

Dynamics of Ions in Soils Irrigated with Saline Reject

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Abstract

The objective of this work was to evaluate the variation in the electrical conductivity and the mobilization of ions present in reject brine from desalination plant of brackish well water in three types of soil. The mobilization of the contaminant ions in the reject brine was studied in glass percolation columns, which were filled with soil of contrasting textures (eutrophic CAMBISOL, typic dystrophic Red OXISOL, ENTISOL Quartzipsamment). Experiments were repeated three times each, and the initial and final concentrations of the ion contaminants were analyzed. The pollution potential of this residue was determined by the retardation factor and dispersion-diffusion coefficient of Ca^{2+} and Mg^{2+} , besides the variation of electrical conductivity along the profile of each soil studied. In the Red Oxisol, Ca^{2+} and Mg^{2+} ions move with greater ease resulting in possibility largest of potential of ground water contamination. In Entisol Quartzipsamment presented higher Mg^{2+} (R) ion advancement speed, that is, higher subsurface contamination power for these ions. The eutrophic Cambisol presented low diffusion-dispersion coefficient in all the evaluated ions and, therefore, lower mobility of the ions in the soil profile, and consequently, a greater possibility of contamination when irrigated with reject brine.

Keywords: irrigation, semi-arid, water reuse, reverse osmosis, calcium, magnesium

1. Introduction

The rational use of water in irrigated agriculture has been a recurrent discussion along the last decades, especially with respect to water quality (Ayers & Westcot, 1999; Silva et al., 2007; Anami et al., 2008). The use of water with high contents of salts results in the salinization of agricultural soils, causing disorders of physical and chemical nature in these soils, besides limiting crop development (Miranda et al., 2011; Mesquita et al., 2015; Sá et al., 2015). Since the water in some wells has high content of salts, desalinators have become necessary to make its use viable, and reverse osmosis desalination is one of the most employed techniques in arid and semi-arid regions (Santos et al., 2010a; Cosme et al., 2011; Oliveira et al., 2016).

Brackish water desalination through reverse osmosis allows the use of water for human consumption and agriculture. However, besides purified water, this process generates saline waste with high potential of soil salinization, which requires adequate disposal (Santos et al., 2011). In general, the final disposal of the saline waste in the soil results in its salinization, thus compromising its chemical and physical quality. In this context, this waste poorly managed in agriculture may pose risks to the environment, promoting soil salinization and reduction of agricultural production (Garcia et al., 2008; Dias et al., 2010; Santos et al., 2011).

The percolation column is a tool used to simulate the behavior of solute movement through the soil. It is based on the principle of accommodation of previously treated soil with well-known physical characteristics, followed by the application of the solution to be studied in the soil, with subsequent infiltration, and the collection of the predetermined pore volumes. Importantly, the dimensions of the column are measured in order to calculate the pore volume to be collected (Silva et al., 2012; Matos et al., 2013; Pinho et al., 2014; Silva et al., 2016).

Given the above, the study on the dynamics of ions present in the saline wastewater disposed in the soil is of extreme importance for the evaluation of the contamination potential, either of soil and/or water sources; in addition, the ions present in this water will show different behaviors for each type of soil (Oliveira et al., 2016).

Therefore, the present study aimed to evaluate the variation in electrical conductivity and mobilization of calcium (Ca) and magnesium (Mg) ions present in saline wastes from the brackish water desalination process in three types of soil, in order to contribute with information on the polluting potential of these waters.

2. Material and Methods

The experiment was carried out at the Soil Physics Laboratory from Rural Federal University of Semi-Árido (UFERSA). Three soil types of Caatinga bioma from different regions of Baraúna and Natal, Rio Grande do Norte State, were used. The classification of the soils and their locations are shown in Table 1.

Table 1. Studied soil classifications and taken locations of sample

| Classification (SiBCS) | Location (RN) |
|-----------------------------|--------------------|
| Eutrophic CAMBISOL | Baraúna |
| Typic Dystrophic Red OXISOL | Alagoinha, Mossoró |
| Entisol Quartzipsamment | Boa Fé, Mossoró |

Note. SiBCS: Brazilian Soil Classification System.

Each percolation column was filled with one type of soil sample, and the experiment was performed in triplicate, producing a total of nine experimental units. The soil was filled to a height of 0.20 m within the percolation column, with a crushed stone layer of 0.005 m (1.00 to 0.50 mm) as a base to facilitate drainage and to prevent loss of soil material (Figure 1).

