems utilizing aerial photographs of the location obtained from the Mexican Institute of Statistics and Geography, INEGI [19]. From the aerial photographs a digital mosaic was developed where 11 visible control points were used where their coordinates were geo-referenced in the field through a GPS system. The statistical interpretation of Pb concentration in the soils was carried out using the Gstat software, this is a computer program for geostatistical modeling, prediction and simulation [20]. With the Gstat software an information sheet was built including the concentration ranges of Pb using the Kriging method.

Results

The concentration of lead in the soil samples varies from 8 to 7672 μg kg^{-1}, with an average of 1397 μg kg^{-1}. Soil samples were ranked in function of its lead concentration as shown on Table 1.

The largest group of the soil samples has a lead concentration ranging from 400 to 1000 μg kg^{-1}. 28.1% of the samples have lead concentration that is less than 400 μg kg^{-1}, while 20.2% of the samples have lead above 2000 μg kg^{-1}.

Regarding the zone, and the population activity, sampled areas in Vetagrande were distributed in three regions, the kindergarten where all the town children from 2 to 6 years are attending, the playground area, where children from 10 up to 17 years old attend regularly to play, and the downtown area where the houses concentration is larger, in these areas 43 samples were taken. Soil samples distribution and the mean lead concentration are shown on Table 2. Another 46 samples, not included in Table 2, were taken from the hills around the town.

The spatial distribution of the lead concentrations in soil samples was obtained using the method of geo-statistics estimates, where the distribution is defined by ranges. This treatment uses the measured lead concentrations to estimate the concentration in sites where soil samples were no obtained. For the geo-statistical estimation the study area of 1.6 km^2, was divided into blocks of 20 × 20 m and 5 cm of thickness. Results are summarized on Table 3.

Table 1 Ranges of the concentration of Pb in soil

Range of Pb distribution in soil (μg kg^{-1})	Number of samples	Relative number of samples (%)
0–200	20	22.5
200–400	5	5.6
400–1000	27	30.3
1000–2000	19	21.4
>2000	18	20.2
Total	89	100

Table 2 Levels of Pb in soil distributed by areas

	Kindergarten	Games area	Downtown
Number of samples	10	7	26
% of samples with <400 μg kg^{-1}	0	14.28	30.76
% of samples with ≥400 μg kg^{-1}	100	85.71	69.23
Average Pb concentration in μg kg^{-1}	1901	1489	724
Range of lead level in soil in μg kg^{-1}	3207	3564	2327

Table 3 Pb concentration in the blocks

Pb in soil (μg kg^{-1})	Number of blocks	Relative %
0–200	374	9.3
200–400	333	8.3
400–1000	1281	31.9
1000–2000	916	22.8
>2000	1114	27.7
Total	4018	100

To visualize the lead concentration in the study area a different color was used to identify the lead concentration ranges: For 0–200 μg kg^{-1} was used light green, for 200–400 μg kg^{-1} was used green, for 400–1000 μg kg^{-1} was used yellow, pink was used for 1000–2000 μg kg^{-1}, and red for blocks with lead concentration larger than 2000 μg kg^{-1}. In Fig. 1 a color map shows the distribution of lead concentration. Here, areas with larger lead concentrations are those with active mining tails, chutes, grinding plant, benefit plant deposits where the minerals are processed, the tailing damn and the vein that goes through a part of the population.

Discussion

The lead concentration in soil samples from Vetagrande town has been measured and the lead distribution all over the town has been identified. The average concentration from the 89 samples is 1397 μg kg^{-1} being larger to 400 μg kg^{-1} that the US Environmental Protection Agency recommends as limit in soils for residential use [21, 22]. The presence of such high levels of lead, in combination with poor hygienic habits and malnutrition produce a high risk of lead intake in children and pregnant women [16, 23].

