Environ Earth Sci
DOI 10.1007/s12665-013-2456-2

ORIGINAL ARTICLE

Geochemical processes controlling the groundwater transport of contaminants released by a dump in an arid region of México

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Received: 28 August 2012 / Accepted: 25 March 2013
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Abstract The Vado Carranza dump, located in the Mexicali Valley, Baja California, northwest Mexico, was operated for more than 15 years receiving about 30 tons/day of solid wastes. The disposed wastes were periodically burned in open air. The presence of a shallow aquifer in the area makes the groundwater vulnerable to contamination processes. The purpose of this study was the evaluation of heavy metals content (Cu, Cd, Ni, Pb and Zn) in soil and groundwater in the vicinity of this dump. The results indicate high content of metals in soil, mainly at a superficial level, with the highest concentrations in the areas where burning of wastes occurred. Elevated concentrations of cadmium and copper were detected in groundwater with the highest concentrations occurring in monitoring wells located in the north side of the dump, downward of groundwater flow. Although the high content of metals in soil can be attributed to the burning of waste, other sources of pollution could be the agricultural irrigation in the vicinity of the dump. The program PHREEQC was used to model the geochemical evolution of groundwater. Results suggest that evaporation of the contaminated waters circulating below the landfill is one of the key processes that explain the increased concentration of contaminants in groundwater and its seasonal variations. As groundwater flows away from the dump, evaporation can concentrate the chemicals making the water more toxic. These results are important because they illustrate processes that are likely to occur in landfills located in other desert areas of the world.

Keywords Dump site · Groundwater evaporation · Semiarid zones · Heavy metals · PHREEQC · Mexicali

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Introduction

In most developing countries, solid wastes are being dumped on land surface without adopting any acceptable sanitary landfilling practices (Vasanthi et al. 2008). After the 1940s, Mexico has experienced a substantial increase in its generation of urban solid wastes (USW). In addition, a change in waste characteristics occurred mainly due to industrial development and a remarkable population explosion. These changes, combined with the common disposal practices, led to the unrestricted emergence of large open dumps that lack the structure needed to protect the environment. Currently, about 30 % of solid wastes generated nationwide are deposited in controlled and uncontrolled open dumps (INEGI 2005). In these sites, the burning of wastes is a common form of treatment, which increases their potential to contaminate the environment and affect human's health.

Areas located near landfills are largely exposed to groundwater contamination given the potential source of pollution that generation of leachate represents. The nature

Published online: 13 April 2013

of this contamination depends on the composition of the leachate, which, in turn, depends on the nature of the disposed wastes, on the chemical and biochemical processes responsible for decomposition and on the available volume of water (Mor et al. 2006). The risk of contamination increases when the USW disposal sites are built without the proper safety elements, such as protective barriers against leachate infiltration, and when they are located in areas of shallow water table.

In arid and semiarid regions, leachate generation has often been underestimated mainly due to the scarcity of precipitation, which is frequently considered negligible and may result in insignificant infiltration (Al-Yaqout and Hamoda 2003). However, advances in irrigation and other

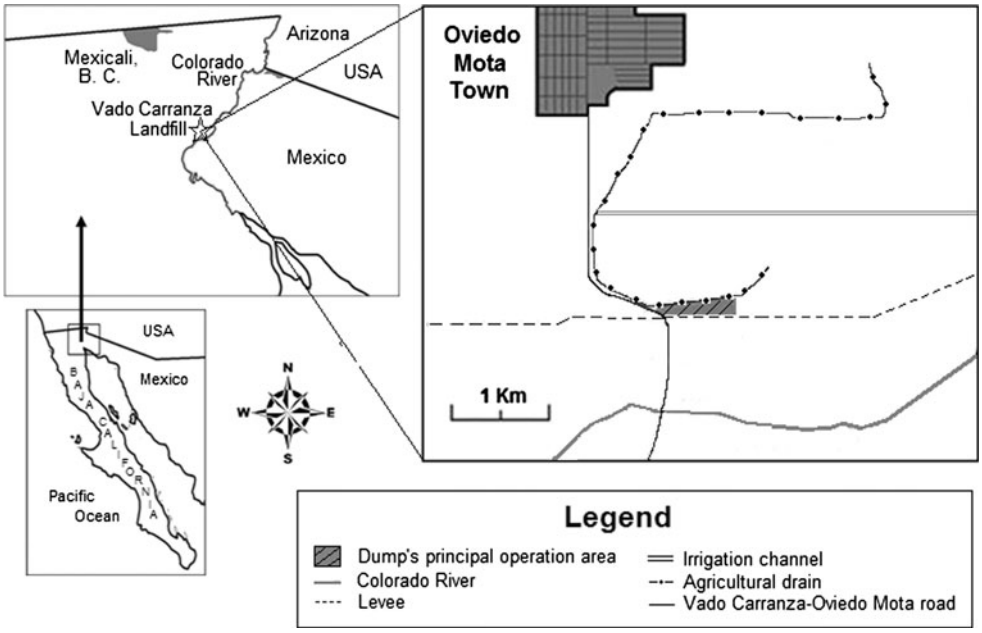

Fig. 1 Location of Vado Carranza dump in Mexicali Valley close to Colorado River

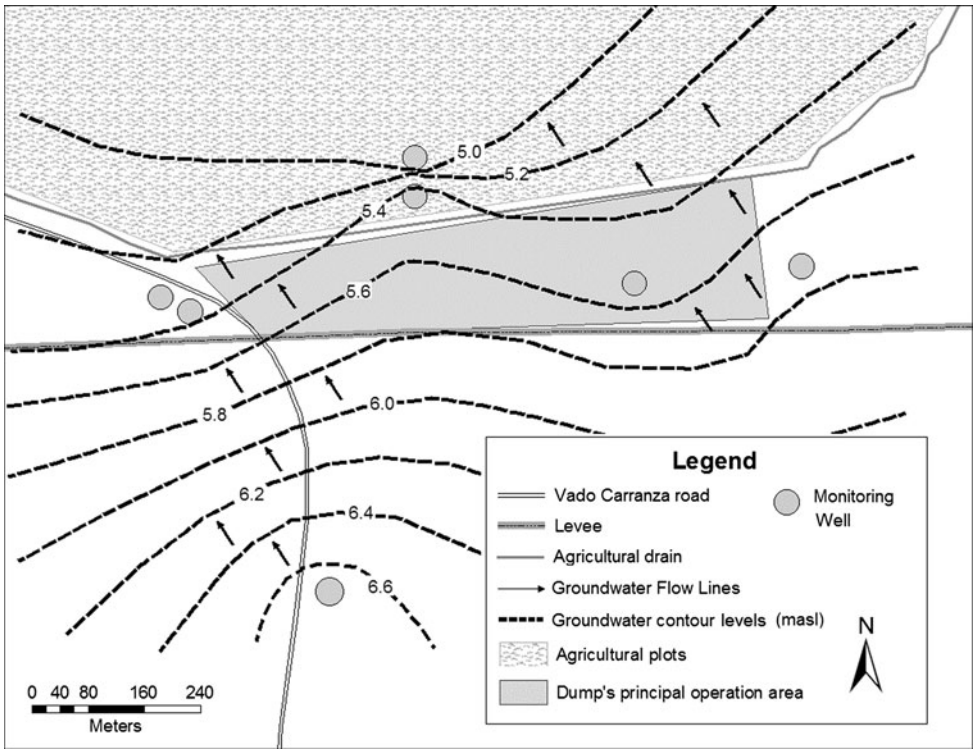

Fig. 2 Groundwater direction flow in the study area, modified from Valdez-Carrillo (2010)

systems of water distribution may alter the water cycle of those zones, adding water artificially or activating previously exhausted sources and therefore, increasing the potential infiltration. Isolation systems used in conventional landfills to minimize infiltration include high density plastic membranes and low-permeability, well-compacted clay barriers. However, such clay layers are vulnerable in climates where arid or semiarid conditions prevail, whereby the clay cover tends to desiccate and crack, resulting in drastically higher infiltration (Sadek et al. 2007). In addition, the high evaporation rates common to regions with arid or semiarid climate can affect shallow aquifers causing a substantial increase in the content of major and minor dissolved constituents and consequently, in salinity (Nicolli et al. 2010).

