ISSN : 0974 - 7451 Volume 7 Issue 9

Environmental Science
An Indian Journal

Trade Science Inc.

Current Research Paper

ESAIJ, 7(9), 2012 [343-348]

Heavy metal quantification in community soils impacted by mining activities in the northern mountains of Oaxaca, México

Adela Hernández-Hernández, Jaime López-Luna, Elizabeth González-Terreros*
Instituto de Estudios Ambientales, Universidad de la Sierra Juárez, Av. Universidad s/n,
Carr. Guelatao-Ixtlán, Ixtlán de Juárez, Oaxaca, C.P. 68725, (MEXICO)
E-mail: eliza799@hotmail.com
Received: 2nd August, 2012 ; Accepted: 18th August, 2012

ABSTRACT

This work was conducted in two seasonal times to quantify As, Cd, Cr and Pb, in community soils impaired by mining tailings. Soils were physico-chemically characterized, metals extracted by acid digestion and then determined by ICP-OES. Significant differences were observed between dry and rain season, with the highest metal level content in the dry season. The concentrations of As and Pb recorded in most soils were of serious concern; even though in the control soil used as a no-polluted reference soil. Important synergistic relationships were observed among metals and physico-chemical parameters.

KEYWORDS

Mining tailings;
Community soils;
Heavy metals;
Quantification.

INTRODUCTION

With the modern civilization and the industrial revolution started the most destructive actions, altering and distorting the biological recycling of soil chemical compounds[1]. The mining has been one of the anthropogenic activities generating a great quantity of tailings containing sludge rich in heavy metals (Figure 1). This way, the parent soil of the mine is degraded or lost irreversibly. The resulting soil suffers a serious impact during the mining exploitation, becoming frequently unstable and more else, its structural forming materials are not suitable for biological activity development and the natural process of soil formation[2].

Heavy metals are of extreme concern because of their toxicity; since soluble compounds are rapidly absorbed in the human body where enzyme activity is inhibited. Very small dose might produce serious physiologic or neural consequences[3]. Metal pollution is spread

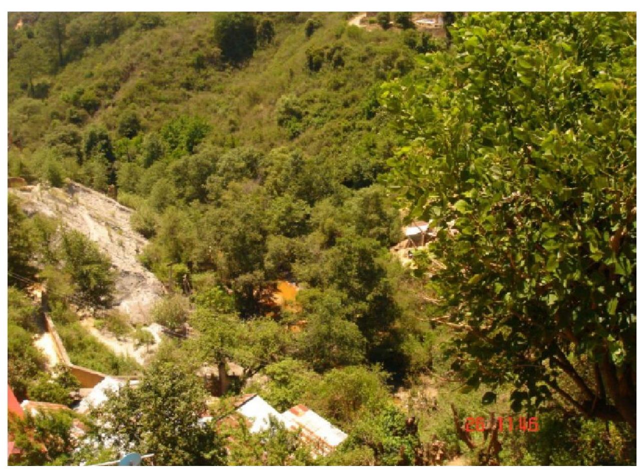

Figure 1 : Photograph showing the mining tailings (without vegetal cover) on the riverside in the community of Natividad, Oaxaca, México.

over there, but soil is the main receiver of heavy metals from anthropogenic sources, as it is shown at the Municipality of Natividad, Ixtlán de Juárez (latitude 17º 17'/17º 19' N, longitude 96º 24'/96º 27 W), the northern mountains of Oaxaca State, México; where the heavy metals follow a dynamic course, rather than getting stabilized. The dynamics of heavy metals in soil can be classified in four mainly categories: mobilization to fresh or ground water, atmospheric volatilization, biological uptake and, soil retention by different mechanisms (heavy metals in the soil solution, adsorption, complexes formation, and precipitation)[4].

Mining pollution is an ancient issue but still is of great concern for the environment and human health. As a short remembrance, the colonial exploitation of gold and silver in the State of Oaxaca started at the beginning of the XVI century, mainly in Valle Central and El Istmo, causing huge havocs among the indigenous population, which was diminishing due to the extremely hard work and abuses imposed by the "pernicious gold idolatry from the Spaniards". The mining in Oaxaca reached its maximum splendor in the XVIII century[5]. In Natividad was established the Compañía Minera Natividad y Anexas S.A. de C. V., but the industrial mining activities started 200 years ago, since then causing environmental alterations in the surrounding soils and water bodies, due to the residuals generated.

