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Migration of total chromium and chloride anion in the Rocha River used for estimating degradation of agricultural soil quality at the Thiu Rancho zone

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Abstract: The Rocha River is a receptor to receive wastewater from household, hospital and industry, from where contaminants are transported in the river, affecting biodiversity and the ecosystem of the area. In this paper we estimated the maximum transport of total chromium and chloride anion by applying the analytical model of Ogata & Banks (1961), and the results obtained are grouped into three zones: Contaminated, transition, and uncontaminated. The analytical model was applied with 13 samples collected from the river piezometers installed near Rocha, where they are arranged in two lines, *i.e.* RH-1 to RH-6 as the first line and RH-9 to RH-12 as the second line. The total chromium concentrations range from 0.16 mg/L (RH-1) and 0.11 mg/L (RH-9) at the closest points to Rocha River, to 0.13 mg/L (RH-7) and 0.03 mg/L (RH-12) at the most remote points to the river. The advance of the pollutants does not exceed 50 meters with respect to the axis of the Rocha River.

Keywords: Total chromium; Chloride anion; Contamination; Rocha River; Thiu Rancho

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Introduction

Today heavy metals are not only generated by a natural process, but also generated through anthropogenic activities. These metals are frequently detected in sediments and in the water that are stored or transported by lakes and rivers. Since the last decade, environmental pollution has become more serious, the importance of monitoring and determination of some heavy metals are very important for scientific analysis (Dundar *et al.* 2006). However, restoring groundwater is difficult due to geological complexity (Sookhak *et al.* 2018a, 2018b, 2019a, 2019b). The remediation time is long and the cost is very high (HUANG Yong *et al.* 2019).

San Simón University (UMSS) has been investigating Rocha river pollution since 1998. Moreover many relevant studies have been

conducted on Rocha River, among which the microbiological study was performed by Maldonado *et al.* (1998), and the heavy metals in sediment and chironomids were studied by Romero *et al.* (2000). Recent studies include the assessment of Rocha River contamination through the potential non-point pollution index (PNPI), where sources of contamination are identified by land use (Terrazas, 2018).

1 Location

The study site is located in the community of Rancho Thiu, which belongs to the Canton Township Mallco Rancho Sipe Sipe Quillacollo province, from the department of Cochabamba.

2 Methods

To estimate the maximum range of pollutants and total chromium and chloride anion, analytical

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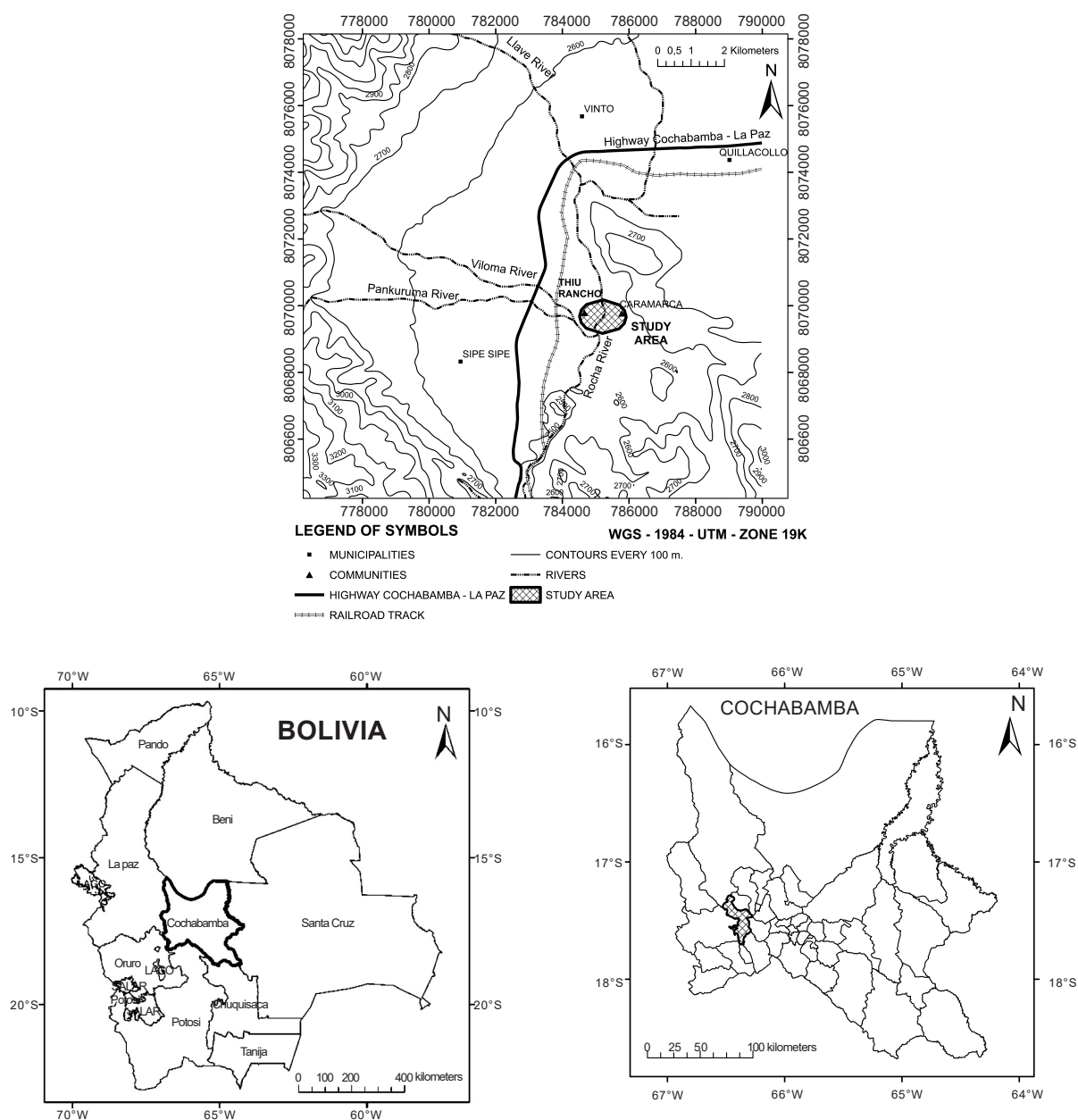