Since the 1960s, hydrochemistry modeling has been used to analyze the natural and anthropogenic environmental impacts on aquatic systems (Merkel and Planer-Friedrich 2008). Hydrochemical models provide useful information about the geochemical processes that affect the solutes content of groundwater and their spatial and temporal distribution. Therefore, groundwater modeling is an integral part of water resources assessment, protection and restoration studies, regulations, and engineering designs (Kumar 2012).

There have been many investigations to study the effect of landfill leachate on groundwater quality from physical and chemical data (e.g., Israde et al. 2005; Vasanthi et al. 2008; Kale et al. 2010). Other studies have focused on the biogeochemical processes in natural attenuation of contaminants in groundwater and landfill leachate (e.g., van Breukelen and Griffioen 2004). There is also research related to the modeling of reactive transport of solutes in leachate and groundwater (e.g., Brun et al. 2002). However, to the best of the knowledge of the authors, the assessment of the environmental impact of open dumps on nearby aquifers in arid and semiarid areas has not yet been published. Hence, modeling the chemical evolution of groundwater to understand the main geochemical processes involved in the transport and fate of contaminants, such as the effect of water evaporative process, is still needed. The assumption of little or no precipitation percolation through the solid waste layers (buried or surficial) changes when the landfill is located in an area with a shallow water table. Such is the importance of collecting data that reveal the environmental impact of sites under these conditions.

The aim of this research was to evaluate the quality of groundwater and soil in an open dumpsite of USW by means of their content of major ions and heavy metals (Cu, Cd, Ni, Pb, and Zn), and to model the chemical evolution of groundwater. The results of this characterization provide information on the main geochemical processes involved in the transport and fate of solutes in areas with low rainfall, high evapotranspiration, and shallow aquifers.

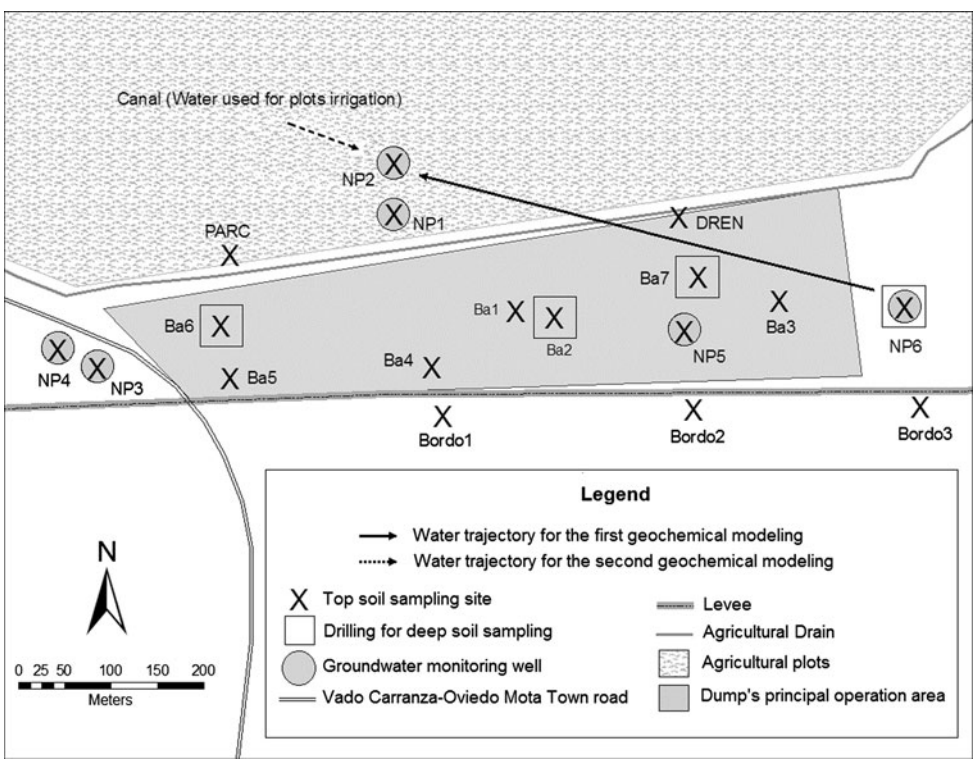

Fig. 3 Distribution of groundwater and soil sampling sites

Study area

The municipality of Mexicali is located in the state of Baja California, in northwestern Mexico. It has a population of 936,826 inhabitants. Of this number, more of 653,000 live in Mexicali city while the rest are distributed in about 1,740 registered villages along the Mexicali Valley. This population's distribution has led to a spreading in the generation of USW thereby, increasing both the number of clandestine dumps and official dumps. The study area consists of an open dump located in the Mexicali Valley, about one kilometer from the Colorado River, within the riparian corridor. The central geographical coordinates are 32°12′12.9″ North and 115°09′19.3″ W (Fig. 1). Its elevation varies between 8.0 and 9.4 m above sea level (m.a.s.l.) and the operational area covers approximately 13 hectares (ha). For more than 15 years, this site received about 30 tons/day of USW, most of them constituted by plastics, organic, and ferrous metal wastes. Separation and recycling of ferrous and aluminum wastes have been of commercial interest while the rest of the waste fractions have been burned in the open air. The site is bordered to the north by several plots of flood irrigation and the nearest human settlement is the Oviedo Mota town, located at 2.7 km from it. The water table is located at an average depth of 3 m from the surface and the local direction of groundwater flow is oriented southeast–northwest (Valdez-Carrillo 2010; Fig. 2). Groundwater has a high content of dissolved solids ranging between 1,000 and 2,200 mg/L. In contrast, surface water used for agricultural irrigation contains an average of 760 mg/L dissolved solids.

The annual rainfall average is 54 mm, January being the wettest month with an average of 9.3 mm and May the driest with an average of 0.15 mm. The annual average temperature is 22.5 °C with July as the hottest month with an average of 32.7 °C and January as the coldest with an average of 13 °C (INEGI 2001). Maximum temperature in summer is above 40 °C and the annual evaporation rate is 325 mm. Despite the arid climate, there is an available volume of 1,850 Hm^3/year of water from the Colorado River that supplies water to irrigate more than 200,000 ha of agricultural land in the Mexicali Valley.

Irrigation water contributes to keep the water table in a shallow level. The Colorado River flow is well controlled all along its path by several dams to be use in agriculture, industry, and urban areas. Along the Mexicali Valley, this river maintains its flow by gaining water from irrigation returns and from treated wastewater discharges (Ramírez-Hernández et al. 2006). The predominant soil type in the study area is the xerosol. This type of soil has three subunits: haplic, luvic, and calcic. The haplic xerosols have moderate cation exchange capacity, pH between 6.6 and 8, light brown to pale brown color, and medium to coarse texture; meanwhile the xerosols luvic contain a horizon of clay layers that favors the retention of moisture. Calcium xerosols tend to accumulate calcium carbonate in the subsoil (INEGI 2001).

