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Diffusional transport of chloride and phosphate in soils of the North Central Region of Córdoba (Argentina)

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***Abstract*— The kinetics and energy changes of chloride and phosphate adsorption in soils can be determined using mixed bed ion-exchange resin. Attending on this need, this work purpose was to determine the coefficients of diffusion of phosphate and chloride in soils of the North Central Region of Córdoba (Argentina). With disturbed samples were prepared soil columns with moisture at saturation, assessing the transport of phosphate and chloride. The average diffusion coefficients for phosphate ranged from 2.59 $\times 10^{-8}$ cm^2 s^{-1} and 9.59 $\times$ 10^{-8} cm^2 s^{-1} and the average for chloride was 4.20 $\times$ 10^{-6} cm^2 s^{-1} ($\pm 5\times 10^{-8}$). Phosphate ion has strong restrictions to diffusional movement, given its intense interaction with the solid matrix while chloride suffers only restrictions associated with the physical environment available to transport. From there, the grade of interaction of the species in diffusion with the solid phase of the soil, determines its pollutant potential and the importance of the form in which the spatial distribution of the fertilizers is done.**

***Keywords*— Chloride adsorption, phosphate adsorption, diffusion coefficients, soils fertility, ion transport.**

I. INTRODUCTION

Predicting flow and transport processes in soil is crucial in many areas of soil and environmental sciences. Modelling the transport and dispersion of substances requires knowledge of the parameters that determine its rate of diffusion [1]. Diffusive transport is the major mechanism responsible for the movement of ion phosphate to plants roots [2]. Evaluation of ion chloride diffusion is very important to investigate how this ion may turn into potential contaminant. Understanding the magnitude and variability of water and solute fluxes in the vadose zone is required to assess the risk of potential contamination of ground water resources [3].

The kinetics and energy changes of chloride and phosphate adsorption in soils can be determined using mixed bed ion-exchange resin [4]. Modelling the process requires an understanding of the parameters that determine the rate of ion diffusion in soil. Attending on this need, this work purpose was to determine the coefficients of diffusion of phosphate and chloride in soils of the North Central Region of Córdoba (Argentina).

II. MATERIALS AND METHODS

2. 1 Study area and sampling

The work was carried out in six locations of the north central region of the province of Cordoba (from 31°24' S, 64°07' W to 31°43' S, 63°55' W), Argentina. The soils were classified as Typic Haplustolls [5]. Composite soil samples (n = 25 subsamples) from the A horizon were taken for diffusion experiments. Undisturbed soil samples from 0-7 and 7-14 cm were taken to determine bulk density (BD).

In each of these composite soil samples, the following analyses were performed: soil organic matter (SOM) through the Walkley and Black procedure [6], extractable phosphorus (P_{ext}) [7] and extractable chloride by potentiometric analysis (Cl_{ext}). The properties of the soil studied are presented in Table I.

2. 2 Diffusion experiments

The samples were arranged in columns of water-saturated soil and placed in a thermostated camera at 30 ºC to generate diffusional flow from a fertilized section (900 mg Cl^-/kg soil and 1000 mg $H_2PO_4^-$/kg soil) towards a non-fertilized column. After 7, 14 and 21 days, three sample of each treatment were separated, frozen, and sectioned every 250 µm.

2.3 Determination of the time/concentration profiles.

In each section of soil, ions were extracted using Amberlite IRN-150 mixed bed ion exchange resin. The elution of ions from the exchange resin was performed with a solution of $NaNO_3$ 0.1 M, which, in addition, provided an adequate adjustment of ionic strength for chloride potentiometric analysis.

The concentration of chloride was measured using a specific electrode ORION 94-17 and the reading was recorded with an ORION 710A equipment. The concentration of phosphate in extracts was measured by spectrophotometry at 890 nm [7].

