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Electrical Conductivity and Chemical Composition of Soil Solution: Comparison of Solution Samplers in Tropical Soils

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ABSTRACT: Soil solution samplers may have the same working principle, but they differ in relation to chemical and physical characteristics, cost and handling, and these aspects exert influence on the chemical composition of the soil solution obtained. This study was carried out to evaluate, over time, the chemical composition of solutions extracted by *Suolo Acqua*, with the hydrophilic membrane (HM) as a standard, using soils with contrasting characteristics, and to determine the relationship between electrical conductivity (EC) and concentration of ions and pH of soil solution samples. This study was carried out under laboratory conditions, using three soils samples with different clay and organic matter (OM) contents. Soil solution contents of F^-, Cl^-, NO_3^-, Br^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, were analyzed, as well as inorganic, organic, and total C contents, pH, and EC, in four successive sampling times. Soil solution chemical composition extracted by the *Suolo Acqua* sampler is similar to that collected by the HM, but the *Suolo Acqua* extracted more Na^+ and soluble organic C than the HM solution. Solution EC, cation and anion concentrations, and soluble C levels are higher in the soil with greater clay and OM contents (*Latossolo* and *Cambissolo* in this case). Soil solution composition varied over time, with considerable changes in pH, EC, and nutrient concentrations, especially associated with soil OM. Thus, single and isolated sampling of the soil solution must be avoided, otherwise composition of the soil solution may not be correctly evaluated. Soil solution EC was regulated by pH, as well as the sum of cation and anion concentrations, and the C contents determined in the soil liquid phase.

Keywords: electrical conductivity, water soluble carbon, soil liquid phase, soil solution extraction methods.

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INTRODUCTION

Soil solution samplers differ in size, length, diameter, pore diameter, shape, and the physical properties of their components (Litaor, 1988). Depending on the type and physical and chemical properties of the sampler membrane, there may be limitations on evaluating the contents of chemical elements in solution due to the adsorption or desorption of cations and anions in the samplers (Silva et al., 2004; Kiggundu et al., 2010). Components used in the manufacture of porous cups may also increase solution sampling time, due to biochemical reactions between the sampler membrane and the solution (Ross and Bartlett, 1990; Wolt, 1994). Some sampler membranes have selective pore diameters that prevents the entrance of clay particles and organic materials, altering the composition of the soil solution (Litaor, 1988; Spangenberg et al., 1997). Variation in the volume of solution collected by the sampler is also commonly reported (Grossmann and Udluft, 1991), as well as pore plugging, which prevents the use of samplers in successive extractions of the solution (Di Bonito et al., 2008; Falcon-Suarez et al., 2014). All the aforementioned factors determine the relative efficiency of samplers and may further alter the determinations of chemical composition of the soil solution.

Comparing ceramic samplers with porous Teflon solution samplers, Zimmerman et al. (1978) reported no clogging of pores in long-term sampling, or changes in the solution nutrient concentrations when the Teflon sampler was used. The ceramic sampler retained more NH_4^+, PO_4^{3-}, NO_3^-, NO_2^-, and silicon compared to Teflon. Despite its improved performance, the authors report that the Teflon sampler cost is high, which restricted its use in many studies. A big problem of a ceramic sampler is its capacity to adsorb anions and release cations, such as Ca^{2+}, Mg^{2+} and Al^{3+} (Litaor, 1988). Adsorption of ions (Menendez et al., 2003; Kiggundu et al., 2010) and even increased release of Ca^{2+} and Mg^{2+}, overestimating their concentrations in solution (Silva et al., 2004), are other limitations reported for ceramic solution samplers.

