Mobility of Heavy Metals (Pb, Cd, Zn) in the Pampeano and Puelche Aquifers, Argentina: Partition and Retardation Coefficients

L. M. Jakomin, L. Marbán, S. Grondona, M. Glok Galli & D. E. Martínez

Bulletin of Environmental Contamination and Toxicology

ISSN 0007-4861
Volume 95
Number 3

Bull Environ Contam Toxicol (2015)
95:325-331
DOI 10.1007/s00128-015-1602-9

Bulletin of Environmental Contamination and Toxicology

Volume 95 Number 3 September 2015

Contents continued on back cover

128 BECTA6 95(3) 279–420 (2015) ISSN 0007-4861

Springer

To visit Springer on the Web:
http://www.springer.com

To e-mail the journal:
bect@springer.com

Springer

Bull Environ Contam Toxicol (2015) 95:325–331
DOI 10.1007/s00128-015-1602-9

Mobility of Heavy Metals (Pb, Cd, Zn) in the Pampeano and Puelche Aquifers, Argentina: Partition and Retardation Coefficients

L. M. Jakomin[1] · **L. Marbán**[2] · **S. Grondona**[3] · **M. Glok Galli**[3] · **D. E. Martínez**[3]

Received: 19 September 2014 / Accepted: 8 July 2015 / Published online: 17 July 2015

Abstract The prediction about metals behaviour in soil requires knowledge on their solid–liquid partitioning. Usually it is expressed with an empirical distribution coefficient or Kd, which gives the ratio of the metal concentration in the solid phase to that in the solution. Kd values have been determined for Zn, Pb and Cd from samples representing the two most exploited aquifers in Argentina, Pampeano and Puelche, at three different locations in the province of Buenos Aires. The Pampeano aquifer presented higher Kd values than the Puelche aquifer. Comparing Kd values, different relationships could be observed: (a) Pampeano aquifer: Pb > Zn > Cd, and (b) Puelche aquifer: Pb > Cd > Zn. Kd for Cd seems to be linked to cationic exchange capacity, but solid phases precipitation can be more determining for Pb and Zn.

Keywords Pampeano aquifer · Puelche aquifer · Distribution coefficient · Heavy metals

The distribution or partition coefficient, Kd, is one of the most important parameters applied in contaminant migration studies on aqueous solutions in contact with suspended, superficial, and subsuperficial solids in an equilibrated system. It expresses the relative tendency of an element to become adsorbed (Appelo and Postma 1993). This is defined as the relationship between the concentration of the contaminant associated to the solid and the concentration of the contaminant in the aqueous solution of the system, once the equilibrium is reached.

$$\mathrm{Kd} = \mathrm{mmol\ per\ g\ solid/mmol\ per\ mL\ water} \tag{1}$$

The Kd can also be used to estimate the potential adsorption of the dissolved contaminant in contact with the sediment. The inverse relationship is applied in the retardation factor, an empiric parameter that describes the relationship between the velocity of the contaminant transport and the velocity of the groundwater (Domenico and Schwartz 1990; Appelo and Postma 1993).

$$\mathrm{R_f} = \mathrm{V_w}/\mathrm{V_c} = 1/1 + (\mathrm{K_d} \cdot \rho/\varepsilon) \tag{2}$$

where R_f is the retardation factor, V_w is water Darcy velocity, V_c is the compound velocity, ρ is the specific weight and ε the porosity of the solid material.

From Eqs. 1 and 2 it can be observed that if a compound is not adsorbed (i.e. all remains in solution) Kd value is 0 and then R_f is 1, which means that the compound is moving at the same velocity of water. A non-conservative solute which is adsorbed has a $Kd > 0$, resulting in a lower velocity. If the compound is a contaminant, therefore low Kd values imply a faster displacement, and consequently, a higher potential to contaminate water in the porous media. On the opposite, if the Kd value is high the contaminant displacement is low and contamination tends to be attenuated (Bethke and Brady 2000).