TABLE I
PROPERTIES OF THE SOIL FROM EACH LOCATION, SOIL ORGANIC MATTER (SOM), BULK DENSITY (BD), EXTRACTABLE P (P_{EXT}) AND EXTRACTABLE CHLORIDE (Cl_{EXT})

Site	SOM (mg kg^{-1})	BD (Mg m^{-3})	P_{ext} (mg kg^{-1})	Cl^{-}_{ext} (mg kg^{-1})
Las Arrias	24.3	1.19	93.3	37.9
Cañada de Luque	18.0	1.20	93.5	32.9
Jesús María	17.9	1.16	67.9	31.3
Monte Cristo	13.7	1.34	34.3	22.2
Piquillín	14.1	1.29	69.1	21.5
Pilar	14.9	1.29	42.4	13.6

2.4 Calculation methods.

To estimate the diffusion coefficient (*D*) at transient state, the general diffusion equation was:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad 1$$

The system was of cylindrical symmetry, with flow in an infinite medium from $x<0$ to $x>0$. In the soil columns in contact, at $t = 0$, $C = C_0$ for $x > 0$ and that $C = C_{fert}$ for $x < 0$, being C_0 the concentration in the not fertilized soil, and C_{fert} the concentration in the enriched soil. The analytical solution for this experimental geometry is [8]:

$$C_{(x,t)} = C_o + \tfrac{1}{2} erfc\left(\frac{x}{2\sqrt{Dt}}\right)\cdot\left(C_{fert} - C_o\right) \qquad 2$$

The results of the analysis of sections of soil columns were fitted by nonlinear regression to the Ec. (2), in order to estimate the diffusion coefficients for Cl^- and PO_4^{3-}.

III. RESULTS & DICUSSIONS

Phosphate concentration profiles, obtained after 14 days of contact between columns of fertilized soil and non-fertilized, are presented in Figure 1.

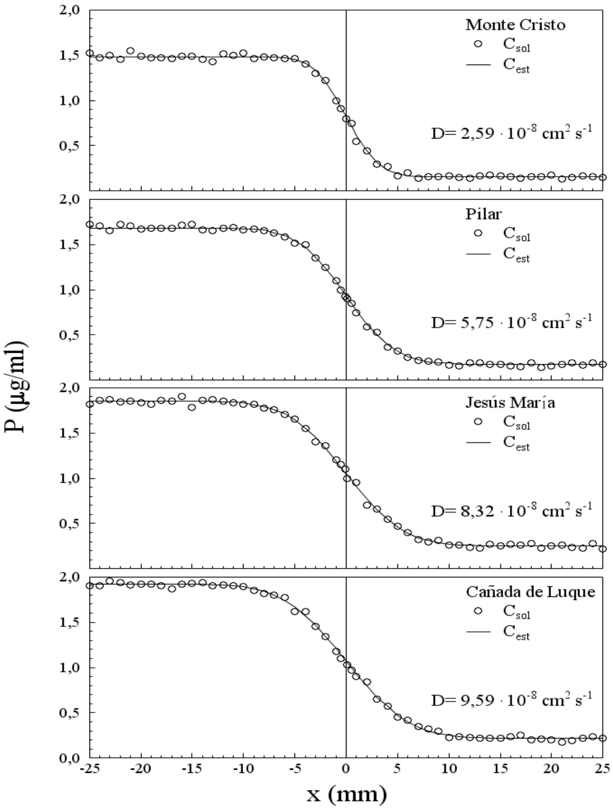

Fig.1: Profiles of phosphorus concentration after 14 days of diffusion. D: Diffusion Coefficient. Continuous lines: simulated concentration profiles using Ec 2.

The average diffusion coefficients for the phosphate ion, estimated applying the equation (2), were found between 2.59×10^{-8} cm^2 s^{-1} and 9.59×10^{-8} cm^2 s^{-1}. These values are within the highest cited for this nutrient [9], and are compatible with cases in which the soil provides an adequate level of extractable phosphorus for the crops, as it was pointed out by different authors [10,4].