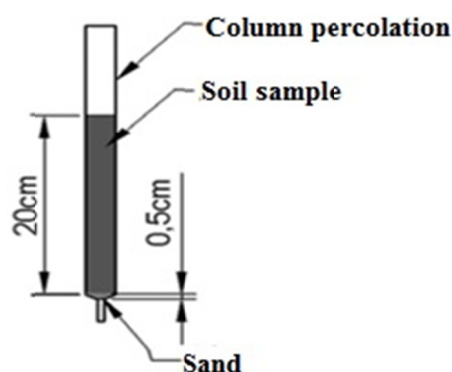


Figure 1. Schematic drawing for assembling and filling the percolation columns soil micro arthropods collecting was made with an Uhland-type. Soils were taken from the top 20 cm deep layer in a zigzag pattern for the percolation study to ensure that representative samples were obtained from each site. Soil samples with deformed structures were taken for analyses of the chemical and physical parameters. To perform the analyses, samples were used as air-dried fine earth (ADFE), obtained by air-drying, crumbling and sieving (< 2 mm). To perform soil bulk density and total porosity, collecting of soil samples of un-deformed structures were made with Uhland-type, stainless steel auger 5 cm in diameter and 5 cm in height. The physical and chemical analyses followed the recommendations outlined in the Manual of Soil Analysis Methods (Embrapa, 1997)

The assessment physical parameters included: particle size distribution by pipette method utilizing sodium hexametaphosphate as a chemical dispersant; solid density (ρ_s) by the volumetric flask method; soil density (ρ) by volumetric ring method and, total porosity (α) as described in Equation 1.

$$\alpha = \left(1 - \frac{\rho}{\rho_s} \right) \times 100 \quad (1)$$

Where, α is the total calculated porosity (%), ρ is the soil density, (kg dm^{-3}), and ρ_s is the solid density (kg dm^{-3}). Results are shown in Table 2.

Table 2. Distribution of particle size, texture classification, soil density (ρ), solid density (ρ_s), and calculated total porosity (α)

| Soil | Particle size distribution | | | Texture classification (SBCS) | P | ρ_s | α |
|-----------------------------|-----------------------------------|-------|--------|-------------------------------|------|-----------------------------|----------|
| | Sand | Silt | Clay | | | | |
| | ----- (g kg ⁻¹) ----- | | | | ---- | (kg dm ⁻³) ---- | (%) |
| Eutrophic Cambisol | 662.80 | 96.50 | 240.70 | Frank-clay-sandy | 1.46 | 2.47 | 40.89 |
| typic dystrophic Red Oxisol | 823.80 | 28.40 | 147.80 | Sand-frank | 1.68 | 2.51 | 33.07 |
| Entisol Quartzipsamment | 897.50 | 21.60 | 80.90 | Sand | 1.64 | 2.59 | 36.68 |

Note. SBCS: Brazilian Society for Soil Science; ρ : soil density; ρ_s : solid density; α : calculated total porosity.

Measured chemical characteristics were: Soil pH (H₂O) determined in a solution of 1:2.5 soil-water mixture, electrical conductivity of the saturated soil-paste extract (EC_s), exchangeable calcium (Ca²⁺) and magnesium (Mg²⁺) by complexometry after extraction with KCl 1 mol L⁻¹, exchangeable aluminum (Al³⁺) by extraction with KCl 1 mol L⁻¹ and titrated with NaOH 0.025 mol L⁻¹, available phosphorus (P), sodium (Na⁺) and potassium (K⁺) extracted in Mehlich-1 and determined by spectrophotometry visualization (P) and detected by flame photometry (Na⁺ and K⁺), the potential acidity (H+Al)—quantified by titration with 0.025 mol L⁻¹ NaOH after extraction with calcium acetate at a concentration of 0.5 mol L⁻¹ with a pH of 7.0 and, soil organic matter (SOM) - as assessed by 0.005 mol L⁻¹ ferrous ammonium sulfate titration after being heated in a uniform plate with 0.02 mol L⁻¹ potassium dichromate (Table 3).