Normally the Kd can be measured experimentally by batch or column tests (EPA 1999; Hopp et al. 2002; Beck and Jankowski 2000; Roy et al. 1992; Stradberg and Fortkamp 2005). Although this measurements would be more

---

✉ D. E. Martínez
demarti@mdp.edu.ar

[1] Ministerio de Planificación Federal, Inversión Pública y Servicios, Subs. de Recursos Hídricos, Buenos Aires, Argentina

[2] INGEIS Universidad de Buenos Aires – CONICET, Buenos Aires, Argentina

[3] Instituto de Investigaciones Marinas y Costeras, Instituto de Geología de Costas y del Cuaternario, CONICET-Universidad Nacional de Mar del Plata (UNMdP), Mar del Plata, Argentina

accurate and recommended in site specific studies, Kd can be also estimated using multiple regression models to find equations describing Kd dependence on metal properties and soil characteristics (Carlon et al. 2004). Briefly, a quantity of sediment is mixed with a contaminant solution of known concentration. This is brought into contact with the sediment and shaken for 72 h. Then, it is separated and the concentration of the associated contaminant is determined by calculating the difference between the initial and final contaminant contents. These experiments are quick, and aspects such as the solid/solution relationship, time of contact, shaken and centrifugation velocity, and the control of pH and temperature should be considered (Roy et al. 1992; Jeppu and Clement 2012). In some studies applied to radioactive isotopes, it is necessary to include some additional parameters to Kd in order to obtain better results (Samper et al. 2010). The importance of biofilms on metals adsorption has been recently highlighted by Drahota et al. (2014).

In spite of the significance of this parameter in the mobility of contaminants, such as metals, experimental values are little known in the sediments forming the two main aquifers Argentina. The Pampa plain constitutes the most populated and productive agro-economical region in the country. The sub-region named Wet Pampa has its main source of water supply in two aquifer systems, Pampeano and Puelche aquifers. There is a general good knowledge of their hydraulic and hydrochemical conditions due to their wide area distribution and relatively easy accessibility. Nevertheless, in relation to contamination events, there are only few references about partition coefficient values for several chemical species (Martinez et al. 2006; Albouy et al. 2009; Matteoda 2012).

In this contribution, Kds of three heavy metals (Zn, Cd and Pb) were obtained at three different locations in the province of Buenos Aires (Fig. 1) on representative samples of the Pampeano and Puelche aquifers. This information would increase the knowledge of the hydrogeological behavior of the two main aquifers in Argentina and the mobility of the studied heavy metals.

The Pampa plain in Argentina is divided in many hydrogeological regions (Auge 2004), mostly based in their geomorphology and the relationship between the two main aquifers. This study was developed in the areas corresponding to the Northeastern and Depressed hydrogeological regions (Fig. 1). These areas show a similar stratigraphic and hydrogeological scheme, which determines the hydrogeological units:

Pampeano aquifer formed by Pampeano and Post-Pampeano sediments (Plioceno-Holoceno), which are mainly of aeolian origin. The sediments composition is silt-sandy, with variable clay proportion up to 30 % and low organic matter content. Nevertheless the presence of interbeded paleosoils results in an average organic matter content of 5 %. The recharge of the Pampeano aquifer is produced by rain infiltration through permeable superficial deposits, making it highly vulnerable to contamination. Pampeano is a phreatic aquifer, whose thickness varies between 120 m in the northeast and 0 m in the lower rivers' basins of the area (Auge 2004).

Puelche aquifer formed by Puelches sands (Pliocene-Lower Pleistocene) and underlies the Pampeano aquifer in the NE of the province of Buenos Aires (Auge et al. 2002). It is formed by fluvial sand deposits, having very low clay and organic matter contents. It is a semi-confined aquifer and is the most exploited in Argentina providing water for Buenos Aires city and the satellite suburban localities (approximately 15 million inhabitants). It is recharged directly from the Pampeano aquifer by vertical filtration and its thickness oscillates between 20 m and 90 m (Auge et al. 2002).

Methodology

Sediment samples were obtained from borehole drilling samples' archives of the Department of Hydrological Services of the National Institute of Water. Samples were collected from drilling debris of two wells located in the Ezeiza and Tres de Febrero districts, both situated within the Reconquista and Matanza rivers basins, in the Northeastern hydrogeological region. Moreover, another well is placed in the Chascomús district, within the Salado river basin, in the Depressed Pampa hydrogeological region (Auge 2004) (Fig. 1).

In the Ezeiza district, the Pampeano aquifer sediments were selected from samples at 14–24 m depth and the Puelche aquifer sediments came from samples at 47–51 m depth. In the Tres de Febrero district, sediments were taken from the 28–34 m depth as representative of the Pampeano aquifer and from the 56–64 m depth as representative of the Puelche aquifer. In the Chascomús district, samples were taken from 24 to 30 m depth for the Pampeano aquifer and from 96.5 to 112 m depth for the Puelche aquifer. Standard size particle distribution, organic matter content and cation exchange capacity (CEC) were determined for each sample.