The hydrophilic membrane (HM) is characterized as a non-destructive method for solution extraction since it can be set up directly in the soil. The main body of the HM is composed of a cylindrical tube made from an inert hydrophilic polymer membrane with a 0.1 µm micropore designed to retain soil organisms and high molecular weight compounds found in the soil solution. The hydrophilic membrane is selective to some soluble C fractions and organo-metallic complexes found in the soil solution (Spangenberg et al., 1997; Sigfusson et al., 2006). The HM is used as a reference in solution extraction methods since adsorption or sorption of ions present in the liquid phase is not reported for this sampler (Spangenberg et al., 1997; Knight et al., 1998). Furthermore, the HM quickly and easily samples the soil solution, with minimal intervention in its chemical composition (Argo et al., 1997). In addition, the technical efficiency of HM is recognized worldwide, especially for evaluating nutrient availability in soils (Meijboom and van Noordwijk, 1992) and in substrates for plant growth (Argo et al., 1997). However, the HM has not yet been tested under the conditions of Brazilian crop fields or compared to samplers currently used for sampling soil solutions in Brazil.

Because of the advantages and technical characteristics of HM and because it is an imported product, it is necessary to compare it with a sampler of national origin, the *Suolo Acqua*, which has a low price, is made with a hard plastic body, and is filled with an inert material. The *Suolo Acqua* sampler is not selective to high molecular weight organic molecules and it does not interfere in the composition of the solution sampled. In addition, the use of vacuum-conditioned tubes along with the *Suolo Acqua* may allow sampling of the soil solution in an automated way and in a shorter time than the HM. *Suolo Acqua*, due to its easy installation and handling, allows successive samplings of the soil solution and can be used either in crop fields or in small pots. Thus, the *Suolo Acqua* sampler tested here may serve as an alternative method for evaluating the EC, pH, soluble C fractions, and ion concentrations in the soil solution, technically matching the performance of the standard sampler (HM) most used in the market. The *Suolo Acqua* sampler does not retain or release ions; it collects the soil solution in a shorter time and its pores do not clog over time or after successive use.

Soils differ over time in terms of ion concentrations in the soil solution, with variations in the levels of nutrients, pH, and EC; and the chemical composition of the soil solution depends on soil water content, the soil layer sampled, and the targeted nutrient (Miranda et al., 2006). Thus, sampling the solution at only one time does not reflect its variations in composition over different climatic seasons.

We hypothesized that, over time, variations in solution composition are more evident in the soil with high OM and clay contents in comparison to soils with low clay and C contents since in rich clay-textured soils, the reservoirs and pools of nutrients that can be mineralized are higher, increasing the salt and ion contents in the soil solution. Changes in soil pH depend on the characteristics of the soil studied and this is a key factor regulating the concentration of ions in the soil solution. The performance of *Suolo Acqua* in evaluating the chemical composition of the solution is similar to the HM sampler, although a greater recovery of C is expected in the solution sampled by the *Suolo Acqua*. Specific objectives were to evaluate the pH, EC, and concentration of anions and cations in the solution extracted by the *Suolo Acqua* and by the hydrophilic membrane samplers. We also compared the chemical composition of solutions from soils with contrasting texture and OM contents. The variations in solution composition over time were also investigated.

MATERIALS AND METHODS

Two solution samplers were tested, the hydrophilic membrane (HM), which is a reference method in the market, and *Suolo Acqua* (patent BR 20 2014 026836 2), a sampler developed at the Soil Science Department, Universidade Federal de Lavras, Lavras, MG, Brazil. Solution sampling was performed in three soil samples with sharp differences in their degrees of fertility, and clay and organic matter (OM) contents. The soils investigated were classified as *Neossolo Quartzarênico - RQ* (Typic Quartzipsamment), *Latossolo Húmico Distrófico - LHd* (Humic Hapludox) *and Cambissolo Háplico Tb Distrófico - CXbd* (Typic Dystropepts), according to the Brazilian System of Soil Classification (Santos et al., 2013) and the USDA Soil Taxonomy (Soil Survey Staff, 2010). Soil samples were collected under natural conditions from the 0.00-0.20 m soil depth, air dried, macerated, and sieved (2 mm). Chemical and physical characteristics of the soil samples investigated are shown in table 1.

