

Full Length Research Paper

Heavy metals In agricultural soils and Irrigation wastewater of Mixquiahuala, Hidalgo, Mexico

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Agricultural soils irrigated with wastewater pose a significant risk in the accumulation of heavy metals, a problem that affects agriculture and human health. An investigation was conducted on the concentration of heavy metals in agricultural soils and wastewater used for irrigation in plots of Mixquiahuala, Hidalgo. It analyzed the potential of hydrogen (pH), electrical conductivity (EC) and total extractable heavy metals in water and soil: As, Cd, Cr, Hg, Ni, Pb and Zn. Heavy metals were determined by using an Inductively Coupled Plasma (ICP) Perkin Elmer Optima 5300 (Inductively Coupled Plasma), using the methods recommended by the EPA (Environmental Protection Agency) and APHA (American Public Health Association). The study was conducted in November 2009. The sampling was conducted in two replications for both soils and wastewater. It compared the concentration of heavy metals with the criterion of Norma Oficial Mexicana-001-ECOL-1996. Based on these results, the concentration of extractable metals in agricultural soils of Mixquiahuala, Hidalgo, was presented in the following order: Pb > Ni > Cd > As > Cr > Hg. Water for agricultural irrigation did not present problems for use based on the concentration of As, Cd, Hg, Ni, Cr and Zn. However, lead concentration exceeded the maximum permissible limits in 40% of water samples analyzed. Considering the limits established in Spain, the concentrations of As, Ni and Cd exceeded permissible levels in 20, 60 and 60% respectively, of the samples analyzed.

Key words: Heavy metals, agricultural soil, maximum permissible limits.

INTRODUCTION

In the state of Hidalgo, Mexico, it is located the irrigation district 112 Ajacuba, where the main source of irrigation water is wastewater from Mexico City. This water has been used for irrigation for over 80 years (Vazquez et al., 2001; Prieto et al., 2007). According to some studies, this water has high concentration of detergents, fats, oils and trace metals that affect the soils (Siebe, 1994; Sanchez, 2006). The problem of high levels of heavy metals such as lead, nickel and cadmium in soils (Corinne et al., 2006), and in wastewater used for irrigation, mainly lies in the fact that they can be accumulated in these systems that are critical to agriculture. Heavy metals are dangerous because they are non-biodegradable, bio-

available and toxic for different crops (Mahler, 2003; Garcia and Dorransoro, 2005). Some of these heavy metals are mercury, arsenic and chromium (Lucho et al., 2005).

These elements are usually found as natural components of earth's crust, as minerals, salts and other compounds that can be absorbed by plants and incorporated into the food chain (Rooney et al., 2006; Zhao et al., 2006). They can pass into the atmosphere by volatilization and can be mobilized into surface water or groundwater. They cannot be easily degraded, destroyed naturally or organically since living beings do not have specific metabolic functions for them (Abollino et al., 2002).

An increasing trend in soil metal concentrations is reported in places where wastewater has been used for irrigation (Garcia et al., 2000; Hettiarachchi and Pierzynski,