Sediment samples were placed in contact with seven metal solutions of increasing concentration in a 1:10 relationship. Moreover, blank samples were performed and included. Using this sediment/solution relationship, the more convenient analytical results were obtained to be able to construct the adsorption isotherms. Solution densities of 1 g/cm^3 were assumed, independently of their composition. The initial concentration was denominated C_0. It was continuously shaken at 29 rpm for 72 h. After that,

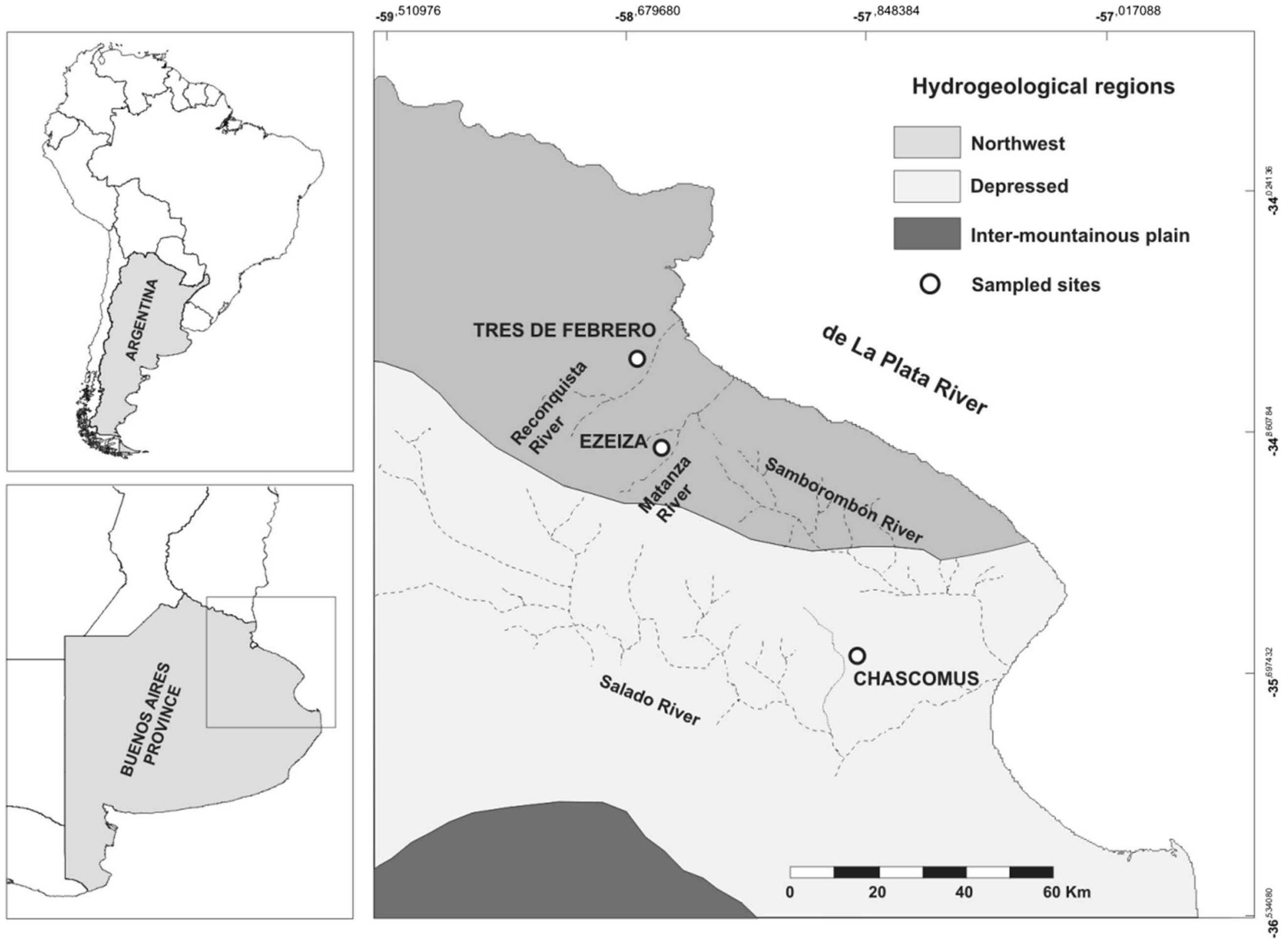

Fig. 1 Hydrogeological regions of the province of Buenos Aires s and location of the used samples