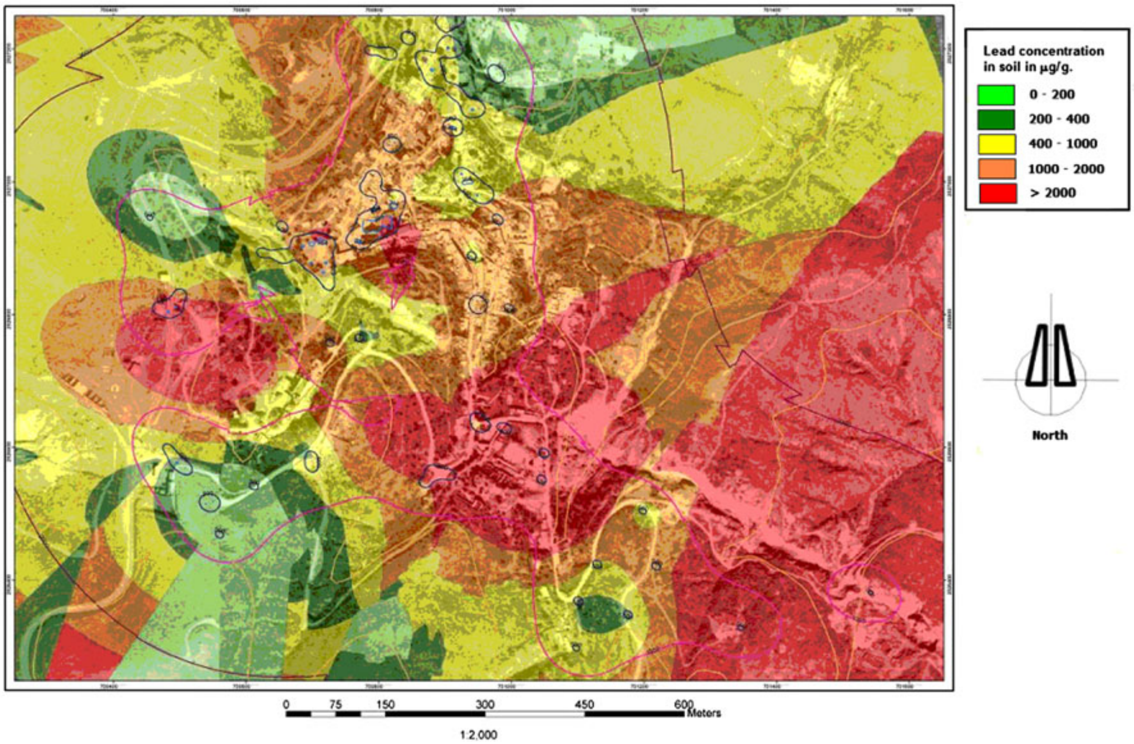

Fig. 1 Spatial distribution of lead concentration in Vetagrande town

Only 28% of the samples have less than 400 µg kg^{-1}, this group has an average concentration of 136 µg kg^{-1}, these locations are viable for residential use. On the other hand 72% of the sampled sites have lead concentrations above the criteria value.

The kindergarten of the town is located approximately 50 m from the main mine vein and approximately 100 m from the grinding plant of the mining company; soil samples taken in the kindergarten area have an average lead concentration of 1901 µg kg^{-1}. Considering that the maximum allowable level in Germany [24, 25] for a kindergarten is of 200 µg kg^{-1}, the value found in Vetagrande is approximately nine times higher than this value. These levels indicate that the soil is a potential source of lead intoxication for the susceptible population because children's organism has the capacity of absorbing lead in higher percentages than adults [26]. 8% of the samples analyzed were taken in the playground area in the community, from those, an average lead value of 1489 µg kg^{-1} was obtained, being larger to, 400 µg kg^{-1} that is recommended, as limit of lead concentration in soil used for recreational purposes, in US and Germany. This concentration is 372% above the 400 µg kg^{-1}, this playground area is located near a high school where children and teenagers spent their free time, therefore due to high concentration of lead represent a risk area to the health.

The lead concentration observed at the downtown area are attributed to the geo-morphology of the place, and the wind and rain erosion that makes the dragged material end up deposited in this area, this is probable the explanation for the inferior levels of lead in comparison to the deposits and mining waste, and it coincides with the direction of the main vein.

The highest lead values are distributed in a preferential direction corresponding to the main vein and with the residue areas including the grinding plant, located in this same orientation, this is not the case for the benefit plant, for this area is found with values which are of little significance. The extraction activity of the metals in the zone generated as tailings that historically were deposited on the surface, dispersed without control. It was until 1996 that the Mexican environmental legislation body did established the control regulations for environmental protection, where mining activities were included [27].

Currently the mining activity is carried out through a scale of only one company, with a grinding plant locate at SW direction from the population and a benefit plant that includes a tailing damn to the NE, located approximately 500 m from the population, therefore it can be considered, that Vetagrande is eminently an industrial zone according to the EEC norms [24, 25].

The old deposits of mining residues, as well as the mineralized areas of Vetagrande, are the main sources of bioavailable Pb. The lead concentration in soil found in this study around the kindergarten, playground area, and the downtown suggest that they must be considered a risk for human health.

Conclusions

Since its early years up to nowadays, mining activity in Vetagrande has been the main cause of current lead levels in soil. The mine vein, and mine infrastructure, as well as the mine tailings zone, located along the strip oriented to the NW and SW, and the grinding plant, release Pb affecting Vetagrande town. Lead is transported through erosion produced by wind and rain and it settles in the soil. Dust particles, with lead, are deposited in the community, mainly in the downtown. 71.9% of the sites from where soil samples were taken are not appropriate for residential use, 20% are not suitable for industrial use. The mean concentration of lead at the kindergarten area is 190 μg kg^{-1}, therefore could be considered as a risk zone for health. The SIG, with factorial and Kriging indicator under different combinations of variations and pollution probabilities of soil with Pb, provide an alternative procedure for delineating the areas that contain high variation and high pollution probability, enabling the identification of the pollution sources for lead. The lead concentration in soil is a source of contamination in Vetagrande that can affect the health of population living nearby the studied areas. Lead is intake mainly by ingestion, being bio available through its presence in soil.

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