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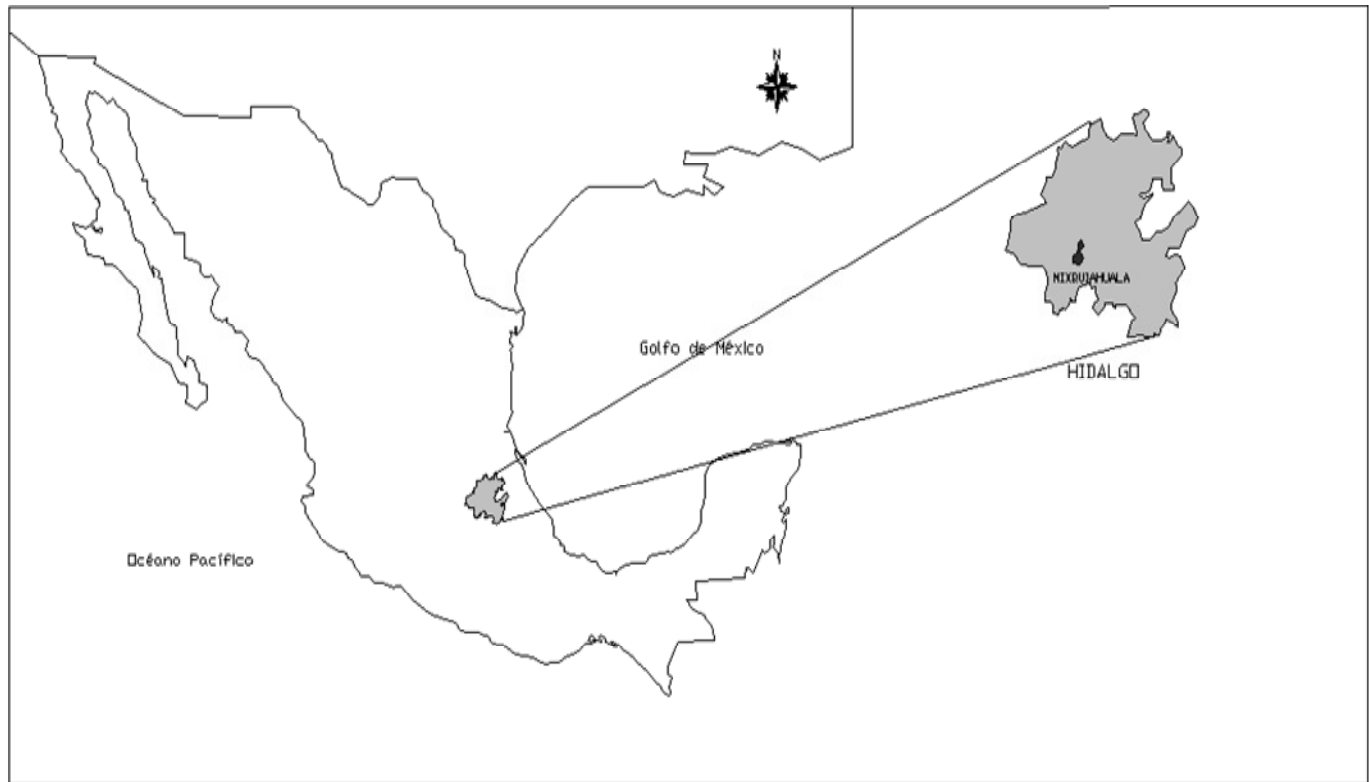


Figure 1. Location of the study area.

2002). There was ample research on the risk of heavy metals on health and the environment (Spain et al., 2003). Several authors have shown the risk of contamination by heavy metals in water (Yang et al., 1996; Ramos et al., 1999; Topalian et al., 1999; Santos et al., 2002; Taboada-Castro et al., 2002; Lee and Moon, 2003; Montes-Botella and Tenorio, 2003; Smolders et al., 2003; Lucho et al., 2005; Mapanda et al., 2005; Tahri et al., 2005; Prieto et al., 2007), in the accumulation of heavy metals in soils and sediments (Fytianos et al., 2001; Ho and Egashira, 2001; Moor et al., 2001; Ramos-Bello et al., 2001; Lin, 2002; Moral et al., 2002; Davor, 2003), and the potential risk to human health due to the accumulation of heavy metals in plants (Zhou et al., 2000; Fytianos et al., 2001; Long et al., 2003; Wang et al., 2003; Qi-Tang et al., 2004; Ismail et al., 2005; Mapanda et al., 2005; Prieto et al., 2009).

The objective of this study was to determine the concentration of heavy metals such as: As, Cd, Pb, Hg, Cr and Ni, in soil and wastewater used for irrigation in plots of the district 112-Ajacuba, Hidalgo. The concentration of these elements was compared to the maximum permissible limits established in the NOM-001-ECOL-1996.

METHODOLOGY

The study was conducted in the irrigation district 112-Ajacuba,

it is located Mixquiahuala, Hidalgo, Mexico (Figure 1). This region is placed in the southwestern part of the state, in a region called "Valle del Mezquital". It is located the following geographical coordinates: 20°11'51" N latitude, 90°11'51" W longitude, and an altitude of 1996 m.

Samples of soil and water were taken in different plots, irrigated for over 80 years with wastewater. Samples were taken in November 2009, after irrigation. Water samples were acidified with nitric acid, adding 2 ml/L, according to NOM-014-SSA1.1993. Heavy metals of soil samples were extracted using DTPA solution as described by Araujo do Nascimento et al. (2006).

Parameters analyzed in the samples were pH, EC (both in relation 1:2) with an EXCEL 20/pHmeter-mV-conductivity meter, heavy metals (As, Ni, Cr, Pb, Hg and Cd), using an ICP Perkin Elmer 5300 Optima model. Analyses were performed in the Environmental Sciences Laboratory located at Colegio de Postgraduados. In this study, As, Ni, Cr, Zn, Pb, Hg and Cd were considered for their toxicological relevance for plants, the differences of these metals in their behavior in soils and their availability for crops (Cd > Pb > Cr) (Scheffer and Schachtschabel, 1984). It is important to mention that sampling and analysis were performed according to procedures of APHA (1995) and EPA (1983).

The recovery values obtained in fortified samples for metal analysis were as follows: As 109.1, Al 99.7, Cr 99.46, Cu 99.25, Hg 106.15, Zn 98.21, Cd 100.35, Pb 96.93 and Ni 98.24%, which are within the recommended range and near to 100% (EPA, 1996), so there was no interference in the samples analyzed.