Soil samples were characterized as follows: pH in water, SMP pH, EC, Ca^{2+}, Mg^{2+}, Al^{3+}, potential acidity (H+Al), Al saturation (AlS), base saturation (BS), total carbon (C), organic matter (OM), total nitrogen (N), NH_4^+-N, NO_3^--N, buffered (pH 7) cation exchange capacity (CEC), effective CEC (eCEC), S-sulfate, K^+, P-extracted by the Mehlich-1 solution, remaining P, Zn^{2+}, Fe^{2+}, Mn^{2+}, Cu^{2+}, and B, following the analytical procedures described in Santos et al. (2009). Electrical conductivity and pH were determined in a soil:water ratio of 1:2.5 (0.01 dm^3 of dried soil:25 mL H_2O), which was stirred for 30 min, allowed to stand for another 30 min, and stirred again for 30 s; the solution EC and pH were then measured. Total C content was determined by dry combustion in an automated analyzer (Elementar brand, Vario TOC Cube model). The solution EC was determined in a TECNAL-TEC 4MP conductivitymeter. Soil textural fractions were quantified according to the Bouyoucos method (Claessen, 1997).

Description of the solution sampler

The *Suolo Acqua* sampler (Figure 1a), proposed in this study as an alternative sampler to HM, is constituted by an internal inert filter membrane previously decontaminated in successive

Table 1. Fertility properties, electrical conductivity (EC), and granulometry of the three studied soils

Property	Latossolo Húmico Distrófico[(1)]	Neossolo Quartzarênico	Cambissolo Háplico Tb Distrófico
pH(H_2O)	5.5	5.2	5.6
pH(SMP)	5.4	6.1	6.0
P (mg dm^{-3})	4.2	14.0	2.6
K (mg dm^{-3})	101	39	59
Ca^{2+} ($cmol_c$ dm^{-3})	3.2	0.4	2.3
Mg^{2+} ($cmol_c$ dm^{-3})	1.2	0.1	0.4
Al^{3+} ($cmol_c$ dm^{-3})	0.4	0.6	0.3
H+Al ($cmol_c$ dm^{-3})	7.9	4.0	4.2
eCEC ($cmol_c$ dm^{-3})	5.1	1.2	3.1
CEC ($cmol_c$ dm^{-3})	12.0	4.6	7.0
BS (%)	35	14	40
AlS (%)	8.3	53	8.7
C (%)	6.5	0.9	3.0
OM (dag kg^{-1})	7.1	1.6	3.7
Total N (g kg^{-1})	5.9	1.1	3.3
EC (μS cm^{-1})	76	35	62
Rem. P (mg L^{-1})	7.3	41	27
Zn^{2+} (mg dm^{-3})	2.2	0.6	2.8
Fe^{2+} (mg dm^{-3})	47	79	116
Mn^{2+} (mg dm^{-3})	16	3.7	22
Cu^{2+} (mg dm^{-3})	0.7	0.3	1.1
B (mg dm^{-3})	0.1	0.1	0.1
S (mg dm^{-3})	7.5	5.1	9.9
NH_4^+-N (dag kg^{-1})	35	22	29
NO_3^--N (dag kg^{-1})	23	28	27
Mineral N (dag kg^{-1})	58	50	56
Clay (g kg^{-1})	510	40	350
Silt (g kg^{-1})	150	30	190
Sand (g kg^{-1})	340	930	460

(1) Soil nomenclature according to the Brazilian System of Soil Classification (Santos et al., 2013). (2) P: P extracted in the Mehlich-1 solution; Rem. P: remaining phosphorus; eCEC: effective cation exchange capacity; CEC: buffered (pH=7) cation exchange capacity; BS: base saturation; AlS: aluminum saturation; C: total carbon; OM: organic matter; S: S-sulfate; Clay, silt, sand: quantified according to the Bouyoucos method.