Methodology

Water sampling

A piezometric network consisting of six monitoring wells was installed for groundwater sampling (Fig. 3). Piezometers were constructed with PVC tube of 2 in diameter and 20 ft long. Groundwater samples were taken from each piezometer and surface water was collected from a channel that is used in agricultural irrigation, located around 1 km north of the dump site. There were six sampling campaigns from April 2008 to February 2009. Samples were collected using a manually operated vacuum system as described by Fetter (1993). Piezometers were purged before sampling. Once the groundwater level recovered, samples for anions and metals were taken in two polyethylene bottles of 500 mL.

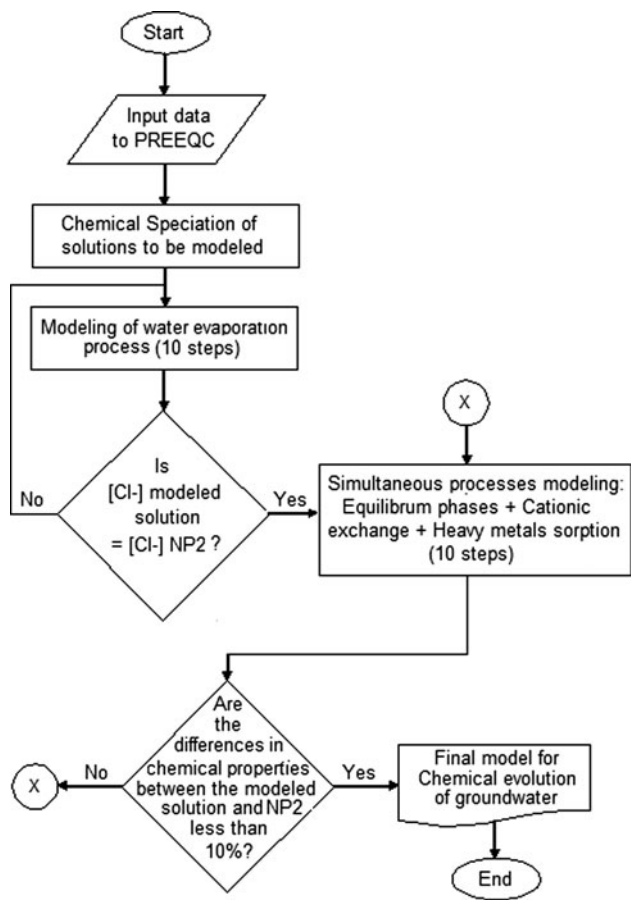

Fig. 4 Flux diagram for the Vado's Carranza dump groundwater geochemical modeling using the program PHREEQC

Table 1 Heavy metals in groundwater from the Vado Carranza dump

Metal	Date	Ground water						Surface water
		NP1	NP2	NP3	NP4	NP5	NP6	Canal
Cu	Apr 08	0.35	0.48	0.55	0.50	0.60	0.52	0.35
	Jun 08	0.32	0.30	0.26	0.24	0.22	0.11	0.11
	Aug 08	0.27	0.26	0.19	0.25	0.17	0.13	0.09
	Oct 08	0.25	0.31	0.23	0.23	0.16	0.11	0.09
	Dec 08	0.28	0.32	0.27	0.30	0.19	0.15	0.10
	Feb 09	0.31	0.35	0.22	0.21	0.21	0.14	0.13
AVG ± SD		0.30 ± 0.04	0.34 ± 0.08	0.29 ± 0.13	0.29 ± 0.11	0.26 ± 0.17	0.19 ± 0.16	0.15 ± 0.10
Cd	Apr 08	0.052	0.061	0.045	0.037	0.030	0.028	BDL
	Jun 08	BDL	BDL	0.02	BDL	BDL	BDL	BDL
	Aug 08	0.021	0.051	0.035	BDL	0.037	0.037	0.023
	Oct 08	0.038	0.042	0.042	0.036	0.041	0.036	0.031
	Dec 08	0.033	0.032	BDL	BDL	BDL	0.021	0.025
	Feb 09	BDL	0.035	BDL	BDL	0.023	BDL	BDL
AVG ± SD		0.036 ± 0.013	0.044 ± 0.012	0.036 ± 0.011	0.037 ± 0.001	0.033 ± 0.008	0.031 ± 0.008	0.026 ± 0.004
Ni	Apr 08	0.048	BDL	0.026	0.020	0.030	BDL	BDL
	Jun 08	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Aug 08	0.023	0.024	BDL	BDL	0.023	BDL	0.025
	Oct 08	0.021	0.025	BDL	BDL	0.034	0.026	0.025
	Dec 08	BDL	0.022	BDL	BDL	BDL	BDL	BDL
	Feb 09	0.026	0.029	BDL	BDL	BDL	BDL	BDL
AVG ± SD		0.030 ± 0.013	0.025 ± 0.003	–	–	0.029 ± 0.006	–	0.025 ± 0.000
Pb	Apr 08	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Jun 08	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Aug 08	0.033	0.072	BDL	BDL	BDL	BDL	BDL
	Oct 08	BDL	0.050	BDL	0.049	BDL	BDL	BDL
	Dec 08	BDL	0.045	BDL	BDL	BDL	BDL	BDL
	Feb 09	0.034	0.038	BDL	BDL	BDL	BDL	BDL
AVG ± SD		0.034 ± 0.001	0.051 ± 0.015	–	–	–	–	–
Zn	Apr 08	0.031	0.033	0.053	0.042	0.038	0.038	0.056
	Jun 08	0.043	0.059	0.030	0.047	0.051	BDL	BDL
	Aug 08	0.056	0.054	0.058	0.064	0.050	0.040	0.050
	Oct 08	0.061	0.061	0.059	0.059	0.055	0.051	0.053
	Dec 08	0.060	0.047	0.043	0.040	0.046	0.048	0.044
	Feb 09	0.061	0.051	0.051	0.042	0.047	0.043	0.042
AVG ± SD		0.052 ± 0.012	0.051 ± 0.010	0.049 ± 0.011	0.049 ± 0.010	0.048 ± 0.006	0.044 ± 0.005	0.049 ± 0.006

Detection limits: Cu 0.06; Cd 0.02; Ni 0.02; Pb 0.03; Zn 0.03

AVG Average, *SD* standard deviation, *BDL* below detected limit

Soil sampling

Two types of soil samples were collected in January 2009 (Fig. 3), superficial and deep samples were taken according to the recommendations of the Mexican Standard NMX-AA-132-SCFI-2006 (DOF 2006). Eighteen samples of topsoil were collected in the following way: six of these samples were taken next to each monitoring wells (identified as NP1 to NP6); three at the southern boundary of the site, which is defined by a small hill (samples labeled bordo 1 to bordo 3); seven samples are from areas where the solid wastes are disposed and burned (Ba1 to Ba7); one soil sample corresponds to an agricultural plot which is located north of the dumpsite (PARC); one more corresponds to the side of a drain (drain) also located to the north. The vertical sampling consisted of the implementation of four boreholes where soil sampled were collected every 30 cm up to a depth of 1.5 m in each hole.

Chemical analysis

Water samples were acid digested, according to article 10.3 of the Mexican Standard NMX-AA-051-SCFI-2001 (SE 2001). Treatment of the soil samples consisted of a plate acid digestion (USEPA 1996). Water and soil samples were analyzed using atomic absorption spectrometry.

Monthly potential evapotranspiration (MPE)

In order to estimate the effect on groundwater by the evapotranspiration, we used the Thornthwaite Method (Thornthwaite and Mather 1957) to calculate the monthly potential evapotranspiration in the study area. This method incorporates the average monthly temperature and the latitude of the study area. The Thornthwaite equation is $MPE = 16\ NM\ [10TM/I]^a$ where MPE is the monthly potential evapotranspiration (in millimeters), NM is a monthly adjustment factor related to the daylight hours, $I = \Sigma\ [TM/5]\ 1.5$ where TM is the average monthly temperature in Celsius degrees, and $a = 6.7 \times 10^{-7}\ I^3 - 7.7 \times 10^{-5}\ I^2 + 1.8 \times 10^{-2}\ I + 0.49$.