Fig. 1 Location map of the study area

model was applied (Ogata and Banks, 1961). The model requires the following data: Hydraulic conductivity (K), distribution coefficient (K_d), pollutant concentrations (C), and retardation (R).

The hydraulic conductivity (K) was estimated by performing Slug-Test analysis with piezometers installed to apply the methods of Hvorslev (1951) and Bouwer and Rice (1976), from which the weighted average hydraulic conductivity was estimated.

The distribution coefficient was estimated by the concentrations values of total chromium presented in aqueous form and sediments. However for the chloride anion this value is zero.

The retardation factor (R) is determined based on the variables of effective porosity (n_e), sediment density (ρ_b) and the distribution coefficient (K_d).

3 Results and discussion

Table 1 shows the values of the hydraulic conductivity from various methods (Hvorslev, 1951; Bouwer and Rice, 1976), and Fig. 2 shows the spatial location of the piezometers installed in the vicinity of Rocha River.

The results of the average hydraulic conductivity from the previous methods exhibit little variation. The variation among these methods

is due to several factors, for example, different authors could have made different assumptions in their study.

The hydraulic conductivity value applied to the analytical model (Ogata and Banks, 1961) is

the average value obtained from the method of Hvorslev (1951), because the aforementioned assumptions made by the author are consistent with the observed conditions (such as lithology) when installing the piezometers.

Table 1 Values of average hydraulic conductivity

Line	Distance	Hvorslev	Bouwer and	Hvorslev	Bouwer and rice	Hvorslev	Bouwer and rice
RH-7 to RH-1	(m)	K (m/s)	rice K (m/s)	K _b (m/s)	K _b (m/s)	K (m/day)	K (m/day)
RH-1	1.60	5.4E-05	4.1E-05				
RH-2	5.15	7.7E-07	6.0E-07				
RH-3	4.41	8.3E-07	6.3E-07				
RH-4	1.73	7.9E-07	6.0E-07	1.0E-06	8.0E-07	0.09	0.07
RH-5	1.75	1.1E-06	8.1E-07				
RH-6	1.74	2.5E-06	1.9E-06				
Total (m)	17.24						
Line	Distance	Hvorslev	Bouwer and	Hvorslev	Bouwer and rice	Hvorslev	Bouwer and rice
RH-12 to RH-1	(m)	K (m/s)	rice K (m/s)	K _b (m/s)	K _b (m/s)	K (m/day)	K (m/day)
RH-12	1.17	6.6E-07	5.0E-07				
RH-11	2.18	6.4E-06	5.0E-06				
RH-10	4.75	5.0E-06	3.7E-06				
RH-9	4.59	1.7E-05	1.3E-05	4.2E-06	3.2E-06	0.37	0.28
RH-8	1.94	9.9E-06	7.6E-06				
JRH-1	1.12	6.0E-06	4.4E-06				
Total (m)	15.75		Average =	2.6E-06	2.0E-06	0.23	0.17