washings with hydrochloric acid and deionized water, covered by porous hard plastic whose internal body is connected to a flexible silicone tube. The operating principle of *Suolo Acqua* consists of the application of vacuum suction, which generates a potential gradient in the soil around the capsule, inducing soil solution to flux into the porous membrane. The collected soil solution is then stored in a 20 mL previously conditioned vacuum tube (Figure 1b). The hydrophilic membrane sampler is composed of a chemically inert porous hydrophilic polymer (blend of polyethersulfone and polyvinylpyrrolidone) of 0.1 μm pore diameter, with a 2.5 mm outer diameter and a 1.4 mm inner diameter; the HM is attached to a 0.10 m length PVC pipe, which is directly coupled to a luer-lock type connector. Inside the PVC pipe, there is a stainless steel wire used to reinforce the sampler structure.

Soil solution sampling

Solution samplers were installed in a 0.740 dm^3 pot filled with 0.700 dm^3 of each soil tested, whose weights differ depending on the soil density: 1.150 Mg m^{-3} (RQ), 700 Mg m^{-3} (LHd),

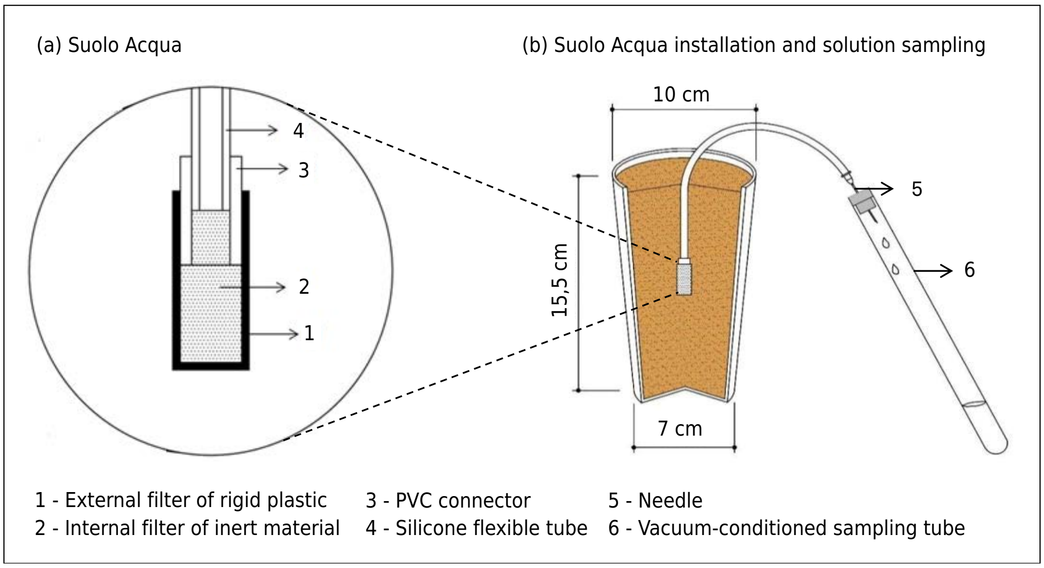


Figure 1. Schematic diagram of the *Suolo Acqua* sampler and its constituent parts (a) and *Suolo Acqua* installation and solution sampling procedure adopted for the pot used to incubate the soil samples (b).

and 750 Mg m^{-3} (CXbd). The sampler was installed so as to keep it in the center of each pot. Solution samplers were carefully inserted in soils, and fine soil with aggregates of approximately 1 mm were lightly compressed around the sampler capsules to prevent air bubbles and discontinuity of the soil-water-sampler system. After sampler installation, deionized water was added to reach soil water content near field capacity. Soil moisture was kept at this level for a period of 12 h, aiming at equilibrium between the soil and its liquid phase. The soil solution was sampled at 0, 2, 4, and 14 days after beginning soil incubation. Soil solution samples were collected with a 20 mL tube previously conditioned to -70 kPa vacuum pressure. This standardized vacuum level was generated with the aid of a vacuum pump, allowing the collection of about 15 mL of soil solution. A hypodermic needle was placed at the end of the solution header pipe of each sampler, and this needle was inserted in the rubber sealing cap of the plastic tube used to store the soil solution. After 10 h, the solution collected in the vacuum-conditioned tubes was filtered through membranes of 0.45 μm pore diameter and stored in the refrigerator at ±3 °C for further analyses.