Geochemical modeling

The program PHREEQC (Parkhurst and Appelo 2000) was used to simulate the geochemical evolution of groundwater in the study area. For this purpose, major ions, physicochemical parameters and direction of groundwater flow were taken from Valdez-Carrillo (2010). Two models were tested for the six sampling periods.

The basis for the first model was the direction of groundwater flow (southeast–northwest). Therefore, the starting point was water composition from NP6, which evolves geochemically to produce water with the characteristics observed in NP2 monitoring well (Fig. 3). This well showed the highest amount of dissolved solids for all sampling campaigns with an average of total dissolved solids (TDS) of 2,200 mg/L. Simulation for the second model was carried out considering the potential infiltration of channel water used to irrigate plots located north of the dump. Piezometer NP2 is located beside one of these plots. This model tested the geochemical evolution of water from the irrigation channel (Canal) to a type of water with the composition observed in NP2 (Fig. 3). The first step for both models was to perform chemical speciation of the initial solution (NP6 or Canal). At this stage, concentrations for each of the elements of interest and saturation indexes for the different mineral phases were obtained. In a second stage, waters from NP6 and Canal were evaporated up to the point of matching Cl^- concentration in NP2. The total number of steps used for evaporation was 10. This approach was based on the conservative behavior of Cl^- (Appelo and Postma 2005). In a final modeling stage, three simultaneous processes were tested to match the rest of the chemical species: phase equilibria, cation exchange, and adsorption of metals. Chemical speciation and mineral assemblage from NP2, NP6, and Canal serve as the basis for phase equilibrium. Chemical equilibrium with CO_2 (g) and O_2 (g) was also considered. An average value for logarithmic partial pressures of carbon dioxide ($\log P_{CO_2} = -1.6$) and a fixed one for oxygen ($\log P_{O_2} = -1.21$) were used considering Henry's Law and the average oxygen concentration in NP2 (2.4 mg/L). Agricultural lands show the highest P_{CO_2} values where respiration is at a maximum and it generally tends to increase with depth.

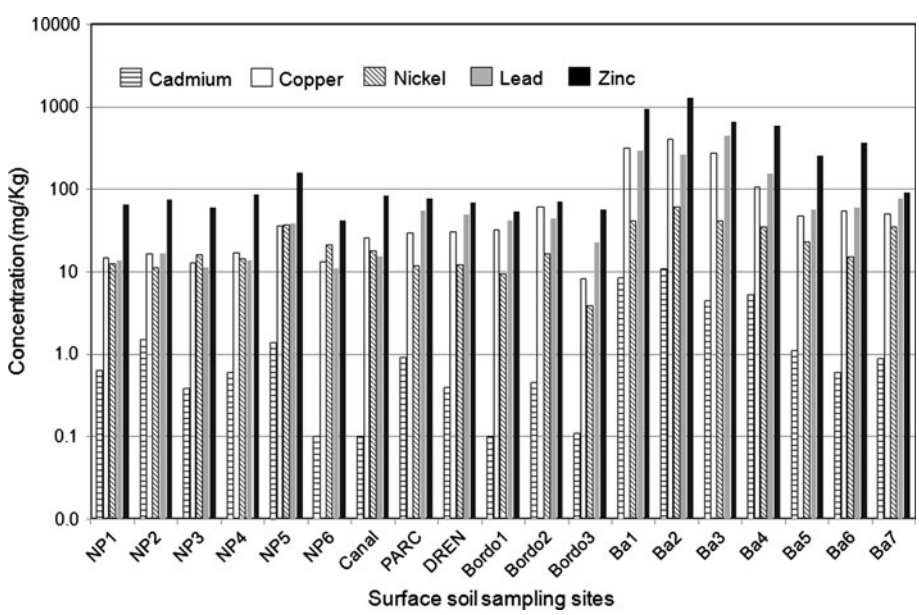

Fig. 5 Heavy metals in surface soil samples

This type of land can achieve CO_2 concentrations above 6 %vol (Appelo and Postma 2005). P_{CO_2} values used in the simulations are within the range for this kind of soils. The adsorption process of heavy metals was simulated using iron hydroxides because it is the type of adsorbent used by the program PHREEQC and one of the most common adsorbent materials. An iterative process was followed to ensure that the concentrations of chemical species in the final solution were close to the composition of NP2, within an error lower than 10 % when possible (Fig. 4).

Results and discussion

Heavy metals in water

Table 1 shows the results for the content of heavy metals in water. In general, the content of copper and cadmium are higher than those reported in groundwater by other authors (Aiuppa et al. 2005; Kale et al. 2010). Copper presented a mean water content of 0.26 ± 0.11 mg/L, during the first sampling campaign (April 2008) when the highest concentration for this metal was found, reaching up to 0.6 mg/L. This time of the year corresponds to the irrigation season of cultivation plots adjacent to the dumpsite. This suggests that the copper content in local groundwater may be influenced by both actions related to solid waste disposal and agricultural activities. No research has been conducted at the site to confirm this assumption; however, given that copper-based fertilizers and pesticides are widely used in agriculture (Oliveira-Filho et al. 2004), it is reasonable to anticipate addition of Cu from agrochemicals into the groundwater system. Kale et al. (2010) reported copper concentrations reach up to 0.88 mg/L in groundwater in the area of a solid waste landfill in the city of Pune, India. The average cadmium had content in water of 0.035 ± 0.008 mg/L. Israde et al. (2005) reported amounts of cadmium in groundwater reaching up to 0.23 mg/L in a dump's area in Morelia, Mexico. For metals nickel, lead, and zinc results are generally in the range of concentrations reported in other studies (Aiuppa et al. 2005; Kale et al. 2010). Nickel showed an average content of 0.026 ± 0.005 mg/L. In the case of lead, in general the metal is found below the detection limit with the exception of some samples from wells NP1 and NP2. The NP2 monitoring well presents a lead concentration reaching 0.072 mg/L, above the average value of 0.05 mg/L reported in the studies previously cited. Finally, zinc had a mean value of 0.049 ± 0.010 mg/L, and was the metal with more stable concentration value throughout the sampling period.

Heavy metals in surface soil

Surface soil samples Ba1, Ba2, and Ba3, which exhibit the highest concentrations of heavy metals, correspond to