Table 3. Characterization of soil chemical properties

| Soil | pH | EC _s | SOM | P | K ⁺ | Na ⁺ | Ca ²⁺ | Mg ²⁺ | Al ³⁺ | (H+Al) |
|------|---------|-----------------------|-----------------------|-------|------------------------------|-----------------|------------------|---|------------------|--------|
| | (water) | (dS m ⁻¹) | (g kg ⁻¹) | ----- | (mg dm ⁻³) ----- | ----- | ----- | (cmol _c dm ⁻³) ----- | ----- | ----- |
| 1 | 7.46 | 0.06 | 10.99 | 2.28 | 166.87 | 21.74 | 6.24 | 2.50 | 0.00 | 8.58 |
| 2 | 5.35 | 0.06 | 8.80 | 1.41 | 35.29 | 15.96 | 0.98 | 0.49 | 0.06 | 3.82 |
| 3 | 6.00 | 0.06 | 6.51 | 9.10 | 55.24 | 17.66 | 1.55 | 1.17 | 0.02 | 0.33 |

Note. pH - hydrogen potential, EC_s - electrical conductivity of the saturated soil-paste extract, SOM - soil organic matter, P - available phosphorus, K⁺ - potassium, Na⁺ - sodium, Ca²⁺ - calcium, Mg²⁺ - magnesium, Al³⁺ - aluminum and, (H+Al) - potential acidity. Soil 1 = Eutrophic Cambisol; Soil 2 = typic dystrophic Red Oxisol; Soil 3 = Entisol Quartzipsamment.

The reject brine sampling was taken in the Boa Fé rural community in Mossoró, Rio Grande do Norte State, Brazil. This community has a desalination plant by reverse osmosis that provides treated water to the population and, as a result of the desalination process, also generates reject brine.

The chemical characteristics of the saline tailings measured in this study were pH, electric conductivity (EC_w), potassium (K⁺), sodium (Na⁺), calcium (Ca²⁺), magnesium (Mg²⁺), chloride (Cl⁻), and the sodium adsorption ratio (SAR), which was determined according to the methodology described by Tedesco et al. (1995) (Table 4).

Table 4. Reject brine chemical analysis

| pH | EC _w | K ⁺ | Na ⁺ | Ca ²⁺ | Mg ²⁺ | Cl ⁻ | SAR |
|------|-----------------|-----------------------------------|--|--|---|-----------------|------|
| | | ----- (dS m ⁻¹) ----- | ----- (mmol _c L ⁻¹) ----- | ----- (mmol _c L ⁻¹) ----- | ----- (mmol _c L ⁻¹) ^{1/2} ----- | | |
| 7.42 | 10.15 | 0.80 | 4.11 | 31.49 | 25.21 | 89.70 | 0.76 |

Note. pH - hydrogen potential; EC_w - electrical conductivity; K⁺ - potassium; Na⁺ - sodium; Ca²⁺ - calcium; Mg²⁺ - magnesium; Cl⁻ - chloride; SAR - sodium adsorption ratio.

According to the EC_w data, the water is highly brackish (EC_w = 10.15 dS m⁻¹), and it appears, according to the guidelines proposed by Ayers and Westcot (1999), that the reject brine have a severe use restrictions due to salinity risks (EC_w > 3.00 dS m⁻¹). Additionally, according to the same authors, the chloride ion has a severe degree of restriction (Cl⁻ > 10 mmol_c L⁻¹).

To fill the percolation columns, volume was calculated using the dimensions of 390 mm height and 34.52 mm diameter. The soil was weighed to determine a bulk density measure and for total porosity calculations. Before filling the soil, the gravel layer was moistened to facilitate packing of the soil, thus reducing the chance of the soil passing the gravel. The determination of soil volume, pore volume, soil saturation and percolate collection are described in Oliveira et al. (2016).

Each solution sample was placed on properly identified collectors with each soil, repetition, and pore volume to be collected. All collectors were closed and sealed with adhesive tape to prevent possible loss. Then, the samples were allocated and stored in a freezer at an optimum temperature to avoid evaporative loss.

After reaching a permanent outflow in the percolation column, a five-pore volume pulse of displacing solution was applied, collecting effluent fractions with a 0.5-pore volume, which were placed in plastic containers with pressurized covers and frozen for further analysis. The K, Na and Cl concentrations in the effluent were determined (C). The relative concentrations (C/C_0) for each ion were calculated, C_0 being the concentration in the shifter fluid.

The retardation factor (R) and the dispersion-diffusion coefficient (D) values were obtained from the DISP program (Borges Júnior & Ferreira, 2006). As input data for the program, the following variables were used: flow, total porosity, soil column height (20 cm), pore volume, and experimental relative concentration.

The output variables were the R and D values, which were analyzed by the Tukey test at a 5% probability ($P < 0.05$). The Tukey test with a 5% probability was used to analyze the experimental data using SISVAR software (Ferreira, 2011).