temperature, pH, and any change in the adsorbent or solution were recorded. pH remained invariable in 7.4 ± 0.5, excepting in Zn experiments where a decrease to 6.35 was observed and then a new experiment was performed stabilizing pH at 7. The solid phase was separated from the liquid by filtration or centrifugation, and enough supernatant was collected and preserved to determine the contaminant concentration. Aqueous extracts were analyzed in the Laboratory of the Agro-Environmental Sector of the "Instituto de Geocronología y Geología Isotópica" (INGEIS, Buenos Aires University) according to ICP 2070 Spectrometer operator guide Nro. 079369 Rev. A. BAIRD Analytical. The inductively coupled plasma-atomic emission spectrometry (ICP-AES) was performed using Sequential Atomic Emission Spectrometer Baird 2070, Argon high purity grade (99.996 %). Argon auxiliary gas flow rate 1 L/min, Argon coolant gas flow rate 8.5 L/min, flow rate through peristaltic pump 3 cm^3/min, Argon carrier gas pressure 172.5 kPa, Power, Optical cell zerny-Turner 850 W, optical length 1 m, scanning speed 400 nm/s, diffraction grid 1800 grooves/mm, slit 0.01 nm, generator of radiofrequency 40.68 MHz, detector hotomultiplier (PM). Certipur® ICP multi-element standard solution IV was used to prepare solutions 0.05–100 mg/L for Cd and 0.10–100 mg/L for Pb and Zn, all of them in 0.5 % nitric acid. Limits of quantitation (LQ) were 0.05 mg/L for Cd, and 0.10 mg/L for Pb and Zn.

The quantity of adsorbed solute by adsorbent mass is calculated as:

$$x/m = (C_0 - C) \times V/m \qquad (3)$$

where x/m = quantity of adsorbed solute by unit of adsorbent mass, C_0 = concentration of the initial solute before the exposure to the adsorbent, C = solute concentration after exposure to the absorbent in equilibrium, V = volume of contaminant solution added in the reaction container, m = adsorbent mass.

For the construction of the isotherm, at least 5 solid/solution relationships were analyzed using the x/m datum.

The concentration in equilibrium C, log C or C/x/m, as well as the x/m, log x/m or C were plotted in the "x" and