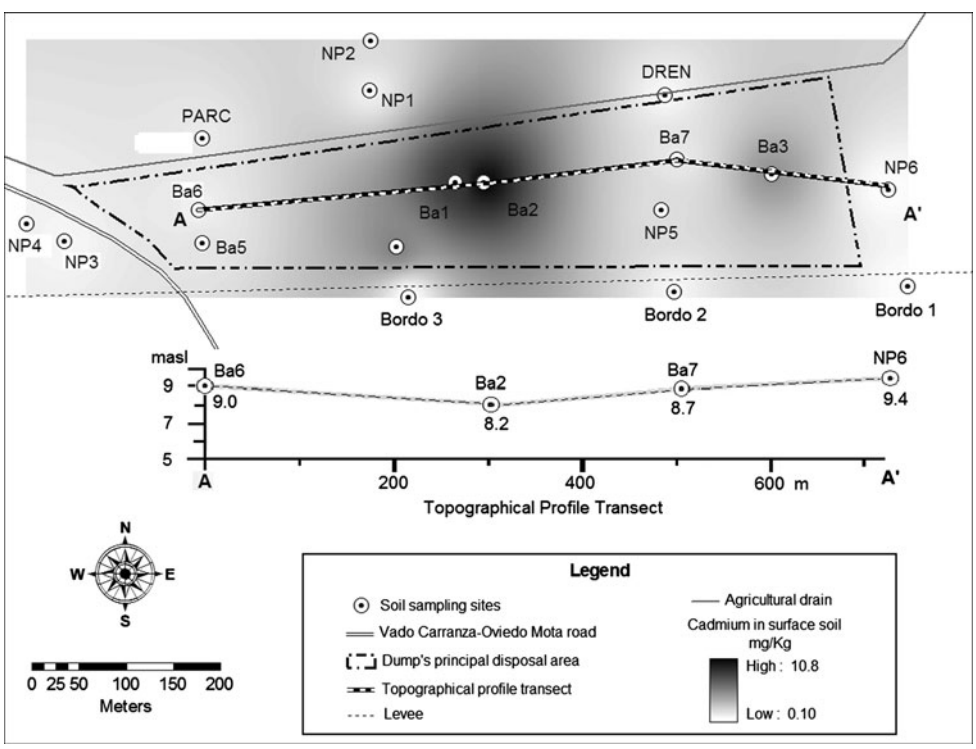

Fig. 6 Cadmium in surface soil and soil topographical profile in the study area

areas where USW burning occurs (Fig. 5). In general, samples Ba1 to Ba7 showed heavy metal contents that are higher than the values reported in other studies for uncultivated soils (Siegel 2002). The results obtained for samples from open burning of waste areas are comparable with others studies about urban solid wastes incineration processes (Morf et al. 2000). The contents of heavy metals had the following mean values and standard deviation of concentration in mg/kg dry weight: Cu (182 ± 154), Cd (4.6 ± 4.1), Ni (36.3 ± 15.2), Pb (197 ± 150), and Zn (608 ± 425). Note the high content of cadmium. Cadmium is a toxic contaminant to plants and animals (Kookana et al. 1999). The mean concentration of this metal in agricultural soil is generally less than 0.4 mg/kg (Alloway 1990), with a maximum up to 3 mg/kg. Highly contaminated soil contains Cd concentrations up to 10 mg/kg or even more (Kookana et al. 1999). Cd anthropogenic sources include atmospheric fallout from metallurgical industries, application of sewage sludge containing cadmium or other waste on land, and use of phosphates fertilizers in agricultural areas. These activities can lead to unacceptably high concentrations of Cd in soils and associated water resources (Kookana et al. 1999). Figure 6 shows the spatial distribution of cadmium concentrations in the soils of the site and a topographic profile of the dump in the east–west direction from BA6 to NP6. This profile reveals that the more abnormal areas correspond to sites of lower elevation. The content in soil at surface level for the rest of the metals tested followed a pattern similar to that observed for cadmium. At higher elevations the concentration of metals decreased significantly. This behavior suggests that the topography of the dump area plays a role in the distribution of pollutants. When it rains, overland flow could make the contaminated soil particles to move and deposit in the lower elevation area of the site.

Heavy metals in subsoil

Table 2 shows the concentrations of heavy metals in the soil vertical profiles of the four boreholes. In the soil samples with higher metal content the presence of ash and other debris from burning waste was evident. The highest concentrations of metals correspond to the surface samples that are related with the main area of discharge and burning of wastes. In this profile relatively high values at a depth of 30 cm were also found. The metal cadmium, in general, was found in a concentration that exceeds the natural range of uncultivated soil, especially in Ba2. Lithological description shows that the greater retention of metals corresponds to clay bed which agrees with the fact that these materials are the best absorbers of metals and other types of contaminants (Wan Zuhairi 2003).

Table 2 Heavy metals in soil samples from the four boreholes drilled in the Vado Carranza landfill (concentrations in mg/kg dry weight)

Drilling	Depth (cm)	Metal				
		Cu	Cd	Ni	Pb	Zn
Ba6	0–10	54.1	0.6	15.2	60.3	364
	30	14.1	1.4	9.2	13.6	41.5
	60	12.7	1.7	6.9	13.3	33.6
	90	16.6	3.1	7.8	27.9	88.3
	120	30.6	2.9	18.7	15.6	79.7
	150	34.4	3.3	21.3	12.9	85.4
Ba2	0–10	410	10.7	61.7	262	1290
	30	183	6.8	39.8	97.0	646
	60	36.0	4.8	40.3	9.9	74.6
	90	30.0	4.1	37.7	5.7	69.4
	120	41.9	4.3	43.3	9.6	80.8
	150	29.5	5.1	31.1	12.5	72.3
Ba7	0–10	50.1	0.9	34.9	77.3	92.0
	30	32.9	4.2	15.4	21.6	134
	60	10.9	2.2	4.2	10.6	33.1
	90	25.0	3.6	17.4	13.9	65.4
	120	21.1	3.0	8.5	5.5	55.3
	150	22.9	4.1	15.6	8.5	53.6
NP6	0–10	13.0	0.1	21.4	11.0	42.1
	30	14.7	3.6	25.5	17.6	47.8
	60	27.1	1.8	26.3	32.6	80.7
	90	42.8	2.2	26.9	38.3	58.9
	120	30.9	2.3	26.6	44.2	70.0
	150	27.2	2.2	17.6	18.4	55.6

Potential evapotranspiration (PE)

Figure 7 shows the daily mean potential evapotranspiration (PE), the average monthly rainfall, and the amount of irrigation water with their respective date of irrigation. PE was calculated dividing the MPE by the number of days of the corresponding month. PE highest values occurred during July and August, reaching 33 mm/day. In contrast, the months of December and January, at the beginning of the irrigation period, reached an average of 15 mm/day, showing the lowest PE of the year. These conditions cause the increase of the water table during the winter. Temporal variation of TDS for NP6 correlates quite well with PE behavior during the summer, when the water table is deeper and more concentrated in solutes (Fig. 8). For NP2 the TDS content remained relatively constant during the different sampling campaigns. This behavior can be explained considering the interaction of groundwater with the dump site. During the irrigation season, water levels increase and favor dissolution of solutes from the deeper horizons of the dump site, counteracting the phenomenon of dilution caused by the added water.

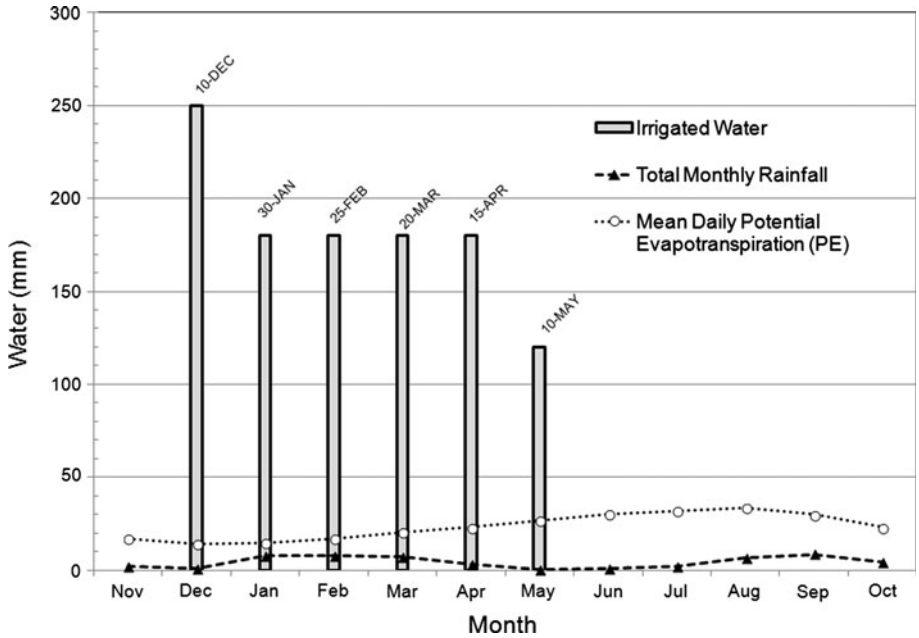

Fig. 7 Daily potential evapotranspiration, irrigated water and rainfall in the study area (the dates, about water irrigation, shown above the *bar graphs* water correspond to specific days on which the activity takes place)