The concentrations of heavy metals in wastewater were compared to the maximum permissible limits of NOM-001-ECOL-1996 (Table 1). The maximum permissible limits, in terms of concentration of heavy metals in irrigation water, was set considering that the accumulation of these elements in the

Table 1. Maximum permissible limits for heavy metals, NOM-001-ECOL-1996.

Parameter	Rivers used in agricultural irrigation		Natural and artificial reservoirs used in agricultural irrigation	
	M.A.	D.A.	M.A.	D.A.
Arsenic	0.2	0.4	0.2	0.4
Cadmium	0.2	0.4	0.2	0.4
Copper	4.0	6.0	4.0	6.0
Chromium	1.0	1.5	1.0	1.5
Mercury	0.01	0.02	0.01	0.02
Nickel	2.0	4.0	2.0	4.0
Lead	0.5	1.0	0.5	1.0
Zinc	10.0	20.0	10.0	20.0

D.A. = Daily average; M.A. = monthly average.

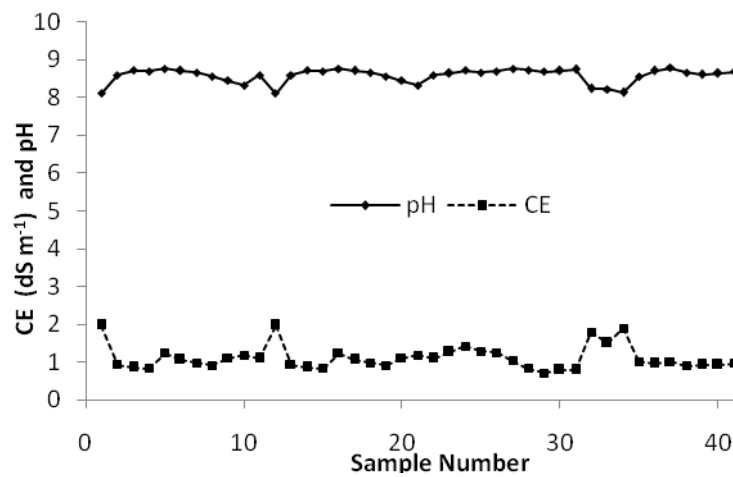


Figure 2. Electrical conductivity and pH measured in the saturation extract of soil samples.

arable layer does not pose a risk for human health

RESULTS AND DISCUSSION

Figure 2 shows the electrical conductivity and the potential of hydrogen measured in the soil extract. The soil pH is slightly alkaline, 99% of the samples showed values above eight, electrical conductivity in the soil showed values below 2 dS m⁻¹, indicating that there is no problem for the growth of crops in the plots, according to Jalali et al. (2008).

Figure 3 shows that the sampled soil presented levels of concentration of extractable heavy metals is in the following order: Pb > Ni > Cd > As > Cr > Hg; for this reason, the elements of greater availability for organisms living in the soils were: Pb, Ni and Cd. Results found in this study are similar to results showed in other studies developed in the region, these results found that Pb, Ni

and Cd tend to accumulate in agricultural soils irrigated with wastewater in the region of study. However, the concentrations found of these metals do not represent a risk according to the limits established by the Mexican official norm, NOM-021-SEMARNAT-200 (SEMARNAT, 1996).

In a study made by Chapela (2010) in the region of this study, soils irrigated with wastewater were analyzed to determine the concentrations of heavy metals. It was found that the concentration trend was Zn < Cu < Pb < Cd, while in this study the concentration trend found was Hg < Cr < Cd < As < Ni < Pb. This Show that the Pb concentrations were higher than the Cd concentrations in this study. Agricultural soils of this Mezquita Valley have been studied by several researchers; these soils have been irrigated with wastewater since more than one hundred years ago (Vazquez et al., 2005).

Heavy metal accumulation in agricultural soils can be a problem when using wastewater to irrigate the soil for