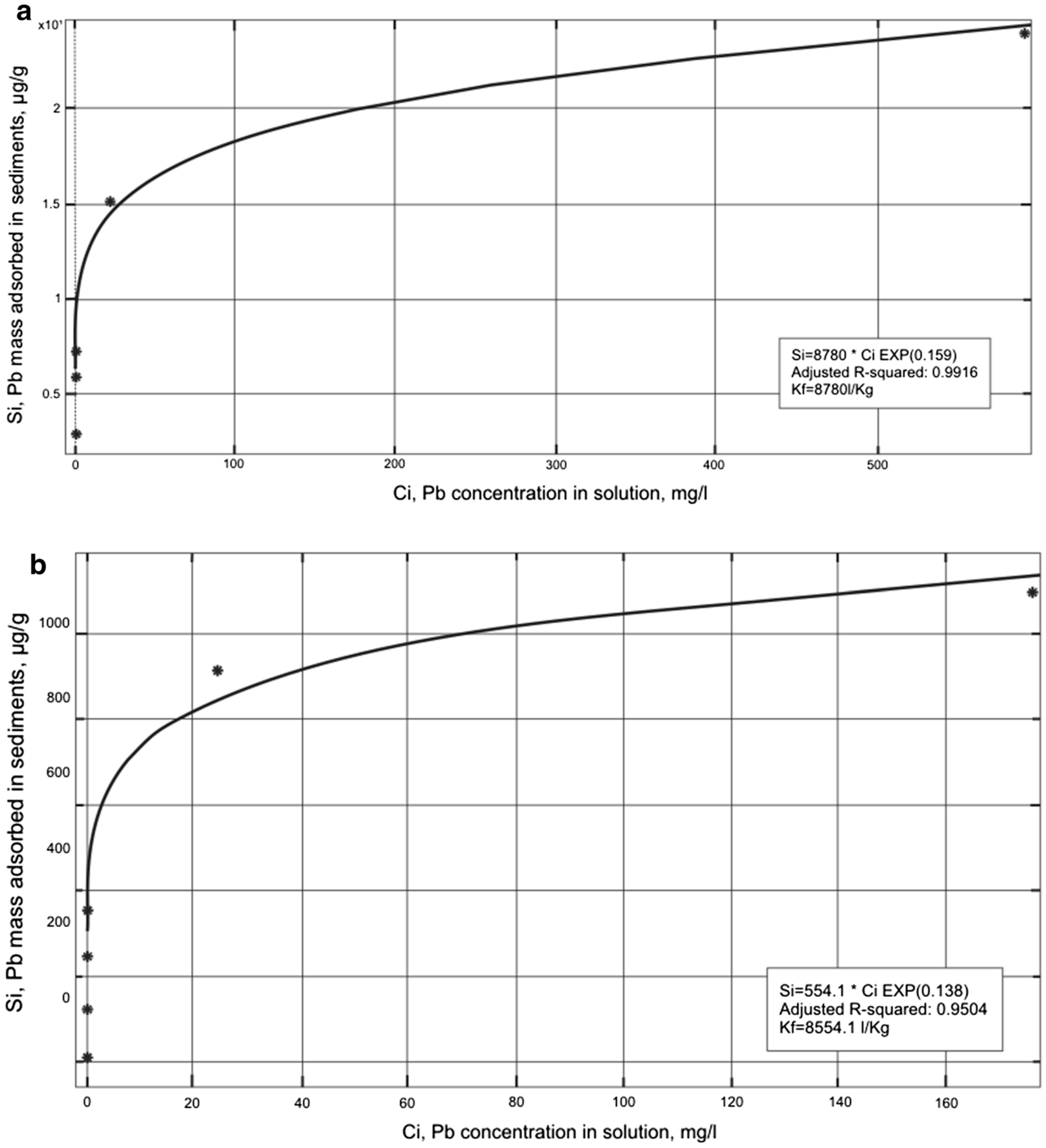

Fig. 2 Pb adsorption isotherm in the **a** Pampeano aquifer and **b** Puelche aquifer of the Tres de Febrero district

"y" axis, as dependent variables, respectively. Data are adjusted and the application of a lineal equation, Freundlich-type or Langmuir-type, have been evaluated. The regression coefficient was calculated and the isotherm with the regression coefficient closest to 1 was used. Together with the adsorption isotherm, the experimental temperature, pH, and concentrations of the stock (C_f) and blank (C_B) solutions, the soil-solution relationship, the initial (C_0) and final (C_f) concentrations, the quantity of solution and adsorbent mass, the equation that corresponds to the best adjustment ($r^2 \approx 1$), and a complete description of the adsorbent were reported. The slope of the adsorption isotherm that is better adjusted corresponds to the Kd value for the analyzed metal when the relationship is lineal.

Another way to obtain the Kd value is:

$$\mathrm{Kd} = ((\mathrm{Vw} \times (C_0 - \mathrm{Cf})/(\mathrm{Msed} \times \mathrm{Cf})) \qquad (4)$$

where Vw = volume of the solution, Msed = weight of the sediment in contact with the solution.From the obtained Kd value, the retardation factor value, defined as the relationship between the velocity of the contaminant and the velocity of water, can be determined as (Deutsch 1997):

$$\mathrm{R} = 1 + (\rho\beta/\eta) \times (\mathrm{Kf}) \times (\mathrm{Caq}) \qquad (5)$$

Table 1 Partition coefficient values (Kd, L/kg)

	Pb	Cd	Zn Without pH control	Zn With pH control = 7
Ezeiza *Pampeano*	7511	1197	884	644
Ezeiza *Puelche*	1427	177	139	131
Tres de Febrero *Pampeano*	8780	914	5633	2558
Tres de *Febrero* *Puelche*	554	63	114	144
Chascomus *Pampeano*	>10,000	44	–	10,160
Chascomus *Puelche*	1682	235	–	160

where $\rho\beta$ = specific weight of the sediment, η = porosity, Kf = distribution or partition coefficient, Caq = concentration of the solute after the adsorption in the aqueous phase.

Results and Discussion

Figure 2a, b shows the isotherms obtained for Pb at both aquifers (Pampeano and Puelche) in the Tres de Febrero well. Eighteen isotherms were obtained according to the best adjustment. In the case of Zn, the experiment was done without controlling pH and with pH stabilized at 7. Kd values obtained in each case are shown in Table 1. It illustrates that, for each metal and considering the three locations, Kd values obtained for the Pampeano aquifer are higher than those corresponding to the same metal in the Puelche aquifer in all cases, except for Cd in the Chascomús district. The comparison among metals showed a different order in Kd values from the largest to the smallest value in the Puelche aquifer than in the Pampeano aquifer being: (a) Pampeano aquifer: Pb > Zn (controlled pH) > Cd; (b) Puelche aquifer: Pb > Cd > Zn. A study including the same metals in soil sediments was performed by Gao et al. (1997) finding a similar metal affinities sequence Pb > Cu ≈ Zn > Cd > Ni > Cr at pH 6.5, and linear isotherm adjustments.