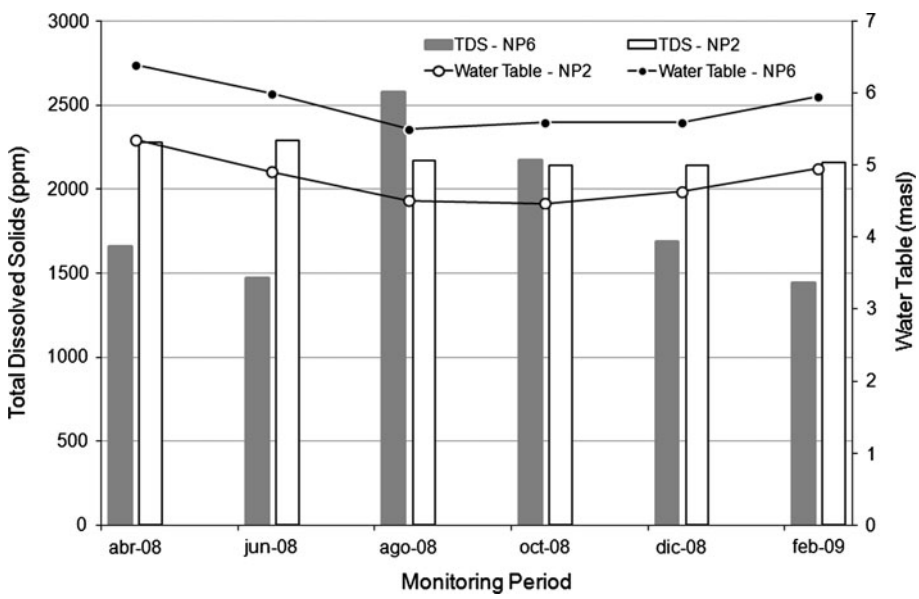

Fig. 8 Temporal evolution of TDS and water table levels of groundwater in the Vado Carranza Dump

Geochemical modeling

First model

Table 3 presents the results obtained in shorthand. It identifies the different processes modeled and the corresponding values of the initial solution (NP6), final solution (NP2) and modeled solution. The difference between the modeled and the solution NP2 observed was measured as an error percentage. The results indicate that the geochemical processes modeled reproduce satisfactorily the chemical evolution of groundwater, as well as the occurrence of other processes not considered in the modeling.

For the six sampling campaigns the results can be generalized as follows:

Water evaporation The results for the modeling of this process are consistent with both agricultural activities and climatic variations in the region. It was necessary to model the evaporation of more water to the campaigns of the winter months (December, February, and April) than those for summer season (June, August, and October). This can be explained by considering that the recharging process originated during the time of crop's irrigation replenish water close to the surface that can evaporate compared with the deep

Table 3 Results of the groundwater geochemical evolution modeling from NP6 to NP2 using the program PHREEQC

1. Modeling of water evaporation process of 10 steps

Quantity of evaporated water: $H_2O_{(g)}$ = 16.8 mol by water Kg (26.7 ± 9.2)[a]

2. Processes modeled simultaneously

2a. Equilibrium phases

Phase	Saturation index	Moles[b]
Calcite	0.0	0
Dolomite	0.0	0
CO_2 (g)	−1.6 (−1.6 ± 0.1)	10
O_2 (g)	−1.2	10
SiO_2	0.0	10

2b. Cationic exchange

Exchanger	Moles interchanged
CaX_2	2.8×10^{-03} ($6.56 \times 10^{-03} \pm 6.6 \times 10^{-03}$)
MgX_2	6.2×10^{-04} ($3.56 \times 10^{-03} \pm 2.6 \times 10^{-03}$)
NaX	1.6×10^{-03} ($2.62 \times 10^{-03} \pm 1.9 \times 10^{-03}$)
CdX_2	4.5×10^{-07} ($9.86 \times 10^{-07} \pm 4.2 \times 10^{-07}$)
ZnX_2	4.1×10^{-06} ($6.64 \times 10^{-06} \pm 4.6 \times 10^{-06}$)
CuX_2	1.13×10^{-03} ($5.75 \times 10^{-03} \pm 4.9 \times 10^{-03}$)
PbX_2	1.95×10^{-05} ($1.79 \times 10^{-05} \pm 1.9 \times 10^{-05}$)

2c. Surface sorption

Site type	Site (moles)	Surface	Area (m^2/g)	Mass (g)
Hfo_wOH	0.003 (0.013 ± 0.008)	Hfo	600	0.01

3. Chemical comparison between modeling solution and NP2

Element	Initial solution NP6	Modeling solution	Final solution NP2	% Error
HCO_3^-	8.1×10^{-03}	7.6×10^{-03}	9.0×10^{-03}	10.8 (23.2 ± 21.9)
Ca	2.2×10^{-03}	1.7×10^{-03}	1.7×10^{-03}	3.2 (2.8 ± 3.4)
Cd	3.3×10^{-07}	4.5×10^{-07}	4.6×10^{-07}	1.0 (1.0 ± 0.5)
Cl	1.7×10^{-02}	2.3×10^{-02}	2.3×10^{-02}	0.1 (0.1 ± 0.1)
Cu	2.1×10^{-06}	4.0×10^{-06}	4.1×10^{-06}	1.1 (2.2 ± 2.1)
K	2.0×10^{-04}	1.7×10^{-04}	1.5×10^{-04}	8.9 (2.3 ± 3.3)
Mg	5.4×10^{-03}	3.0×10^{-03}	3.0×10^{-03}	0.7 (1.1 ± 1.4)
NO_3^-	7.0×10^{-05}	9.3×10^{-05}	2.0×10^{-05}	109.3 (80.7 ± 26.1)
Na	2.8×10^{-02}	3.6×10^{-02}	3.6×10^{-02}	0.3 (1.4 ± 1.5)
Pb	BDL	3.4×10^{-07}	3.5×10^{-07}	1.6 (1.3 ± 1.1)
SO_4^{2-}	9.9×10^{-03}	1.2×10^{-02}	1.2×10^{-02}	4.5 (15.8 ± 16.8)
Zn	6.1×10^{-07}	8.2×10^{-07}	8.3×10^{-07}	0.6 (0.4 ± 0.2)
pH	6.9	7.2	7.4	1.7 (3.7 ± 4.1)

Results are for the third sampling campaign (August 2008)

BDL below detection limit

[a] All parentheses information corresponds to the mean and standard deviation modeling values of the six campaigns

[b] Maximum amount of the mineral or gas that can dissolve

water table and lack of water close to the hotter surface during the summer.

Cation exchange and adsorption of metals The modeling of these processes successfully reproduce the chemical evolution of metals in groundwater with error rates less than 6 %. In the case of heavy metals, the results have satisfactory approximations to the quantities observed in NP2. The average error and standard deviation were as follows: Cu (3.7 ± 3.2 %), Cd (1.3 ± 1.8 %), Pb (2.5 ± 0.9 %), and Zn (0.6 ± 0.7 %).