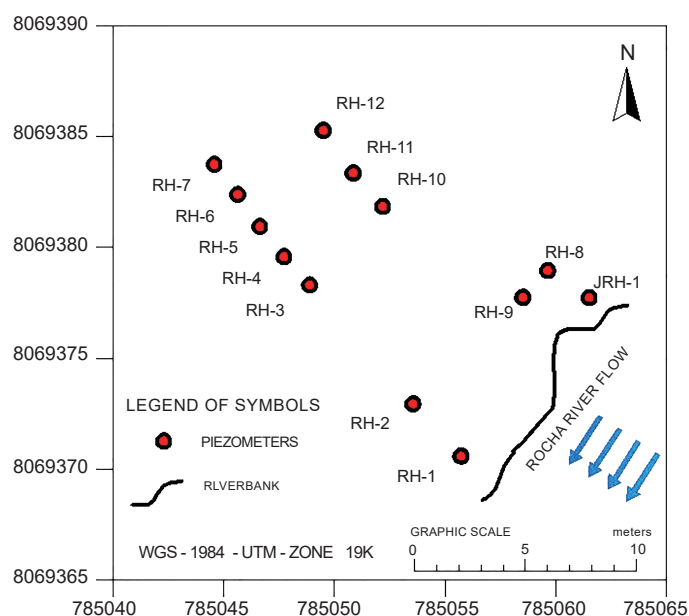


Fig. 2 Planimetric location of the piezometers

Fig. 2 shows the planimetric distribution of the piezometers installed near the Rocha River, from where the soil and water samples were collected.

Fig. 3 shows the linear adsorption isotherm

of total chromium, which is measured in the quantity of total chromium in the sediments vs. adsorbed amount of the total chromium in aqueous form. The slope of the straight line is to

be the distribution coefficient (K_d), in which the Coefficient of Determination value (R^2) is 0.91, indicating the result of the K_d is valid for both analytical and numerical models. The sorption isotherm is linear as presented (Fetter, 1999).

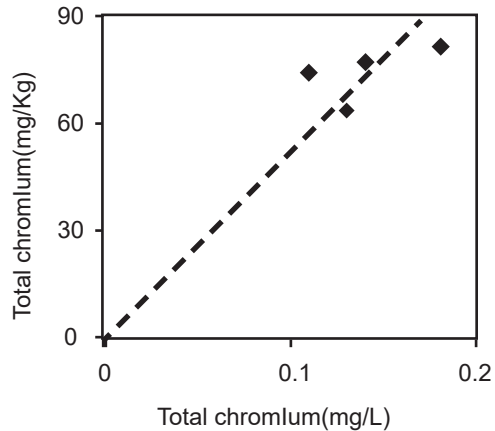


Fig. 3 Linear adsorption isotherm of total chromium

Points deviated from the source in Fig. 3 occur because sampling was performed after a long time to initiate pollution, and for this reason there are no points near the origin. Furthermore, Fig. 3 is produced based on the values in Table 2, in the month of July. The distribution coefficient (K_d) for the chloride anion is zero, because the electric charge is negative.

$$C^* = K_d \cdot C \quad (1)$$

Where:

C^* : Mass of solute sorbed per dry unit of solid (mg/kg).

C : Concentration of solute in solution in equilibrium with the mass of solute sorbed onto the solid (mg/L).

K_d = distribution coefficient (L/kg).

The value of the determined distribution coefficient is $K_d = 517.7$ (L/kg).

Table 2 Chloride concentrations and total chromium

Code	E(m)	N(m)	Z (m.a.s.l.)	Cl ⁻ (mg/L)	01th Jul.		08th Sep.		22th Nov.	
					Total Cr (mg/L)	Total Cr (mg/kg)	Cl ⁻ (mg/L)	Total Cr (mg/L)	Cl ⁻ (mg/L)	Total Cr (mg/L)
RH-1	785055.726	8069370.579	2 400.181	44.03	0.16	83	19.99	<0.02	14.33	<0.02
RH-2	785053.557	8069372.932	2 400.115	46.96	0.18	81.4	22.49	<0.02	18.46	<0.02
RH-3	785048.892	8069378.293	2 400.041	24.46	0.1		24.99	<0.02		
RH-4	785047.734	8069379.566	2 399.958	34.73	0.12		24.99	<0.02		
RH-5	785046.645	8069380.928	2 399.998	26.42	0.11		16	<0.02		
RH-6	785045.646	8069382.373	2 400.062	20.55	0.13	64	15	<0.02	14.57	<0.02
RH-7	785044.591	8069383.728	2 400.093	29.35	0.13		19.99	<0.02		
RH-8	785059.644	8069378.939	2 400.151	48.92	0.14	77.2	34.79	<0.02	23.31	<0.02
RH-9	785058.523	8069377.733	2 400.123	49.9	0.11	73.9	34.79	<0.02		
RH-10	785052.192	8069381.830	2 400.024	44.03	0.09		34.79	<0.02		
RH-11	785050.864	8069383.341	2 400.042	31.31	0.02		24.99	<0.02		
RH-12	785049.511	8069385.260	2 400.017	24.46	0.03	64.7	23.99	<0.02	22.83	<0.02
JRH-1	785061.514	8069377.719	2 400.018				24.99	<0.02	18.46	<0.02
Rocha River	784984.577	8070318.412	2 397.100				104.97	<0.02		