The adjustments obtained through Mathlab for each absorption isotherm function, indicating the type of isotherm and the value of r^2, are shown in Table 2. Very good correlation coefficients for all adjustments can be observed, higher than 0.70 in all cases, and mostly higher than 0.90. Moreover, in most cases, the best adjustments were achieved with the Freundlich isotherm.

The most heavy metal contaminants respected the Freundlich isotherm. Results of Kd experimental determinations indicate that the capacity of sediment adsorption is high, and greater in the Pampeano sediments than in the Puelches sands, producing a significant capacity of attenuation and protecting the Puelche's water. Pampeano's Kds reflect higher values due to the higher content of clays, higher capacity of cationic exchange, and the pH stabilizing power of the calcite.

It is important to point out that Kd determination of Zn needed a strict control of pH and registered erratic behaviors. Zn behaves as an amphoteric element, and at pH close to 6 it began to precipitate as hydroxide. The equilibrium processes produced in Zn solutions can provoke very important variations in pH, so initial pH values were adjusted with adsorbate and solution already in contact, and final pH values were controlled after 72 h in contact. For this element, the processes of precipitation would be the most important ones. The experiments with Pb demonstrate a strong soil adsorption compared with Cd and Zn.

The different origin of the sediments forming the aquifers is reflected in the contents of clay and organic matter that finally determine the CEC. Kd is related to CEC and in the study case a bulk relationship can be established where the Pampeano aquifer having the highest CEC values also showed the highest Kd values (Fig. 3). Nevertheless considering individually each metal the behavior is rather variable. In the Pampeano Aquifer, Kd of Pb and Zn showed an inverse relationship against CEC while Kd for Cd showed a positive correlation, with increasing CEC values. This difference can be explained considering other sinks than adsorption that can result in higher Kd values. The formation of insoluble oxides or carbonates can be the cause, because while PbO_2 or $PbCO_3$ and ZnO_2 or $ZnCO_3$ are practically insoluble, CdO_2 has a solubility of 4.8 mg/L (18°C). Then, Cd is probably in solution as Cd^{2+} and adsorption, linked to CEC, can be the determining process, while Pb and Zn partition is controlled by a solid phase formation. At pH around 7 the stable phases for Pb and Zn

Table 2 Ajustment of adsorption isotherms

	Pb		Cd		Zn Without pH control		Zn With pH control = 7	
	Freundlich	Langmuir	Freundlich	Langmuir	Freundlich	Langmuir	Freundlich	Langmuir
Ezeiza	n = 5	n = 5	n = 6	No converge	n = 8	n = 8	n = 7	No converge
Pampeano	0.9795	0.9157	0.9206		0.9126	0.9804	0.9965	
Ezeiza	n = 6	n = 6	n = 7	n = 7	n = 7	n = 7	n = 6	n = 6
Puelche	0.9057	0.8938	0.9862	0.9082	0.9846	0.8287	0.915	0.718
Tres de Febrero	n = 5	n = 5	n = 8	n = 8	n = 7	No converge	n = 5	n = 5
Pampeano	0.9916	0.6067	0.9946	0.9048	0.8592		0.9939	0.8891
Tres de Febrero	n = 6	n = 6	n = 7	n = 7	n = 6	n = 6	n = 4	n = 4
Puelche	0,9504	0.9615	0.9914	0.9148	0.9846	0.9030	0.9788	0.7742
Chascomus	–	–	n = 6	n = 6	–	–	n = 6	n = 6
Pampeano			0.9755	0.9798			0.9964	0.9899
Chascomus	n = 6	n = 6	n = 6	n = 6	–	–	n = 5	n = 5
Puelche	0.9935	0.8672	0.9914	0.9781			0.828	0.7071