The studied soils, in their different management situations, have higher values of extractable phosphorus than the cited literature. The high values of D agreed with those obtained by Bachmeier [4] who pointed out that the comparatively low value of the affinity constant of Langmuir indicates a position of the desorption reaction shifted to the solution. That situation determines that an important fraction of the nutrient is available for the difusional transport [9].

Sites with higher bulk density had low diffusion coefficients. It was the case of Piquillín, Montecristo and Pilar, where the D was between 2.59×10^{-8} cm^2 s^{-1} and 5.75×10^{-8} cm^2 s^{-1}, suggesting that lower porosity generates additional restrictions to the desorption process. In this sense, Cox et al. [11] established, by measuring the mobility of phosphate in soil columns, that in addition to the chemical characteristics of the soil matrix, physical parameters associated with the porous fraction should be considered to explain the delay in the displacement of the nutrient [3].

In the case of chloride, the average diffusion coefficient was 4.20×10^{-6} cm^2 s^{-1}, while its value in pure water at infinite dilution (25ºC) is 2.03×10^{-5} cm^2 s^{-1}, which means that the restriction provided by the soil environment reduces the theoretical value 5 times, approximately. This is far from the two or three orders of magnitude of difference observed in the reduction of D to phosphate, an ion with strong electrostatic interaction with the adsorbent matrix.

Figure 2 presents the simulated dispersion of phosphate and chloride that would be obtained within 30 days of diffusion. The phosphate ion's diffusion advance in unfertilized soil is in the order of 10 mm, which indicates the importance of the precise location of phosphorus fertilizers in relation to the young plants. The low mobility detected in plots with greater state of physical and chemical degradation shows that there are severe restrictions on the movement of ions by high interaction with the solid matrix. That suggests the requirement of distribute fertilizers using a broadcast method in this type of soils.

In the simulation for chloride diffusion, was noted a strong trend towards equalization of concentrations on either sides of the reference plane ($x = 0$). This indicates that, under similar soil conditions, ions with little or no interaction with the solid phase have high-speed dispersion. This is still further evidence of the potential groundwater pollution that can be caused by this ion [12].

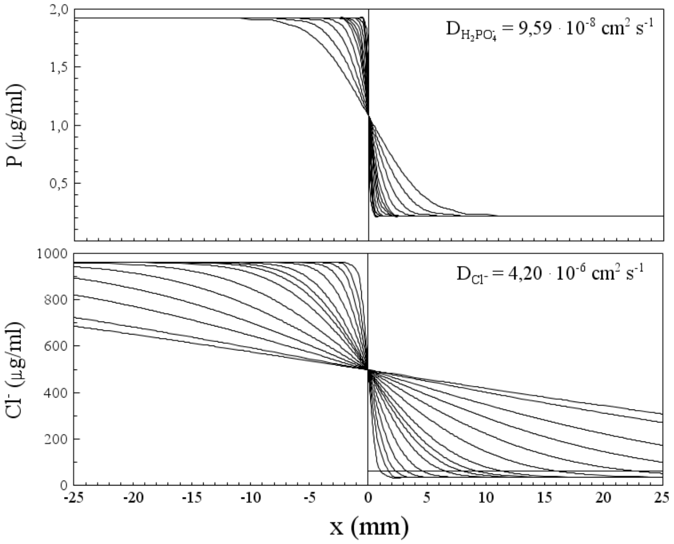

Fig.2: Successive concentration profiles for phosphate and chloride simulated up to 30 days of diffusion.

IV. CONCLUSIONS

The difusional transport parameter is highly sensitive to the physical and chemical conditions of the soil.

Phosphate ions have strong restrictions on their difusional movements given their strong interaction with the solid matrix. The diffusion coefficient of phosphate decreases with the physical degradation of the environment.

The chloride ions have little or no interaction with the solid phase; consequently, they have a high dispersion speed, which turns them into potential pollutants.

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