Table 2 shows bimonthly concentration values, in which it is noted that in September and November, total chromium is below the detection limit of the method used in its determination, whereas in the same period the concentrations of chloride anion are descending, because this sector is a groundwater discharge area, where the exchange of groundwater and surface water of the

river happens (LI An *et al.* 2020).

The total chromium chlorides is decreasing in the transport and this is because the electric charge of the total chromium is positive, which makes it adhere to surface clay materials. The chlorides have negative electric charge, which will not adhere to clay materials because the clay surfaces also have negative charge.

The retardation factor (R) was determined by the value of the obtained distribution coefficient (K_d) with the following Equation.

$$R = 1 + \frac{\rho_b \cdot K_d}{n_e} \quad (2)$$

Where:

R : Retardation factor

K_d : Distribution coefficient (L/kg)

ρ_b : Sediment density (kg/L)

n_e : Effective porosity

Equation 1 and Equation 2 were used in numerous studies of the prediction of the transport of pollutants (Anderson, 1979; Faust and Mercer, 1980; Prickett *et al.* 1981; Srinivasan and Mercer, 1988).

The Rocha River is a recipient of groundwater

in the dry season, because of which the concentration values of total chromium and chloride anion decrease with time in this period, as it is a discharge area as mentioned above.

However, in the flood season Rocha River changes to a recharge zone and it was assumed that the hydraulic head difference is 1 meter ($\Delta H=1$ m) between the Rocha River and the piezometers.

The time step was 30 days, because the maximum rainfall events occur in the months of December, January, and February (Fig. 4).

Fig. 4 shows the variation of piezometric levels of the installed piezometers. It can be observed that the piezometric levels generally fall from March to early November, and then increase until February.

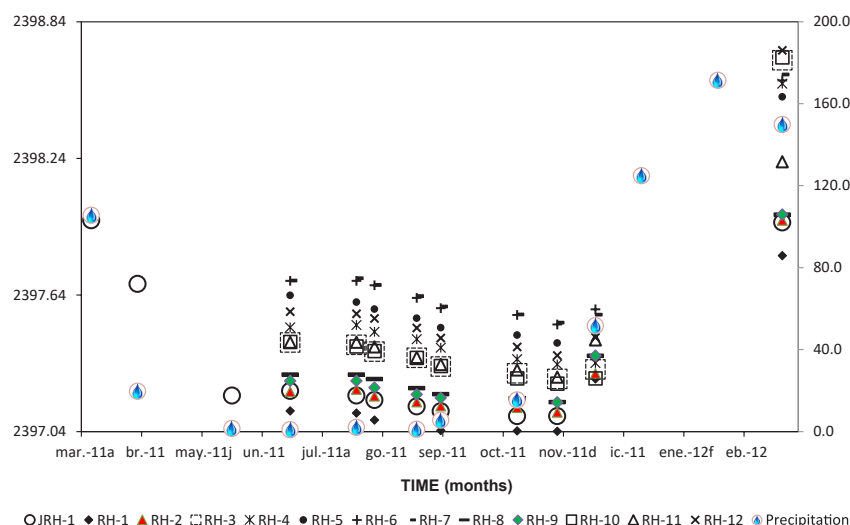


Fig. 4 Piezometric levels and precipitation.