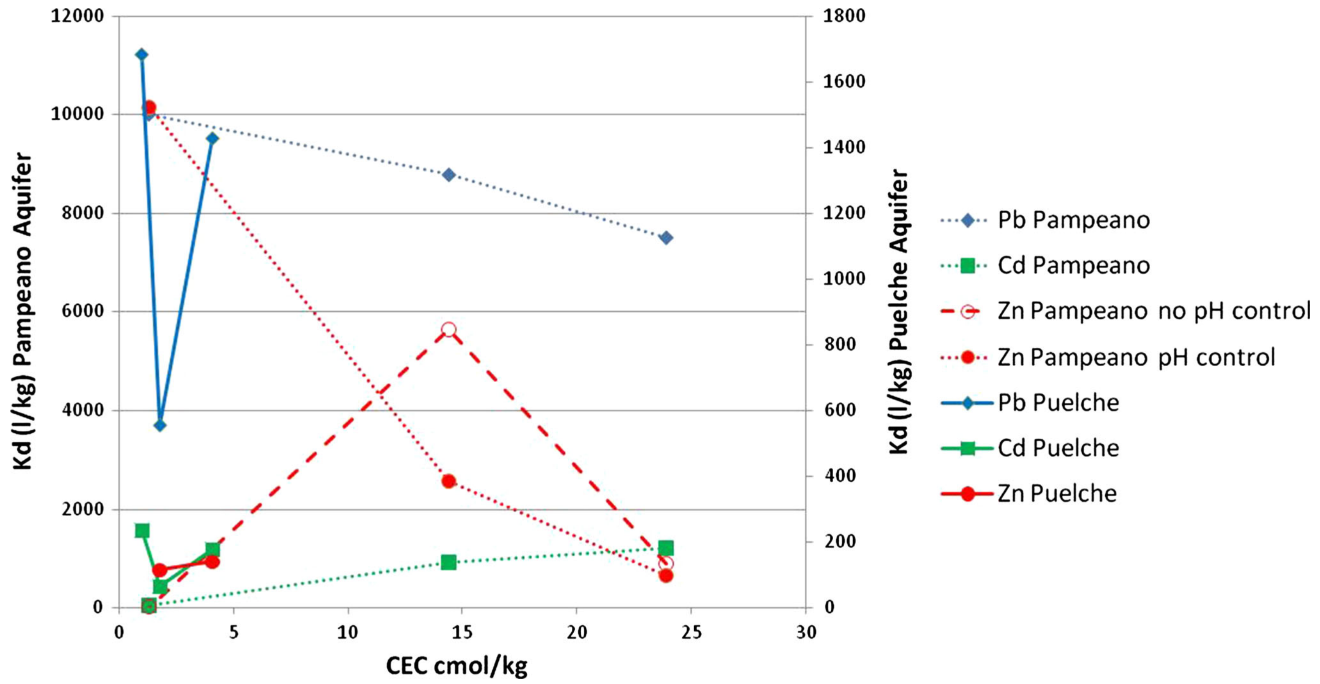

Fig. 3 Kd versus CEC values. *Left Y* axis for Pampeano aquifer values and *right Y* axis for Puelche aquifer values

are carbonates. Low CEC values can be due to lower organic matter content and consequently less redox reactions. It can result in a lower acidification which favors carbonates precipitation and stability. For the Puelche Aquifer, Kd values for Zn and Cd were low and practically constants, while Pb values were relatively higher and more variable, due to the insolubility of PbO_2 and $PbCO_3$.

Few previous data exist in the study zone as comparison values, Martinez et al. (2006) published for the Pampeano aquifer a Kd value for Zn of 300.95 L/kg, which is in the same order of magnitude of the Ezeiza measurements and lower than the obtained for the other locations. In natural sandy sediments, equivalent to the aquifer Puelches, Hassan et al. (1996) determined the minimum values of Kds for the same metals: Cd (45–48 L/kg), Pb (65–67 L/kg) and Zn (249–253 L/kg).

Conclusions

Kd distribution coefficient varied among contaminants. Moreover, depending on the chemistry of the solid and liquid phases, it will be different for the Pampeano and Puelche aquifers. Numerical results provided in this study constitute an basis for future studies on reactive transport of heavy metals in the two most important aquifer systems in Argentina, considering their current use.

Heavy metals tend to be more retained into the Pampeano aquifer sediments than in the Puelche aquifer due to its higher CEC. As the Puelche recharge taking place by leaking from the Pampeano aquifer, its susceptibility for the metal pollution is very low. The main sinks for heavy metals in sediments can be adsorption for Cd, and insoluble oxides or carbonates formation for Pb and Zn. The weak correlation between Kd and CEC for Pb and Zn can be the consequence of the low solubility of the solid phases that can be formed. pH control on the solubility of carbonates can explain changes at field scale.

If the reactive transport of these metals is considered, Pb, with the highest Kd, has a higher retardation factor, followed by Cd and, afterwards, Zn. In this system, Pb would migrate within a smaller area, being attenuated in a smaller area, while Cd and, largely, Zn, would migrate within a larger area, considering similar flow times. This pattern is similar for both aquifers, but retardation is much higher in the Pampeano.