Anions Except for Cl^- the other anions yield results with more errors because these species may experience a wide number of processes that is practically impossible to consider all of them in the modeling. In general, the anions HCO_3^-, SO_4^{-2}, and NO_3^- experience an increase in concentration during the chemical evolution of the well NP6 to NP2. This increase is caused by the evaporation of water and the interaction with the garbage and agricultural activity help make this happen. In the case of HCO_3^- ion differences between modeled and the final solution (NP2) can be attributed to changes experienced by the CO_2 partial

Table 4 Results of the modeling of geochemical evolution from Canal to NP2 using the program PHREEQC

1. Modeling of water evaporation process of 10 steps

Quantity of evaporated water: $H_2O_{(g)}$ = 29.1 mol by water Kg (39.2 ± 5.9)[a]

2. Processes modeled simultaneously

2a. Equilibrium phases

Phase	Saturation index	Moles[b]
Calcite	0.0	0
Dolomite	0.0	0
CO_2 (g)	−1.6 (−1.7 ± 0.1)	10
O_2 (g)	−1.2	10
SiO_2	0.0	10

2b. Cationic exchange

Exchanger	Moles interchanged
CaX_2	3.8×10^{-03} ($6.3 \times 10^{-03} \pm 5.1 \times 10^{-03}$)
MgX_2	4.2×10^{-03} ($2.3 \times 10^{-03} \pm 1.5 \times 10^{-03}$)
NaX	1.2×10^{-02} ($7.5 \times 10^{-03} \pm 3.5 \times 10^{-03}$)
CdX_2	7.8×10^{-07} ($6.3 \times 10^{-07} \pm 4.2 \times 10^{-07}$)
ZnX_2	1.8×10^{-06} ($3.0 \times 10^{-06} \pm 2.1 \times 10^{-06}$)
CuX_2	4.8×10^{-04} ($2.6 \times 10^{-03} \pm 2.0 \times 10^{-03}$)
PbX_2	2.6×10^{-06} ($3.3 \times 10^{-06} \pm 2.5 \times 10^{-06}$)

2c. Surface sorption

Site type	Site (moles)	Surface	Area (m^2/g)	Mass (g)
Hfo_wOH	0.009 (0.008 ± 0.003)	Hfo	600	0.01

3. Chemical comparison between modeling solution and NP2

Element	Initial solution NP6	Modeling solution	Final solution NP2	% Error
HCO_3^-	3.4×10^{-03}	6.9×10^{-03}	9.0×10^{-03}	16.8 (25.0 ± 27.1)
Ca	2.1×10^{-03}	1.5×10^{-03}	1.7×10^{-03}	8.5 (2.8 ± 3.3)
Cd	2.1×10^{-07}	4.2×10^{-07}	4.6×10^{-07}	4.9 (1.7 ± 1.8)
Cl	1.1×10^{-02}	2.3×10^{-02}	2.3×10^{-02}	0.1 (0.1 ± 0.1)
Cu	1.4×10^{-06}	4.0×10^{-06}	4.1×10^{-06}	1.3 (2.2 ± 1.7)
K	2.5×10^{-05}	1.7×10^{-04}	1.5×10^{-04}	7.8 (3.1 ± 4.4)
Mg	2.8×10^{-03}	2.8×10^{-03}	3.0×10^{-03}	5.3 (3.5 ± 3.1)
NO_3^-	1.1×10^{-04}	3.5×10^{-04}	3.0×10^{-05}	155.6 (116.1 ± 56.0)
Na	1.1×10^{-03}	3.5×10^{-02}	3.6×10^{-02}	1.4 (1.6 ± 1.7)
Pb	BDL	3.9×10^{-07}	3.5×10^{-07}	1.6 (1.3 ± 1.1)
SO_4^{2-}	6.3×10^{-03}	1.3×10^{-02}	1.2×10^{-02}	6.8 (10.6 ± 9.6)
Zn	7.7×10^{-07}	8.3×10^{-07}	8.3×10^{-07}	0.0 (0.3 ± 0.5)
pH	8.4	7.1	7.4	1.9 (3.0 ± 2.8)

Results are for the third sampling campaign (August 2008)

BDL below detection limit

[a] All parentheses information corresponds to the mean and standard deviation modeling values of the six campaigns

[b] Maximum amount of the mineral or gas that can dissolve

pressure, a process not considered in modeling, which causes changes in the content of HCO_3^- dissolved and the pH of the water. In addition, the system has been modeled assuming equilibrium conditions which very likely do not occur for the carbonate system in this aquifer. Furthermore, NO_3^- and SO_4^{-2} ions exhibit a behavior in which its content increases as the water evolving from NP6 to NP2 only that unlike the HCO_3^- in this case the solution is generally modeled with content higher than that observed for NP2. This discrepancy suggests the occurrence of another type of process experienced by these anions like the reduction produced by the degradation of organic matter promoted from the activities of solid waste disposal, as is described by Appelo and Postma (2005). Also the degradative process of organic matter is characterized by increasing the content of inorganic carbon which promotes further HCO_3^- dissolving in water (Tesfay and Korom 2006). Also in the modeling did not take into account the amount of NO_3^- and SO_4^{-2} from agricultural activities.

Second model

This model was based on a surface water (Canal) used for crop irrigation and its chemical evolution to obtain a water with NP2 properties. Table 4 presents the results for this modeling for the third sampling campaign. In this case, it was necessary to simulate the evaporation of more water to reproduce the concentration of Cl^- in NP2 because the surface water (Canal) has a lower content of dissolved solids. The cationic exchange and metals adsorption processes satisfactorily reproduce the quantities of heavy metal and cations in NP2 with error percentages below 10 %. With respect to the anions HCO_3^-, SO_4^{-2} and NO_3^-, the differences between modeled and NP2 solutions can be explained taking into account the occurrence of non-modeled processes such as those mentioned in the first model. Finally, in the case of heavy metals the results have satisfactory approximations to the quantities observed in NP2. The errors for these species were: Cd (1.7 ± 1.8 %), Cu (2.5 ± 3.0 %), Pb (2.5 ± 3.0 %), and Zn (0.3 ± 0.5 %).

Conclusions

Groundwater in the study area is characterized by a high concentration of dissolved solids with predominance of Na^+, Cl^-, SO_4^{-2}, and NO_3^- ions. Heavy metals Cu and Cd were found in concentrations that exceed the average values reported in other studies. Monitoring wells with the highest dissolved solids content (NP1 and NP2), are located in downward of local groundwater flow and in the vicinity of farming plots. This suggests the potential of anthropogenic impacts attributable to both, agriculture and waste disposal activities.

High contents of heavy metals were found in surface soil in areas where the burning of solid waste occurs. In general, the order of content of heavy metals was as follows: Zn > Cu > Pb > Ni > Cd. Despite the soils lower cadmium content, compared to the other heavy metals, its concentration is very high considering the values for this metal reported in other studies. The soil heavy metals content is lower at depth, which can be explained by factors such as: the low rainfall that results in a low infiltration rate of solutes and, retardation due to adsorption processes in clay and organic matter contained in the soil.

On the other hand, the water table shows an annual cycle according to the processes of evapotranspiration and irrigation. During the summer, the water table is deeper and more concentrated in solutes, affected by the absences of irrigation water and by evapotranspiration. In the winter lower effects of evapotranspiration along with the beginning of the irrigation season favor the elevation of shallow aquifer. The monitoring wells located inside the dumpsite (NP5) and downward groundwater flow (NP1 and NP2) showed relatively constant dissolved solids content during all of the sampling campaigns. This is explained by gaining salinity through interactions of groundwater with the dump site. During the irrigation season, water levels increase and favor dissolution of solutes from the deeper horizons of the dump site, counteracting the phenomenon of dilution caused by the added water.