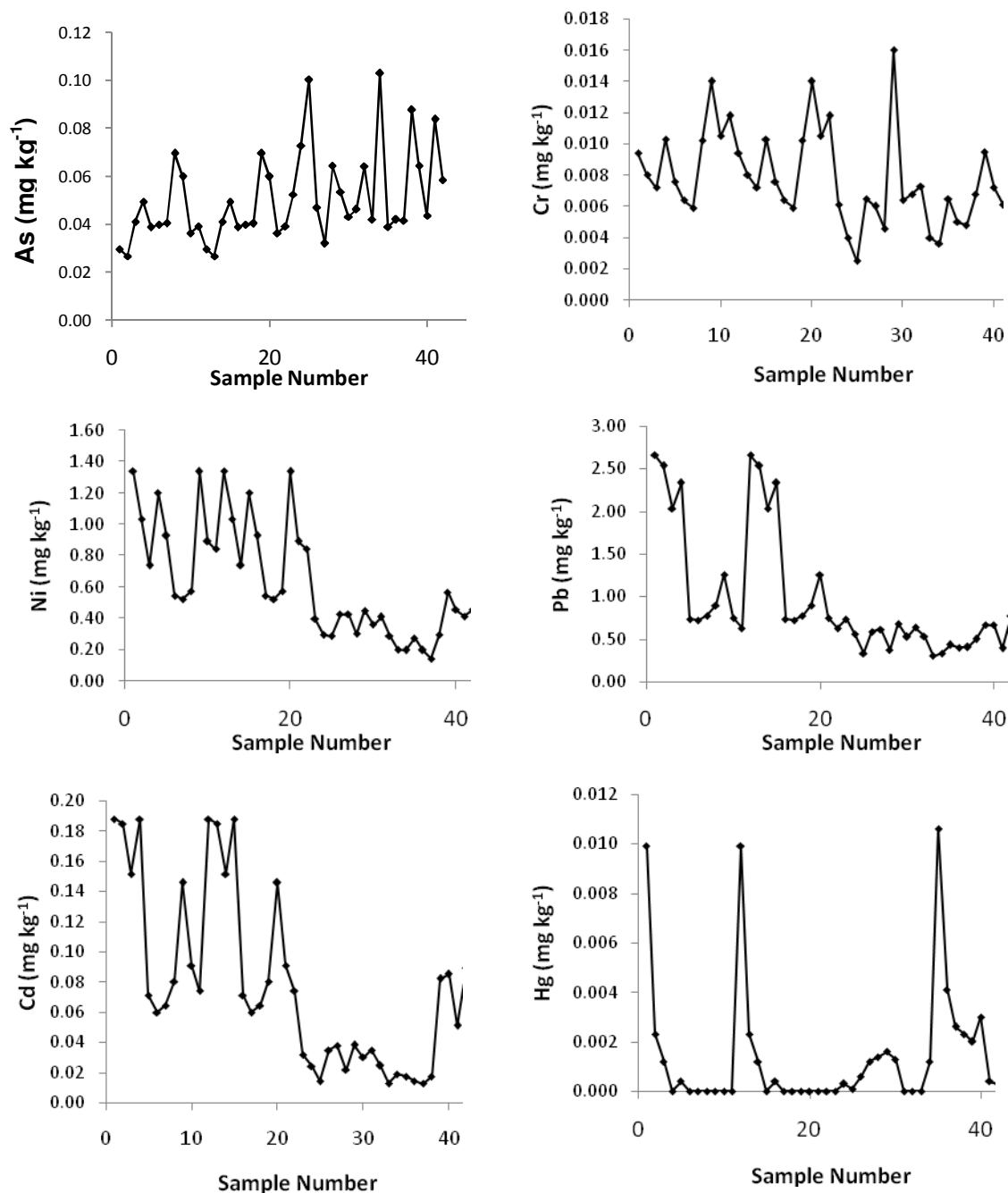


Figure 3. Concentration of heavy metals in agricultural soils.

more than a century. Cajuste et al. (2001) mentioned that in the Mezquital Valley the annual accumulation rate of heavy metals is between 384 and 640 g ha^{-1} . Figure 4 shows the electrical conductivity and the potential of hydrogen measured in wastewater used for irrigation in the plots of Mixquiahuala, Hidalgo. The pH presented values above eight, which means that water is slightly alkaline. The electrical conductivity presented values below 2 dS m^{-1} , which means that water is recommended for use in agricultural irrigation without restrictions,

considering the salinity factor according to Al-Nabulsi, (2001) and Perdomo (2005).

Figure 5 shows the concentration of heavy metals found in wastewater used for irrigation in Mixquiahuala, Hidalgo. According to NOM-001-ECOL-1996, the total concentration of heavy metals such as As, Cd, Ni, Cr, Zn, Hg and Mn present in wastewater analyzed, did not exceed the maximum permissible limits. However, the concentration of Pb exceeded the maximum permissible limit in 40% of the samples analyzed. In a similar way,