With the obtained values listed above, the model of Ogata and Banks (1961) is applied to determine the values observed in July in a one-dimensional way, as described in Equation 3. It has been widely applied to the simulation of groundwater flow and solute transport in fractured porous media (Kavouri *et al.* 2017; Malott *et al.* 2016; Sefelnasr *et al.* 2014).

$$\frac{C}{C_0} = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{x - vt/R}{2\sqrt{D_L t/R}} \right) + \exp \left(\frac{vx}{D_L} \right) \operatorname{erfc} \left(\frac{x + vt/R}{2\sqrt{D_L t/R}} \right) \right] \quad (3)$$

Where:

C_0 : Initial concentration (M/V)

C: Final concentration at a distance of x (M/V)

R: Retardation

D_L : Hydrodynamic distribution coefficient (L^2/T)

v: Flow velocity (L/T)

t: Time (T)

x: Distance (L)

erfc: Complementary error function

Table 3 shows the initial concentration values calculated from Equation 3, where these values were reproduced based on those observed in July in Table 2. It is observed that the analytical model accurately produced the observed values.

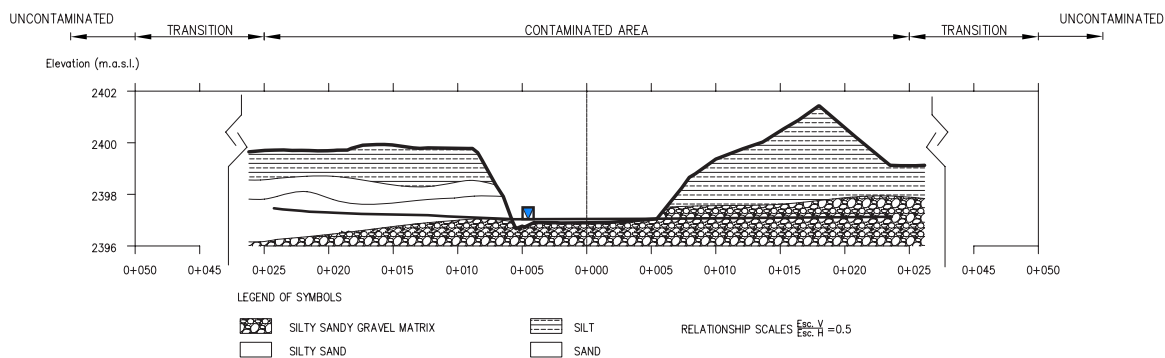
Table 3 also shows the final concentration values predicted by the analytical model, at 25 m and 50 m away from the source of contamination or the closest piezometers to the Rocha River. The final concentration values of total chromium and chloride anion are generally decreasing as they move away from the axis of the Rocha River.

Table 3 Initial concentration and observed as a result of the application of analytical model of Ogata and Banks (1961)

Line	Distance (m)	Time (days)	Total chromium (mg/L)			Chlorides (mg/L)		
			C/Co	Co	C	C/Co	Co	C
RH-1 to RH-6	15.51	30	0.29	0.44	0.13	0.25	84	20.79
RH-9 to RH-12	11.87	30	0.09	0.31	0.03	0.36	68	24.42
RH-1 to RH-6	25	30	0.09	0.44	0.04	0.05	84	4.37
RH-9 to RH-12	25	30	0.00	0.31	0.00	0.01	68	0.52
RH-1 to RH-6	50	30	5.80E-04	0.44	2.55E-04	1.04E-04	84	8.74E-03
RH-9 to RH-12	50	30	1.58E-12	0.31	4.90E-13	1.00E-07	68	6.80E-06

With the results shown in Table 3 and calibration of the analytical model, the area is demarcated into three zones, *i.e.* contaminated, transition and uncontaminated, based on the

change of groundwater flow conditions between recharge and discharge in this sector, which also drives the migration of contaminants. Fig. 5 shows delimitation of the three zones.

**Fig. 5** Delimitation of contaminated, transition and uncontaminated areas

4 Conclusions

The geology of the study area consists of alluvial terrace deposits, shaping them to the typical river bed stratigraphy in Rocha. The stratigraphy of the alluvial terraces found in drill logs were silt, sand, clay, silty sands and gravels in a sandy loam matrix.

The hydraulic conductivity values vary in the range of 0.04 m/d to 3.54 m/d. The variation of local geology, such as distribution of the sediments, grain size, effective porosity, and the degree of compaction, are all contributing factors to the hydraulic conductivity variation.

The hydrogeological parameters obtained from the hydraulic conductivity (K), distribution coefficient (K_d), pollutant concentrations (C), and retardation (R), which are required in the analytical model of Ogata and Banks (1961) are optimal for such application in both analytical and numerical models, because it can accurately predict past

values based on observed values.

The transport of contaminants does not exceed 50 m from the axis of the Rocha River, therefore they do not present any risk to the loss of agricultural soils in the study site as an agricultural area that groundwater is discharging to the river Rocha.

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