The two models presented for the groundwater chemical evolution fit well with the observed values and both models show the importance of water evaporative process in the area; however, the first model that takes into account the flow direction reproduces the chemical evolution of groundwater in the landfill better than the second model, as shown by its lower error percentages. Other geochemical processes that can be inferred from the modeling performed consist of CO_2 partial pressure variations, organic matter degradation from the wastes, reduction process of chemical species such as NO_3^- and SO_4^{-2} given the prevailing anoxic conditions in the aquifer and the cationic exchange and adsorption of heavy metals. The evolution of waters farther away from the site, in comparison with the distances considered in this work, should be investigated. The nature of the geochemical processes taking place in a semiarid region, where groundwater–dumpsite interactions were documented, can be transferred to any arid or semiarid area of the world, where climate can impact the fate and transport of contaminants. This kind of study can give important insight about the movement and concentration of contaminants in desert environments.

Acknowledgments The authors would like to thank National Council of Science and Technology (CONACYT) for financially supporting this research.

References

Aiuppa A, Federico C, Allard P, Gurrieri S, Valenza M (2005) Trace metal modeling groundwater–gas–rock interactions in a volcanic aquifer: Mount Vesuvius, Southern Italy. Chem Geol 216:289–311

Alloway BJ (1990) Heavy metals in soils. Wiley, New York

Al-Yaqout AF, Hamoda MF (2003) Evaluation of landfill leachate in arid climate—a case study. Environ Int 29(5):593–600

Appelo CAJ, Postma D (2005) Geochemistry, groundwater and pollution. A.A. Balkema, Leiden

Brun A, Engesgaard P, Christensen TH, Rosbjerg D (2002) Modelling of transport and biogeochemical processes in pollution plumes: Vejen landfill, Denmark. J Hydrol 256(3–4):228–247

Diario Oficial de la Federación/The Official Gazette of the Federation (DOF) (2006) Norma Mexicana NMX-AA-132-SCFI-2006. Muestreo de suelos para la identificación y la cuantificación de metales y metaloides, y manejo de la muestra/Mexican Norm NMX-AA-132-SCFI-2006. Soil sampling for metal and semi-metal identification and quantification, and sample handling. http://biblioteca.semarnat.gob.mx/janium/Documentos/Ciga/agenda/PPD02/NMX132AA2006.pdf. Accessed 22 January 2013

Fetter CW (1993) Contaminant hydrogeology. Macmillan, New York

Instituto Nacional de Estadística, Geografía e Informática/National Institute of Statistical, Geography and Informatics (INEGI) (2001) Síntesis de información geográfica del estado de Baja California/Synthesis of geographic information of the Baja California state. INEGI, Mexico

Instituto Nacional de Estadística, Geografía e Informática/National Institute of Statistical, Geography and Informatics (INEGI) (2005) Anuario estadístico de México/Statistical yearbook of Mexico. INEGI, Mexico

Israde I, Buenrostro O, Carrillo-Chávez A (2005) Geological characterization and environmental implications of the placement of the Morelia Landfill, Michoacán, Central Mexico. J Air Waste Manag Assoc 55(6):755–764

Kale SS, Kadam AK, Kumar S, Pawar NJ (2010) Evaluating pollution potential of leachate from landfill site from the Pune metropolitan city and its impact on shallow basaltic aquifers. Environ Monit Assess 162(1–4):327–346. doi:10.1007/s10661-009-0799-7

Kookana RS, Naidu R, Barry DA, Tran TY, Bajracharya K (1999) Sorption–desorption equilibria and dynamics of cadmium during transport in soil. In: Magdi Selim H, Iskandar K (ed) Fate and transport of heavy metals in the vadose zone, 1st edn. CRC Press LLC, Boca Raton, pp 107–123

Kumar CP (2012) Groundwater modelling software—capabilities and limitations. J Environ Sci Toxicol Food Technol 1(2):46–57

Merkel BJ, Planer-Friedrich B (2008) Groundwater Geochemistry: a practical guide to modeling of natural and contaminated aquatic systems. Springer, Berlin

Mor S, Ravindra K, Dahiya RP, Chandra A (2006) Leachate characterization and assessment of groundwater pollution near municipal solid waste landfill site. Environ Monit Assess 118:435–456. doi:10.1007/s10661-006-1505-7

Morf L, Brunner P, Spaun S (2000) Effect of operating conditions and input variations on the partitioning of metals in a municipal solid waste incinerator. Waste Manag Res 18(1):4–15. doi:10.1034/j.1399-3070.2000.00085.x

Nicolli HB, Bundschuh J, García JW, Falcon CM, Jean JS (2010) Sources and controls for the mobility of arsenic in oxidizing groundwaters from loess-type sediments in arid/semiarid dry climates—evidence from the Chaco—Pampean plain (Argentina). Water Res 44(19):5589–5604

Oliveira-Filho EC, Matos Lopes R, Roma Paumgartten FJ (2004) Comparative study on the susceptibility of freshwater species to copper-based pesticides. Chemosphere 56(4):369–374

Parkhurst DL, Appelo CA (2000) User's guide to PHREEQC (Version 2)—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, U.S. Geological Survey Water-Resources Investigations Report 99–4259, p 312

Ramírez-Hernández J, Román-Calleros J, Reyes-López JA, Lázaro-Mancilla O (2006) El escenario del agua en el Valle de Mexicali. In: Ramírez-Hernández J (ed) Una visión de la problemática ambiental de Mexicali y su valle, 1st edn. Autonomous University of Baja California (UABC), Mexicali, pp 19–70

Sadek S, Ghanimeha S, El-Fadela M (2007) Predicted performance of clay-barrier landfill covers in arid and semi-arid environments. Waste Manag 27(4):572–583

Secretaría de Economía (SE) (2001) Norma Mexicana NMX-AA-051-SCFI-2001, Análisis de agua—Determinación de metales por absorción atómica en aguas naturales potables, residuales y residuales tratadas—Método de Prueba/Mexican Norm NMX-AA-051-SCFI-2001, Water analysis—Determination of metals by atomic absorption in natural drinking, wastewaters and wastewaters treated—test method. http://www.conagua.gob.mx/CONAGUA07/Noticias/NMX-AA-051-SCFI-2001.pdf. Accessed 21 August 2012

Siegel FR (2002) Environmental geochemistry of potentially toxic metals. Springer, Heidelberg

Tesfay T, Korom S (2006) Modeling groundwater denitrification by ferrous iron using PHREEQC. Technical report. Department of Geology and Geological Engineering, University of North Dakota. http://www.ndsu.edu/wrri/TedrosScottFinal%20Report.pdf. Accessed 22 January 2013

Thornthwaite CW, Mather JR (1957) Instructions and tables for computing potential evapotranspiration and water balance. Drexel Institute of Technology, Laboratory of Climatology, Certenton

USEPA (1996) Method 3050B—Acid digestion of sediments, sludges and soils samples for analysis by flame atomic absorption (FLAA) or inductively coupled plasma atomic emission spectrometry (ICP-AES). http://www.epa.gov/sam/pdfs/EPA-3050b.pdf. Accessed 21 August 2012

Valdez-Carrillo (2010) Impacto de los residuos provenientes de un tiradero a cielo abierto sobre la calidad del agua subterránea. Dissertation, Autonomous University of Baja California, UABC

Van Breukelen BM, Griffioen (2004) Biogeochemical processes at the fringe of a landfill leachate pollution plume: plume for dissolved organic carbon, Fe(II), Mn(II), NH_4 and CH_4 oxidation. J Contam Hydrol 73(1–4):181–205. doi:10.1016/j.jconhyd.2004.01.001

Vasanthi P, Kaliappan S, Srinivasaraghavan R (2008) Impact of poor solid waste management on groundwater. Environ Monit Assess 143:227–238. doi:10.1007/s10661-007-9971-0

Wan Zuhairi WY (2003) Sorption capacity on lead, copper and zinc by clay soils from South Wales, United Kingdom. Environ Geol 45:236–242. doi:10.1007/s00254-003-0871-5