Soil solution analyses

The concentrations of F^-, Cl^-, NO_3^-, Br^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+} were determined by ion chromatography in an ICS 1100 machine (Dionex) equipped with a DS6 conductivity detector. An IonPack AS23 column was used to detect anionic species, and an IonPack CS12A, for cationic species. A solution of 45 mmol L^{-1} Na_2CO_3/14 mmol L^{-1} $NaHCO_3$ was used to elute anions, and 20 mmol L^{-1} H_2SO_4, to elute cations, at a flow rate of 0.25 mL min^{-1}. A volume of 20 μL of soil solution was injected in the chromatograph. The chromatographic standard curve was prepared using certified solutions from Dionex, whose concentrations ranged from 0.1 to 40 mg L^{-1} for anions, and 0.25 to 100 mg L^{-1} for cations. The EC was determined in a TECNAL-TEC 4MP conductivitymeter. The concentrations of soluble inorganic carbon (SIC), soluble organic carbon (SOC), and total soluble carbon (TSC) present in the soil solution were determined in an automatic Total Organic Carbon (TOC) analyzer (Elementar brand, in a liquid module of a Vario TOC Cube model). Certified samples (from Elementar) of potassium acid phthalate and sodium carbonate were used as organic and inorganic C standards, respectively, to calibrate the automated TOC analyzer. Solution EC and pH were measured in unfiltered solution samples within a 24 h collection.

Statistical analyses

A completely randomized experimental design was adopted in a two (solution samplers) × four (sampling times) × three (soil samples) factorial arrangement using three replicates, for a total of 72 experimental plots. Statistical analyses of the data set were performed using analysis of variance at $p<0.05$, and the mean values of the treatments were compared by the F test, using the SISVAR software (Ferreira, 2014). A multiple parameter regression analysis was also performed to evaluate the degree of association of EC with solution pH, ion concentrations, and C contents.

RESULTS AND DISCUSSION

Chemistry of the solution

Solutions extracted by the two samplers differ in relation to Na^+, SOC, and TSC concentrations in the three soils (LHd, RQ, and CXbd) and four sampling times investigated. Statistically significant variations in the concentrations of anions, cations, Σanions, Σcations, Σanions+cations, SIC, SOC, TSC, pH, and EC were verified for the three soils over the sampling period. There was no significant effect of the interaction between solution samplers and sampling time on the chemical properties analyzed in the three soils incubated. Concentrations of anions (F^-, Cl^-, NO_3^-, Br^-, SO_4^{2-}) and Σanions in the solutions extracted by the *Suolo Acqua* are similar to the values reported for the HM (Figure 2). Over the sampling period, the anion concentrations vary, and the magnitude of these variations is soil-dependent. Thus, as the soil incubation period increases, a reduction in the solution F^-, Cl^-, SO_4^{2-} concentrations and sum of anions was verified. The Br^- levels increase over the sampling period, as well as the nitrate contents, at least in soils with higher clay and OM contents than the sandy soil samples.

Differences in the chemical composition of the solution over the sampling period are related to biochemical and chemical processes that occur at the same time as the nutrient transfer rates and reactions between the solid and liquid phase increase. An increase in soil solution pH promotes SO_4^{2-} desorption due to the deprotonation of mineral surfaces (Marsh et al., 1987), while a decrease in H^+ concentrations increased the adsorption of SO_4^{2-} in soil colloids through covalent bonds, with exchange of ligands (Zhang and Yu, 1997). Due to precipitation with cations or adsorption in oxides and other minerals of low chemical activity found in the soil clay fraction, sulfate concentration may also diminish in the soil solution. Over time, soil organic mineralization and nitrification rates may increase, which may explain, at least in part, the increase in solution nitrate concentrations. Thus, variations in solution chemical composition over the sampling period signal the fact that soil solution sampling must be performed over time to correctly evaluate the dynamics of soil chemical composition.