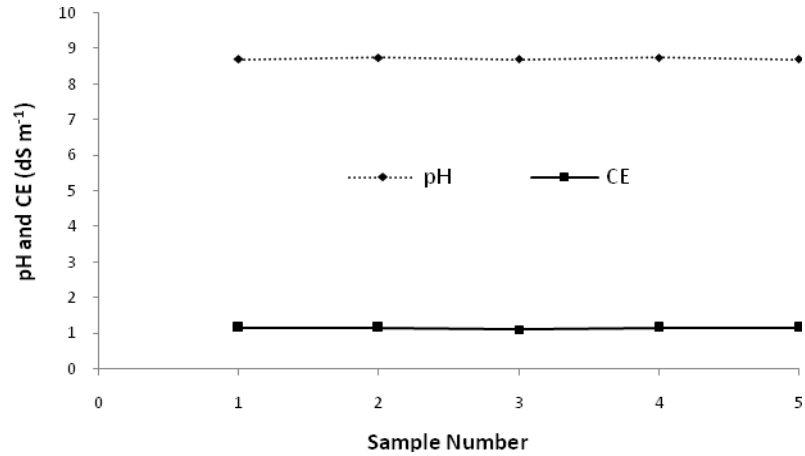


Figure 4. Electrical conductivity and pH measured in wastewater used for irrigation.

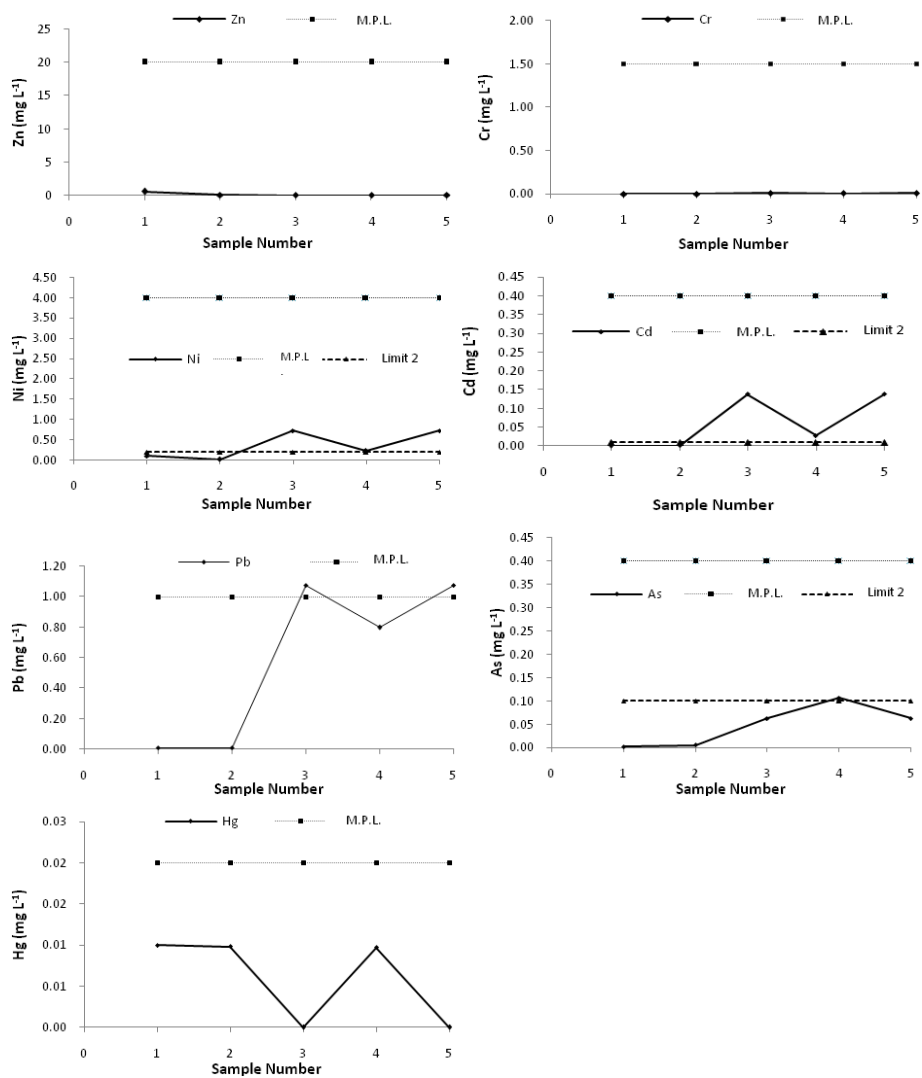


Figure 5. Concentrations and maximum permissible limits of heavy metals in water for irrigation. M.P.L. = Maximum permissible limit (NOM-001-ECOL-1996), limit 2 = maximum permissible concentration in Spain (Urbano, 2001).

Cajuste et al. (1991) and Carrillo et al. (1992) found concentrations of heavy metals such as Ni, Pb and Cr in irrigation water that exceeded the maximum permissible limits. Siebe (1994) concluded that a heavy metal accumulation process is occurring in the Mezquital Valley, where the present study was made. Siebe (1994) showed that heavy metal concentrations of soils irrigated with wastewater were 3 to 6 times higher than heavy metal concentrations of soils under rainfed agriculture.