3. Results and Discussion

The Ca^{2+} ion exhibited a sigmoid behavior in all soils studied, evidencing the adsorptive effect of these soils with Ca^{2+} , allowing to obtain its respective transport parameters under conditions of soil contamination by the excess of salts from the waste of desalinators (Figure 2). For the studied soils, the Latosol and Neosol reach their maximum levels of relative correlation with only 0.6 NPV, which is related to the predominance of macropores, directly responsible for water conduction in the soil during infiltration processes (Silva et al., 2012; Pinho et al., 2014; Silva et al., 2016). In addition, the Cambisol had the highest peak of the Ca^{2+} ion compared with the other soils, even exceeding 1 C/C_0 (Figure 2). This fact can be related to the large presence of calcium carbonate in these soils (Santos et al., 2013), which, after being solubilized, was leached along with the wastewater.

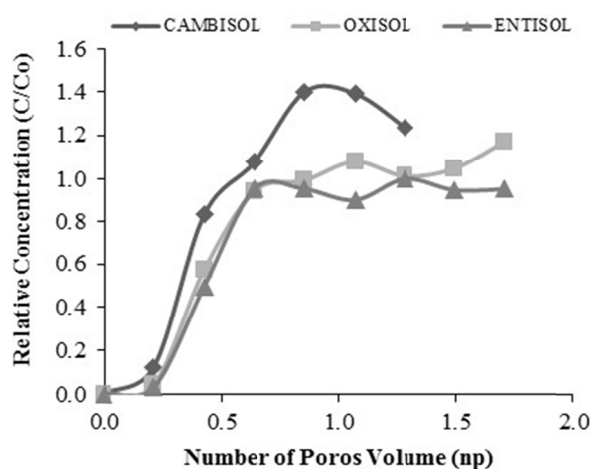


Figure 2. Calcium curve for each soil studied

As can be observed, for the Ca^{2+} ion, the retardation factor (R) was statistically equal for all soils, demonstrating that the slope point is almost equal, i.e., their retention powers were similar for this ion (Table 6). On the other hand, the dispersion-diffusion coefficient was statistically different for all soils, which means that, in each soil, the displacement of Ca is variable, being higher in soils with higher percentage of macropores: Latosol > Neosol > Cambisol (Table 5). With lower values of dispersion-diffusion coefficient (D) for the Ca^{2+} ion, the Cambisol showed higher contamination power; consequently, the Latosol showed lower contamination power by

this ion (Table 5). In an experimental and numerical study on Ca^{2+} behavior in soil of the municipal landfill of Volta Redonda, Souza (2010) concluded that the higher the Ca^{2+} concentration in the contaminating solution, the more it is adsorbed by the soil. This result corroborates with that observed in the present study because, even with the high initial content of Ca^{2+} observed in the Cambisol (Table 3), the presence of a large number of negative charges allows this soil to continue avid for Ca^{2+} ions, and it can be easily salinized compared with the other studied soils.

Table 5. Calcium ion parameters in each soil subjected to Tukey test at 0.05 probability level

| Soil | R | D ($\text{cm}^2 \text{h}^{-1}$) |
|-----------------------------|--------|-----------------------------------|
| Eutrophic CAMBISOL | 0.33 a | 25.07 a |
| Typic Dystrophic Red OXISOL | 0.40 a | 550.61 b |
| Entisol Quartzipsamment | 0.42 a | 109.22 c |

Table 6. Magnesium ion parameters in each soil subjected to Tukey test at 0.05 probability level

| Soil | R | D ($\text{cm}^2 \text{h}^{-1}$) |
|-----------------------------|--------|-----------------------------------|
| Eutrophic CAMBISOL | 0.46 a | 63.71 a |
| Typic Dystrophic Red OXISOL | 0.51 b | 403.09 b |
| Entisol Quartzipsamment | 0.40 c | 148.66 c |

For Mg^{2+} , the sigmoid curve was similar for Latosol, Cambisol and Quartzarenic Neosol. In addition, there was small oscillation in the points of stability of the curve (Figure 3). However, it is noted that the Quartzarenic Neosol has the highest peaks of the Mg^{2+} ion, close to the maximum level of relative concentration ($C/\text{Co} = 1$). This behavior can be explained by the low number of negative charges present in these soils, due to their predominant composition of quartz, and their large number of macropores resulting from the loose structure (Santos et al., 2013), allowing Mg^{2+} ions to move more easily compared with the other soils, due to its lower retardation factor (Table 6). Santos et al. (2010b) found that the adsorption effect of the Mg^{2+} ion in Regolithic Neosol can be observed through its effluent distribution curve, which reflects its highest retardation factor, compared with Ca, Na and K.