The sum of anion concentrations (Σanions) in solution decreased over time for LHd samples as the soil incubation time evolved from 0 to 14 days. Content of anions in solution also changed in the CXbd samples, whereas concentration of anions in the RQ solution only changed slightly over the sampling period. As already mentioned, the magnitude of the diverse processes and reactions between the liquid and solid phase, which are specific to each soil, affect the levels of anions dissolved in the liquid phase. Based on this assumption, the role that soil OM decomposition, microbial activity, and equilibrium reactions between the liquid and solid phase have over the soluble anion contents must be emphasized (Gloaguen et al., 2007). The PO_4^{3-} concentrations were practically zero in the solutions of the three soils over the sampling period, with levels below the detection limit of the method used for determination of soluble P forms. In tropical soils, adsorption of phosphate ions is high, due to the low amount of negative charges and the presence of Fe and Al oxides in the clay fraction of weathered soils, which may explain the reduced levels of P found in the Brazilian soil solution investigated. The reduced amounts of P determined in the soil solutions of the Brazilian soils studied must be highlighted because P scarcity

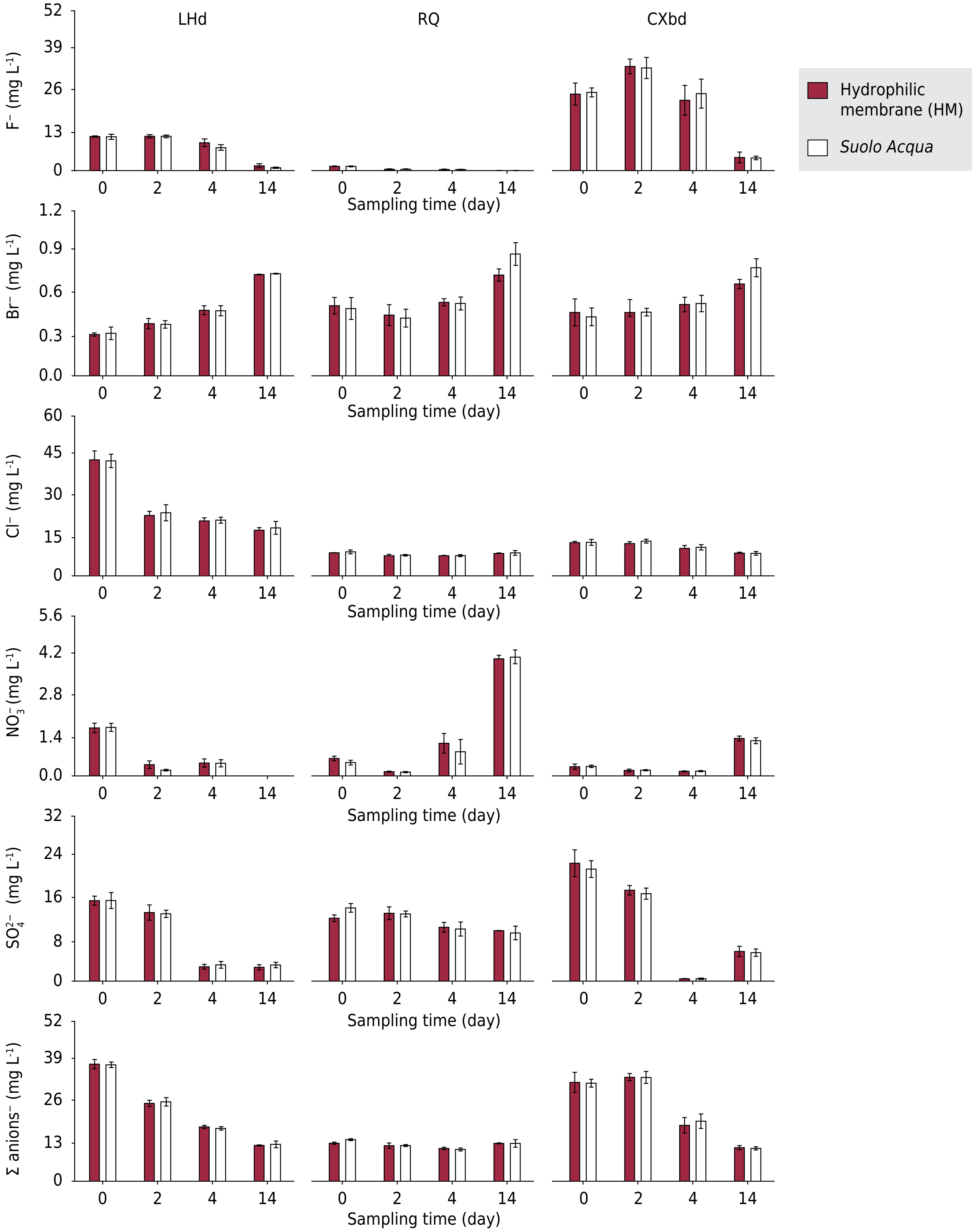


Figure 2. Anion concentrations in the soil solutions sampled by the Suolo Acqua and hydrophilic membrane (HM) at four sampling times. F^- = fluoride; Cl^- = cloride; NO_3^- = nitrate; Br^- = bromide; SO_4^{2-} = sulfate. LHd - *Latossolo Húmico Distrófico*, RQ - *Neossolo Quartzarênico* and CXbd - *Cambissolo Háplico Tb Distrófico*.

is a serious factor limiting high crop yield and enhanced uptake of other nutrients when P-fertilization is not correctly performed in Brazilian crop fields.

The concentrations of cations (NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and Σcations are similar for the two samplers tested (HM and *Suolo Acqua*), but the Na^+ content recovered in solutions extracted by *Suolo Acqua* are higher than the levels measured in the HM solutions in the three soils and sampling times evaluated (Figure 3). Although differences in the chemistry of the solution