Studies about the contamination assessment generated by the mine only exist in the classified archives owned by the company. Therefore, in 2007 PROFEPA-Oaxaca[6] carried out an inspection and, it was verified that Zn and Pb contained in the mine tailings were being dropped to the water bodies of the bordered area, causing a significant impact to the environment and nonfulfillment to the Mexican Normatively. These facts forced to a temporary and partial closing of the mine activities. Joined it, gold seekers (Figure 2) working handmadely without any protection and using acids and mercury salts for extracting silver and gold, spread the heavy metal contamination to the river, to other places of the community and even, to their own housings, posing a serious risk for their inner health.

The economical benefits of the mining activity in Natividad are not directly applied to the population, but rather, they are who suffer the inconveniences of mine tailings poured to the river. Furthermore, dust from mine tailings containing heavy metals, is air transported and spread to the neighbor communities. Despite the environmental doubtful, there are not quantified data of soil and water heavy metal contamination level. Therefore this work was aimed to obtain reliable data of heavy metal pollution of soils adjacent to the mine in two seasonal periods.

Figure 2 : Gambusino (gold seeker) washing mining tailings to recover the precious metal.

MATERIALS AND METHODS

Soils from four sites nearly the mining industry were sampled and a soil from an apparently not impacted area was used as control (Figure 3). The first sampling was carried out on December 2009 for the rain season. The second sampling was carried out on May 2010 for the dry season. The sampling was done at 0 to 20 cm depth covering a surface of $1m^2$, obtaining compose samples according to NMX-AA-132-SCFI-2006[7]. Soil samples were dried at room temperature and sieved through a 2-mm mesh, and then physicochemically characterized.

For total heavy metal content quantification (As, Pb, Cd, and Cr) 0.5 g soil were digested with concentrated HNO_3 and 10% H_2O_2 at 150ºC[8], using a Büchi Digest System K-437. Three replicates of each sample and a blank consisting of 2% HNO_3 were evaluated.

Heavy metals were determined by ICP-OES Optima 7000 DV (Perkin Elmer).

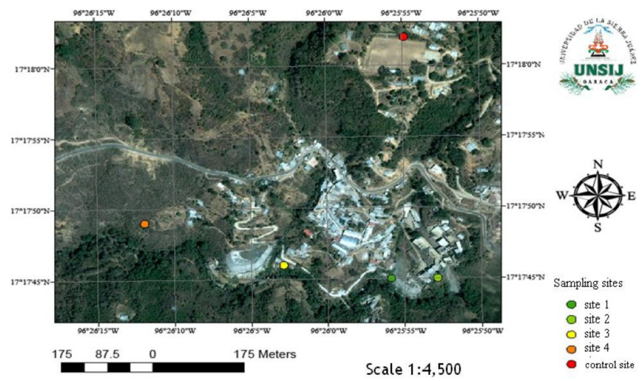

Figure 3 : Distribution of soil sampling sites in the mining community of Natividad, Oaxaca.

Statistical analysis

Analyses of variance (GLM) and means comparison (LSD) were conducted for all parameters measured in rain and dry season. Also Pearson's correlation analyses were performed to establish relationships among metals and soil physico-chemical properties[9].

RESULTS AND DISCUSSION

Soil physico-chemical properties

The five sampled soils were found to mostly content clay and sand (TABLE 1). Heavy metals are strongly adsorbed in soils with higher clay content[10], such as the site 4 and the control soil. Moreover, this kind of soils present high water holding capacity (WHC) meaning restricted metal mobilization since water infiltration is very slow[11]. Otherwise, heavy metals are not importantly adsorbed in sandy soils (site 1, 2 and 3), but these elements could be leached to ground water[12]. Neutral-alkaline pH's were recorded in rain season and dry season, respectively; such a change generated by increased biological activity in rain season. Heavy metals in alkaline soils are more strongly adsorbed than in acidic conditions[13]. Soils from Natividad are not acidic, meaning restricted heavy metal solubility and then mobility. Nonetheless, because of the mine exploitation activities heavy metals could have reached deeper horizons of the soil. Additionally, due to the sharp topography of this place, heavy metals are run off by the pouring rain and transported through the river to local culture soils and soils from other communities. Despite the environmental impact from the mining activities all sampled soils were found not still saline, according to the electrical conductivity values (TABLE 1). Organic carbon represented 98% of total carbon for all the soils studied. Organic carbon in soils is directly related to the quantity and nutrient availability. Organic carbon quantity depends not only on environmental conditions, but also is strongly affected by soil perturbation. Total carbon content differs between dry and rain season due to the increased biological activity in the rain season. It is known that in not perturbed soils the organic matter content is relatively constant[1]. However it is very

TABLE 1 : Physico-chemical properties of soils from the Natividad mining zone.