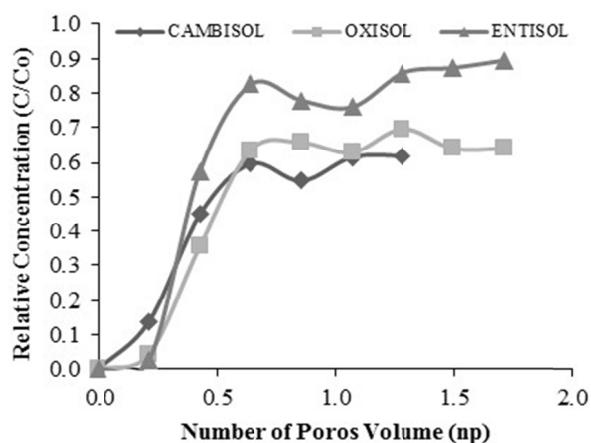


Figure 3. Magnesium curve for each soil studied

As can be observed, for the Mg ion, the retardation factor was statistically different for the soils, demonstrating that the slope point is different for the soils. The dispersion-diffusion coefficient was also statistically different for the soils, which means that, in each soil, the displacement of Mg^{2+} is variable, being higher in the Latosol (Table 6). The D values for the Mg ion, regarding its contamination power, are higher in the Cambisol and lower in the Latosol. Since the R values are statistically different for the studied soils, retention powers of the soils are different for this ion. However, as presented in the study of Ferreira (2006), who worked with conilon coffee

wastewater, the retardation factor and dispersion-diffusion coefficient for the ions K^+ , Na^+ , Ca^{2+} and Mg^{2+} were lower than those of the present study.

For electrical conductivity, the same behavior of chloride was evident in the studied soils (Figure 4). Regarding the chemical characteristics of the studied soils, it is possible to note the reason for each behavior. Since the CEC of the Cambisol was higher compared with the others, this soil has greater potential of ion retention, thus showing higher chances of contamination by the saline waste used. However, as evidenced, for each ion, the Neosol exhibited higher advance speed of K^+ and Cl^- (R), i.e., higher contamination power. Melo (2006), through resident concentration curves, found that the ions advanced more in the column of sandy-textured soil, in comparison to those of medium and clay texture, whose retardation factors are, in general, higher.

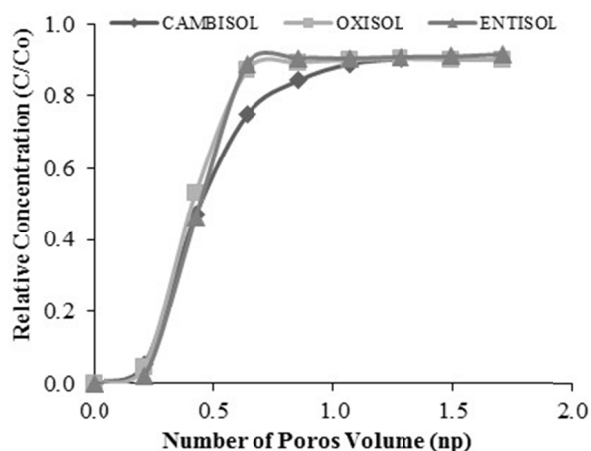


Figure 4. Electrical conductivity curve for each soil studied

Monitoring the mobilization of Na^+ , K^+ and Cl^- ions in the same soils studied in the present research, Oliveira et al. (2016) observed that there was difference in their displacement between the types of soils. These authors observed that K^+ and Cl^- ions exhibited higher advance speed in the Neosol, which showed highest risk of contamination in surface, corroborating the displacement of Mg^{2+} ions observed in the present study (Figure 2). In the Latosol, all ions (Na^+ , K^+ and Cl^-) move more easily, a fact also observed for Ca^{2+} and Mg^{2+} ions in the present study (Figures 1 and 2). Hence, the application of saline waste in this soil leads to great possibilities of water table contamination. For the Cambisol, the small displacement of Ca^{2+} and Mg^{2+} ions, in the present study, has also been observed by the authors for the ions Na^+ , K^+ and Cl^- , denoting that this soil has high buffering power and, consequently, higher risk of salinization compared with the others.

4. Conclusions

In the Red Oxisol, Ca^{2+} and Mg^{2+} ions move with greater ease resulting in possibility largest of potential of ground water contamination.

In Entisol Quartzipsamment presented higher Mg^{2+} (R) ion advancement speed, that is, higher subsurface contamination power for these ions.

The eutrophic Cambisol presented low diffusion-dispersion coefficient in all the evaluated ions and, therefore, lower mobility of the ions in the soil profile, and consequently, a greater possibility of contamination when irrigated with reject brine.

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