Considering the limit 2, established by Urbano (2001), the concentration of As, Ni and Cd exceeded the permissible level in 20, 60 and 60%, respectively, of the samples analyzed. Accumulation of heavy metals in the soil, due to the use of wastewater for irrigation, did not represent a risk for the soil productive potential nor increased to pre-occupant levels the incorporation of metals into the food chain. However, the results of this investigation put in evidence that irrigation with wastewater should not be done during unlimited periods, since heavy metals (such as As, Ni, and Cd) tend to concentrate in the arable stratum of soils and can be absorbed by crops. Consequently, it is important to establish tolerance limits of heavy metal concentration according to the number of years that wastewater will be used for irrigation. To correlate tolerance limits with the number of years that the wastewater can be used, it is necessary to take into account the differences in filter and buffer capacity of agricultural soils, since these will be extinguished faster in sandy soils and slightly acid reaction, than in silty soils and neutral to alkaline reaction, according to Siebe (1994).

Conclusion

The concentration of extractable heavy metals in agricultural soils of Mixquiahuala, Hidalgo, presented levels in the following order: Pb > Ni > Cd > As > Cr > Hg. Heavy metals of greater bioavailability in the soils sampled were Pb, Ni and Cd. Wastewater used for irrigation did not show restrictions for its use considering the concentration of heavy metals such as: As, Cd, Ni, Hg, Cr and Zn. However, the Pb concentrations exceeded the maximum permissible limits in 40% of the water samples analyzed.

REFERENCES

- Abollino O, Aceto M, Malandrino M, Mentaste E, Sarzanini C, Barberis R (2002). Distribution and Mobility of Metals in Contaminated Sites. Chemometric Investigation of Pollutant Profiles. *Environ. Pollut.*, 119: 177-193.
- Al-Nabulsi YA (2001). Saline drainage water, irrigation frequency and crop species effects on some physical properties of soils. *J. Agron. Crop Sci.*, 186: 15-20.
- APHA (1995). Standard methods for examination of water and wastewater. APHA (American Public Health Association), WWA (American Water Works Association), WPCF (Water Pollution Control Federation), Washington D.C., USA.
- Araujo do Nascimento CA, De Oliveira MR, Chaves de Melo E (2006). Distribution and availability of zinc and copper in benchmark soils of Pernambuco State, Brazil. *Comm. Soil Sci. Plant Anal.*, 37(1): 109-125.
- Cajuste LJ, Carrillo-González ER, Cota-González R, Laird J (1991). The distribution of metals from wastewater in the Mexican valley of Mezquital. *Water, Air, Soil Pollut.*, 57(58): 763-771.
- Cajuste LJ, Vázquez A, Siebe G, Alcántar GG, y De la Isla de Bauer ML (2001). Cadmio, níquel y plomo en agua residual, suelo y cultivos en el Valle del Mezquital, Hidalgo, México. *Agrociencia*, 35(003): 267-274.
- Carrillo-Gonzalez R, Cajuste LJ y Hernández L (1992). Acumulación de metales pesados en un suelo regado con aguas residuales. *Terra*, 10: 166-173.
- Carrillo-González R, Cajuste LJ (1995). Behavior of trace metals in soils of Hidalgo, Mexico. *J. Environ. Sci. Health A*, 30: 143-155.