	pH	EC (µS/cm)	WHC (%)	Total C (g/kg soil)	Total N (g/kg soil)	Texture
Rain Season						
Control Site	8.44 ±0.01 aA	230 ±2.00 dA	74.68 ±0.13 aA	44.85 ±0.00 aA	2.63±0.10 aA	clay loam
Site 1	7.98 ± 0.00 bA	290 ±3.00 cA	64.67 ±0.39 cA	34.06 ±0.58 dA	1.76±0.02 cA	sandy clay loam
Site 2	7.02 ±0.01 eA	400 ±0.00 bA	76.88 ±2.09 bA	45.82 ±1.15 bA	1.69±0.01 cdA	sandy loam
Site 3	7.43 ±0.01 dA	770 ±7.00 aA	43.87 ±0.57 dA	22.78±0.00 eA	0.45±0.01 eA	sandy loam
Site 4	7.94 ±0.00 cA	240 ±2.00 dA	78.95 ±1.02 bA	53.25±0.58 aA	4.47±1.06 bA	clay
Dry Season						
Control Site	8.54 ±0.01 aB	200 ±0.00 aB	66.55 ± 0.42 aB	24.05 ±0.57 bB	0.45±0.00 aB	clay loam
Site 1	8.21 ± 0.01 cB	420 ±0.00 bB	59.24 ± 0.87 bB	23.18 ±0.72 bB	0.34±0.05cB	sandy clay loam
Site 2	7.49 ±0.00 eB	1±0.00 cB	83.16 ± 0.35 cB	48.45 ±0.00 bA	0.98±0.00 bB	sandy loam
Site 3	8.24 ± 0.00 bB	250 ±0.00 dB	42.61 ± 1.89 dA	18.00±0.00 cB	0.30±0.00 cB	sandy loam
Site 4	8.14 ±0.02 dB	170 ±0.00 eB	78.20 ± 0.67 eA	48.92±1.15 aB	1.39±0.04 dB	clay

Values are means of three replicates ± standard deviation. Means with the same letter are not significantly different. *P* < 0.05 LSD test. Small letters indicate comparisons among sites. Capital letters indicate comparison between rain season and dry season from the same site.

difficult to establish comparisons since data are scarce and mine activities started 200 years ago. Zarei et al. (2008)[14] reported 0.998-1.013 g total N/kg in soils from a mining zone. These results agree with those obtained from Natividad soils in dry season (0.30-1.39 g total N/kg soil). Conversely, total N was greater in rain season (0.45-4.47 g total N/kg soil) due to increased biological activity and the higher clay content of soil. Groffman et al. (2001)[15] reported less total N content in a disturbed soil when compared to a not environmentally perturbed soil, since microbial and enzymatic activity are impaired by heavy metal toxicity.

Total heavy metal content

The highest heavy metal levels were found in dry season (Figure 4). The control site and the site 3 were expected as the least contaminated soils, since the control site is far away from the mine and the last one is covered by the riverside vegetation. However, both soils presented important As concentration (308.75-334.05 mg/kg soil). For sites 1, 2 and 3 it was found Pb>As>Cr>Cd, while as for site 4 and control site As>Pb>Cr>Cd. Similar results were reported by Cabrera (2008)[16] in soils affected by mine tailings, were 9 trace elements were determined, including As, Pb, Cr and Cd. Heavy metal content significantly diminished in the rain season. It was found Pb>As>Cr>Cd for sites 1, 2, 3 and the control site, in agreement with the dry season. The diminution in heavy metal content

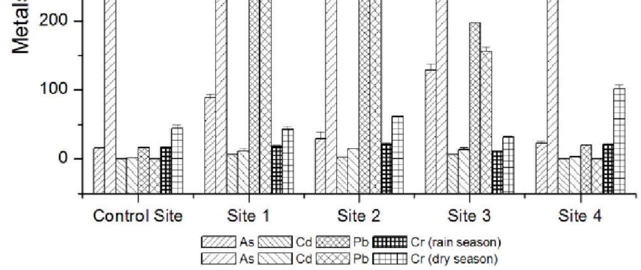

Figure 4 : Heavy metal content of soils affected by mining tailings in Natividad, Oaxaca, determined in two seasonal times.

in the rain season might be due to the run off through the river and metal stabilization or accumulation by the increased biological activity.