References

Albouy R, Lafont D, Carrica J (2009) El acuífero libre del área industrial costera de Bahía Blanca: simulación del transporte de solutos. In: Schulz C, Cabrera MC (eds) Contaminación y Protección de los Recursos Hídricos. Argentine Chapter of the International Association of Hydrogeologists, Santa Rosa, pp 53–62

Appelo CAJ, Postma D (1993) Geochemistry, groundwater and pollution. A.A. Balkema, Rotterdam

Auge M (2004) Regiones Hidrogeológicas. República Argentina y provincia de Buenos Aires, Mendoza y Santa Fe. http://www.alhsud.com/public/ebooks/reghidroarg.pdf

Auge M, Hernández MA, Hernández L (2002) Actualización del conocimiento del Acuífero Semiconfinado Puelches en la Provincia de Buenos Aires, Argentina. In: Bocanegra E, Martinez D, Massone H (eds) Groundwater and human development. Proceedings of the XXXII IAH congress. Argentine Chapter of the International Association of Hydrogeologists, Mar del Plata, Argentina, pp 624–633

Beck PH, Jankowski J (2000) Using Kd—test data in the estimation of contaminant attenuation and risk assessment. In: Sililo O et al (eds) Groundwater: past achievements and future challenges. A.A. Balkema, Rotterdam, pp 697–701

Bethke CM, Brady PV (2000) How the Kd approach undermines ground water cleanup. Ground Water 38:435–443

Carlon C, Dalla Valle M, Marcomini A (2004) Regression models to predict wáter–soil heavy metals partition coefficients in risk assessment studies. Environ Pollut 127:109–115

Deutsch WJ (1997) Groundwater geochemistry: fundamentals and applications to contamination. Lewis, Boca Raton

Domenico PA, Schwartz FW (1990) Physical and chemical hydrogeology. Wiley, New York

Drahota P, Skaloud P, Nováková B, Mihaljevic M (2014) Comparison of Pb, Zn, Cd, As, Cr, Mo and Sb adsorption onto natural surface coatings in a stream draining natural As geochemical anomaly. Bull Environ Contam Toxicol 93:311–315

Environmental Protection Agency (1999) Understanding variation in partition coefficient, Kd, values, volume I. The Kd model, methods and measurement, and application of chemical reaction codes. EPA 402-R-99-004A

Gao S, Walker WJ, Dahlgren RA, Bold J (1997) Simultaneous sorption of Cd, Cu, Ni, Zn, Pb and Cr on soils trated with sewage sludge supernatant. Water Air Soil Pollut 93:331–345

Hassan SM, Garrison AW, Allen HE, Di Toro DM, Ankley GT (1996) Estimation of partition coefficients for five trace metals in sandy sediments and application to sediment quality criteria. Environ Toxicol Chem 15:2198–2208

Hopp L, Buczko U, Durne W, Peiffer RS (2002) A column leaching test for inorganic contaminants. In: Proceedings of the 1st international workshop on groundwater risk assessment at contaminated sites (GRACOS), Posters Leaching Tests, Germany, pp 163–165

Jeppu GP, Clement TP (2012) A modified Langmuir-Freundlich isotherm model for simulating pH-dependent adsorption effects. J Contam Hydrol 129–130:46–53

Martinez D, Mascioli S, Bocanegra E (2006) Determination of Zn partition coefficient and simulation of reactive transport from landfills in Mar del Plata, Argentina. Environ Geol 5:463–469

Matteoda E (2012) Evaluación hidrodinámica e hidrogeoquímica de la cuenca del arroyo El Barreal para establecer línea de base ambiental, con énfasis en la geoquímica del cromo. Ph.D. thesis. Universidad Nacional de Río Cuarto (unpublished), Río Cuarto, Córdoba

Roy WR, Krapac IG, Griffin RA (1992) Batch-type procedures for estimating soil adsorption of chemicals. Environmental Protection Agency. 530/SW-87/00A. EPA, Washington, US

Samper FJ, Ma H, Cormenzana JL, Lu C, Montenegro L, Cuñado MA (2010) Testing Kd models of Cs+ in the near field of a HLW repository in granite with a reactive transport model. Phys Chem Earth 35:278–283

Stradberg J, Fortkamp U (2005) Investigations on methods for site specific determination of the partition coefficient-Kd, for contaminants in soil. Thesis work with additional comments. IVL Swedish Environmental Research Institute