- Chapela-Lara M (2010). Variabilidad temporal en el contenido de metales pesados en suelos regados con aguas residuales en el Valle del Mezquital: México, D.F., Universidad Nacional Autónoma de México, Tesis de maestría.
- Corinne PR, Zhao FJ, McGrath SP (2006). Phytotoxicity of nickel in a range of European soils: Influence of soil properties, Ni solubility and speciation. *Environ. Pollut.*, 145: 596-605.
- Davor R (2003). Heavy metals distribution in agricultural topsoils in urban area. *Environ. Geol.*, 43: 795-805.
- EPA (1983). Methods for chemical analysis of water and wastes (Report No. EPA-600/4-79-020). EPA, p. 544.
- EPA (1996). Method 6010B. Inductively Coupled Plasma-Atomic Emission Spectrometry. U.S. Las Vegas, Nevada. Revision 2.
- Fytianos K, Katsianis G, Triantafyllou P, Zachariadis G (2001). Accumulation of Heavy Metals in Vegetables Grown in an Industrial Area in Relation to Soil. *Bull. Environ. Contam. Toxicol.*, 67: 423.
- García JC, Plaza C, Muñoz F, Polo A (2000). Evaluation of heavy metals pollution on barley crop by agricultural use of municipal solid waste compost. Centro de Ciencias Medioambientales (CSIC). Madrid (Spain). 3rd International Symposium on Geotechnics related to the European Environment. Berlin. Germany. On line in: <http://agrobioenmiendas.iespana.es>.
- García I, Dorransoro C (2005). Contaminación por Metales Pesados. En *Tecnología de Suelos*. Universidad de Granada. Departamento de Edafología y Química Agrícola. <http://edafologia.ugr.es>.
- Hettiarachchi GM, Pierzynski GM (2002). In situ stabilization of soil lead using phosphorus and manganese oxide: Influence of plant growth. *J. Environ. Qual.*, 31: 564-573.
- Ho TL, Egashira K (2001). Solid-solution ratio on extraction of heavy metals by dilute acids from agricultural soils and river-sediments in Hanoi, Vietnam. *Communications in Soil Science and Plant Analysis* 32:643-660.
- Ismail BS, Fariyah K, Khairiah J (2005). Bioaccumulation of Heavy Metals in Vegetables from Selected Agricultural Areas. *Bulletin of Environ. Contam. Toxicol.*, 74: 320-327.
- Jalali M, Merikhpour H, Kaledhonkar MJ, Van Der Zee SEATM (2008). Effects of wastewater irrigation on soil sodicity and nutrient leaching in calcareous soils. *Agric. Water Manage.*, 95: 143-153.
- Lee S, Moon HS (2003). Heavy Metals in the Bed and Suspended Sediments of Anyang River, Korea: Implications for Water Quality. *Environ. Geochem. Health*, 25: 433-452.
- Lin YP (2002). Multivariate geostatistical methods to identify and map spatial variations of soil heavy metals. *Environ. Geol.*, 42: 1-10.
- Long xx, Yang XE, Ni WZ, Ye ZQ, He ZL, Calvert DV, Stoffella JP (2003). Assessing Zinc Thresholds for Phytotoxicity and Potential Dietary Toxicity in Selected Vegetable Crops. *Commun. Soil Sci. Plant Anal.*, 34: 1421-1434.
- Lucho CA, Prieto F, Del Razo LM, Rodríguez R, Poggi H (2005). Chemical fractionation of boron and heavy metals in soils irrigated with wastewater in central Mexico. *Agric. Ecosyst. Environ.*, 108: 57-71.
- Mahler RL (2003). General overview of nutrition for field and container crops. In: Riley, L. E.; Dumroese, R. K.; Landis, T. D. Tech Coords. National Proceeding: Forest and Conservation Nursery Associations. 2003 June 9-12; Coeur d'Alene, ID; and 2003 July 14-17; Springfield, IL. Proc. RMRS-P-33.