In dry and rain season important As levels were recorded since arsenic is commonly found associated to gold and antimony[17] and it should be emphasized that the mine at this municipality has been extracted gold and silver. Differences in As content in the two seasons were remarked by the rainfall from July to December, increasing the metalloid run off. More than 300 mg As/kg soil were recorded in the control soil established as no contaminated reference site. Despite this site is not directly impacted by the mine activities high As levels could be due to the transported particles in the dry season. Arsenic levels in all the soils sampled mainly in the dry season, exceed the 1-10 mg/kg soil background As concentration[18]. These soils are classified as excessively phytotoxic according to US-EPA (1992)[19]. Profepa-México established that 20 mg As/kg soil supposes human health risk and ecological risk. The Cd content in soils is variable but typically the background Cd concentration is about 1 mg/kg soil[19]. Natividad soils are above this limit. The Cd content in soils depends on the parental material. However, mining activities gradually has been increasing the Cd concentration. Again, Cd concentration was found lower in rain season (2.41-6.38 mg/kg) than in dry season (1.5-15.10 mg/kg). Minimal Cd values were recorded for the control site and the site 4 in both seasons while maximum values were observed for the sites 1, 2, 3, nearly the mine dump. Cd tends to be bioaccumulated and is rapidly absorbed in vegetal, animal and human tissues[20]. This element exerts toxicity to all organisms thus at low doses is considered risky for human health. Soils containing 3-10 mg Cd/kg soils are classified as excessively phytotoxic[19]. In the rain season the minimal Cr concentration was obtained for the control site (6.98 mg/kg soil) being the maximal Cr concentration 21.83 mg/kg for the site 4. In the dry season the minimal Cr concentration was 31.78 mg/kg in the site 3 and 102.15 mg/kg in the site 4. In a study of nine soils from an abandoned mine Cr content was found ranging from 2.70 to 35.70 mg/kg soil[20]. Natural Cr occurrence in soil environments is around 1-450 mg/kg, with an average concentration of 50 mg/kg soil[18]. However it should be seriously considered the Cr chemical speciation, since hexavalent Cr is extremely toxic as compared with trivalent Cr[21]. Lead soil contamination is of great concern because of the long time Pb residence into soil that conduces to a dynamic equilibrium with the hydrosphere, atmosphere and biosphere, disturbing the ecosystems; including human beings[22]. In control site and site 4 were recorded the lowest Pb concentration values in both seasons, since these site are far from the mining tailings. In neutral-alkaline soils Pb mobility is very low due to the precipitation of insoluble salts[23]. In the dry season Pb concentration ranged from 104.02 mg/kg soil in the control site to 464.32 mg/kg in the site 2, while in the rain season were recorded 2.9-294 mg Pb/kg soil. Soils containing 50-100 mg Pb/kg are considered extremely toxic[19]. A synergistic relationship was observed between Cd and Pb in both seasons (r 0.857, P<0.0001), while in the rain season a highly significant correlation was observed between Cd and As (r 0.929, P<0.0001) showing also a synegestic relationship that favors metal mobility. A negative correlation (r -0.994, P<0.0001) was observed between As, Cd and total C content in the rain season, since increased biological activity modifies metal dynamics (absorption, oxidation, reduction, plant uptake, organic complexation). It should be highlighted that only total metal content was determined. Sequential and single extractions methods might contribute to better understanding about heavy metal association with soil fractions and heavy metal availability.

As a perspective it can be argued that the brief of offenses to indigenous communities has in mining exploitations the main of its factors. Hundreds of tons of residuals and derived polluting materials collapsed from the mine in the vicinity of this company have spread heavy metal contamination to reach the Capulalpan River impacting the human and wild life[24]. A water sampling promoted by the community in 2012 revealed 177 mg/l As and 117 mg/l Pb, extremely high pollution level and of great risk for human and wild life, according to national and international standards. Gómez (2012)[25] also stated that the mining activities have irreversibly affected 13 aquifers and springs due to filtrations through the mine tunnels. The main pathways exposition to heavy metals in Natividad is the dust particles from mining tailings transported far away by the wind and the tailings run off to the Natividad River that is the water supply for down town communities, flowing finally to the Grande River. The problem can not be solved whereas the mining tailings stay on the riverside. Unfortunately there are not clear plans for environmental management by the mining company or Mexican environmental authorities.

CONCLUSIONS

The high As and Pb concentrations found in the sampled sites poses a serious risk for population in Natividad and surrounding communities, being children and elder people the most physiologically vulnerable to metal toxicity. The control site considered as no-contaminated reference soil was also found to mainly contain As, whose toxicity and effects on human health are well known. Mining tailings keep leaching heavy metals into soils, impacting aquifers. Heavy metals are being spread far away from the contamination source throughout the watersheds and by several skilled miners or gold seekers ("gambusinos" is the term utilized in Mexico) who put into risk their own wealth.

ACKNOWLEDGEMENTS

The authors thank Alejandro Ponce Mendoza and Rocío Gutiérrez Ortíz for technical assistance. This work was supported by CAUP 2EA-0711.

REFERENCES

[1] M.Alexander; 'Introducción a la microbiología del suelo', AGT; México, **(1980)**.

[2] J.M.Becerril, O.Barrutia, P.J.I.García, A.Hernández, J.M.Olano, C.Garbisu; Ecosistemas, **16**, 50-55 **(2007)**.

[3] B.J.Nebel, R.T.Wright; 'Ciencias ambientales: Ecología y desarrollo sostenible', 6th Edition, Prentice Hall Hispanoamericana, S.A., México, **(1999)**.

[4] J.P.Navarro-Aviñó, A.I.Aguilar, J.R.López-Moya; Ecosistemas, **16**, 10-25 **(2007)**.

[5] [FUNDAR] Centro de Análisis e Investigación A.C.; Minería, comunidades y medio ambiente, Investigaciones sobre el impacto de la inversión canadiense en México, México, **(2002)**.

Current Research Paper

[6] A.M.Cruz; Operación de minera en Oaxaca acaba con manantiales de la zona, La jornada, 7 October, 12, **(2007)**.

[7] NMX-AA-132-SCFI-2006, Norma Mexicana de análisis; Muestreo de suelos para la identificación y la cuantificación de metales y metaloides, y manejo de la muestra, **(2007)**.

[8] M.M.S.Vásquez, G.I.Migueles, O.Franco-Hernández, B.Govaerts, L.Dendooven; Eurepean Journal of Soil Biology, **42**, 89-98 **(2006)**.

[9] [SAS] Statistical analysis system v.9; SAS Institute Inc. NC., USA, **(2002)**.

[10] B.M.I.Sánchez; Determinación de metales pesados en suelos de Mediana del Campo Valladolid. Ph.D. Thesis, Valladolid's University, Spain, **(2003)**.

[11] E.D.Enger, B.F.Smith; Ciencia Ambiental: un estudio de interrelaciones, 10th Edition, McGraw-Hill Interamericana, México, **(2006)**.

[12] I.García, C.Dorronsoro; Contaminación por metales pesados. Departament of Edafology and Chemistry, Granada's University, Spain, 12/01/2011, http://edafologia.ugr.es/conta/tema15/introd.htm#anchor1054486.

[13] R.G.Gerriste, W.Van Driel; Journal Environmental Quality, **13**, 197-204 **(1984)**.

[14] M.Zarei, S.Konig, S.Hempel, M.KhayamNekouei, Gh.Savaghebi, F.Buscot; Environmental Pollution, **153**, 1277-1283 **(2008)**.

[15] P.M.Groffman, W.H.Mcdowell, J.C.Myers, J.L.Merriam; Soil Biology and Biochemistry, **33**, 1339-1348 **(2001)**.

[16] F.Cabrera, J.Arizab, P.Madejóna, E.Madejóna, J.M.Murilloa; Science of the Total Environment, **390**, 311-322 **(2008)**.

[17] H.Wild; Kirkia, **9**, 243-264 **(1974)**.

[18] J.Emsley; Nature's building blocks an A-Z guide to the elements, University Press, OXFORD, New York, **(2003)**.

[19] [USEPA] US Environmental Protection Agency; Guide to site and soil description for hazardous waste site characterization, Metals, Washington, **1**, **(1992)**.

[20] L.Li-Teh, C.I.-Cheng, H.Teng-Yuan, Y.Yue-Hwa, M.Hwong-Wen; Environmental Science and Pollution Research, **14**, 49-59 **(2007)**.

[21] J.Hernández, J.Pastor; Environment Geochemistry Health, **30**, 127-133 **(2008)**.

[22] D.E.Kimbrough, Y.Cohen, A.M.Winer, L.Creelam, C.Mabuni; Crit.Rev.Environ.Sci.Technol., **29**, 1-46 **(1999)**.

[23] V.R.Sierra; Fitorremediación de un Suelo Contaminado con Plomo por Actividad Industrial, Tesis de Ingeniería, Buenavista Saltillo, Coahuila, México, **(2006)**.

[24] I.Razo, L.Carrizales, J.Castro, F.Díaz-Barriga, M.Monroy; Water, Air, and Soil Pollution, **152**, 129-152 **(2004)**.

[25] M.Gómez; De Calpulálpam a Wirikuta, La jornada, 24 April, 12 **(2012)**.