- Mapanda F, Mangwayana EN, Nyamangara J, Giller KE (2005). The effect of long-term irrigation using wastewater on heavy metal contents of soils under vegetables in Harare, Zimbabwe. *Agric. Ecosyst. Environ.*, 107: 151-165.
- Montes-Botella C, Tenorio MD (2003). Water Characterization and Seasonal Heavy Metal Distribution in the Odiel River (Huelva, Spain) by Means of Principal Component Analysis. *Arch. Environ. Contam. Toxicol.*, 45: 436.
- Moor C, Lymberopoulou T, Dietrich VJ (2001). Determination of Heavy Metals in Soils, Sediments and Geological Materials by ICP-AES and ICP-MS. *Microchim. Acta*, 136: 123-128.
- Moral R, Gilkes RJ, Moreno-Caselles J (2002). A comparison of extractants for heavy metals in contaminated soils from Spain. *Commun. Soil Sci. Plant Anal.*, 33: 2781-2791.
- Perdomo C (2005). Calidad de las aguas y su relación con los sistemas agrícolas. *Ingeniería Agrícola*, 15: 87-95.
- Prieto G, Lucho CA, Poggi VH, Álvarez SM, Barrado EE (2007). Caracterización fisicoquímica y extracción secuencial de metales y elementos trazas en suelos de la región de Actopan-Ixmiquilpan del distrito de riego 03, Valle del Mezquital, Hidalgo, México. *Revista Ciencia ergo Sum*, 14(1): 69-80.
- Prieto MJ, González CA, Román GAD, Prieto GF (2009). Contaminación y fitotoxicidad en plantas por metales pesados provenientes de suelos y agua. *Universidad Autónoma de Yucatán, México. Trop. Subtrop. Agroecosyst.*, 10(1): 29-44.
- Qi-Tang WZX, Meng Q, Gerard E, Morel JL (2004). Characterization of cadmium desorption in soils and its relationship to plant uptake and cadmium leaching. *Plant and Soil*, 258: 217-226.
- Ramos-Bello R, Cajuste LJ, Flores-Roman D, Garcia-Calderon NE (2001). Heavy metals, salts and sodium in Chinampa soils in Mexico. *Agrociencia*, 35: 385-395.
- Ramos L, Fernández MA, González MJ, Hernández LM (1999). Heavy Metal Pollution in Water, Sediments, and Earthworms from the Ebro River, Spain. *Bull. Environ. Contam. Toxicol.*, 63: 305.
- Rooney CP, Zhao FJ, McGrath SP (2006). Soil factors controlling the expression of copper toxicity to plants in a wide range of European soils. *Environ. Toxicol. Chem.*, 25: 726-732.
- Sánchez GA (2006). Efecto del riego con aguas residuales sobre la calidad de la materia orgánica extractable con agua (MOEA) y las especies de metales pesados en el Valle del Mezquital. Tesis de licenciatura, departamento de Suelos, UACH, México.
- Santos A, Alonso E, Callejón M, Jiménez JC (2002). Distribution of Zn, Cd, Pb and Cu Metals, in Groundwater of the Guadamar River Basin. *Water, Air, Soil Pollut.*, 134: 273-283.
- Scheffer F, Schachtschabel P (1984). *Lehrbuch der Bodenkunde*. 1a Ed., Ferdinand Enke Verlag, Stuttgart, pp. 271-276.
- SEMARNAT (1996). Norma Oficial Mexicana NOM-001-ECOL-1996. Que establece los límites máximos permisibles de contaminantes en las descargas de aguas residuales en aguas y bienes nacionales. Secretaría de Medio Ambiente Recursos Naturales y Pesca. Diario Oficial de la Federación. México.
- Siebe C (1994). Acumulación y disponibilidad de metales pesados en suelos regados con aguas residuales en el distrito de riego 03, Tula Hidalgo, México. *Revista Internacional de Contaminación Ambiental*, 10(1): 15-21.
- Smolders AJ, Lock RA, Van Der Velde G, Medina RI, Roelofs JG (2003). Effects of Mining Activities on Heavy Metal Concentrations in Water, Sediment, and Macroinvertebrates in: Different Reaches of the Pilcomayo River, South America. *Arch. Environ. Contam. Toxicol.*, 44: 314.
- Spain A (2003). Implications of Microbial Heavy Metals Tolerance in the Environment. *Rev. Undergrad. Res.*, 2: 1-6.
- SSA (1993). Norma Oficial Mexicana. NOM-014-SSA1-1993 "Procedimientos sanitarios para el muestreo de agua para uso y consumo humano en sistemas de abastecimiento de agua públicos y privados".
- Taboada-Castro MM, Diéguez-Villar A, Taboada-Castro MT (2002). Effect of soil use and agricultural practices on heavy metal levels in surface waters. *Commun. Soil Sci. Plant Anal.*, 33: 2833.
- Tahri M, Benyaïch F, Bounakhla M (2005). Multivariate analysis of heavy metal contents in soils, sediments and water in the region of Meknes (central Morocco). *Environ. Monit. Assess.*, 102: 405-417.
- Topalián ML, Castañé PM, Rovedatti MG, Salibián A (1999). Principal Component Analysis of Dissolved Heavy Metals in Water of the Reconquista River (Buenos Aires, Argentina). *Bull. Environ. Contam. Toxicol.*, 63: 484.
- Urbano TP (2001). *Tratado de fitotecnia General*. Mundi-prensa, España, p. 895.
- Vázquez AA, Cajuste JL, Siebe GC, Alcántar GG, Bauer de la I ML (2001). Cadmio, Níquel y Plomo en agua residual, suelo y cultivos en el Valle del Mezquital, Hidalgo, México. *Agrociencia*, 35: 267-274.
- Vázquez AA, Cajuste LJ, Carrillo R, Zamudio GB, Álvarez SE, Castellanos RJZ (2005). Límites permisibles de acumulación de Cadmio, Níquel y Plomo en suelos del Valle del Mezquital, Hidalgo. *Terra Latinoamericana*, 23: 447-445.
- Wang QR, Cui YS, Liu XM, Dong YT, Christie P (2003). Soil Contamination and plant Uptake of Heavy Metals Polluted sites in China. *J. Environ. Geochem. Health*, 38: 823-838.
- Yang W, Yang L, Zheng J (1996). Effect of metal pollution on the water quality in Taihu Lake. *GeoJ. (Historical Archive)*, 40: 197-200.
- Zhao FJ, Rooney CP, Zhang H, McGrath SP (2006). Comparison of soil solution speciation and diffusive gradients in thin-films measurement as an indicator of copper bioavailability to plants. *Environ. Toxicol. Chem.*, 25: 733-742.
- Zhou ZY, Fan YP, Wang MJ (2000). Heavy metal contamination in vegetables and their control in china. *Arch. Environ. Contam. Toxicol.*, 16(2): 239.