were hardly observed for the two samplers tested, soils presented different amounts of analytes in their solutions. The concentrations of NH_4^+, Mg^{2+}, Ca^{2+}, and Σcations in the LHd and CXbd samples were higher than those measured in the RQ solutions; however, soluble Na levels were higher in the sandy soil. These higher cation concentrations observed for the LHd and CXbd may be due to the higher clay and OM verified in these soils. An increase in OM and clay contents may enhance the soil CEC and cation availability. In more buffered solid phase soils, cations stored in organic and inorganic colloids can gradually be released to the solution, which may increase cation availability in the soil liquid phase (Ronquim, 2010). Small fluctuations were observed for the soluble Na^+ levels over the sampling period in the three soils investigated. Concentrations of K^+, Mg^{2+}, and Ca^{2+} decreased over the sampling period for the LHd and CXbd samples, but they were not altered for the RQ samples. Similar behavior for concentrations of these three cations in solution matrices was also observed by Miranda et al. (2006) and Oliveira et al. (2011) in solutions from soils under the influence of different land use and management systems.

The SIC concentrations, pH, EC, and Σ(anions+cations) are equivalent for the two samplers, considering the different sampling times. However, concentrations of SOC and TSC were significantly higher in the solutions extracted by *Suolo Acqua* compared to the levels measured in the HM extracted solutions. Greater recovery of C-soluble fractions by *Suolo Acqua* in relation to HM (Figure 4) may be explained by the presumed selectiveness of HM for organic molecules of high molecular weight. The HM pore diameter (0.1 μm) selectivity for some high molecular weight or soluble organo-metallic complexes may explain the lower levels of organic C levels in the HM collected solutions in relation to the *Suolo Acqua* sampler (Spangenberg et al., 1997). The use of *Suolo Acqua* does not result in retention or selectiveness in extraction of organic substances present in the solution because the sampler does not have a defined pore diameter. It should be noted that after extraction, the *Suolo Acqua* solutions were filtered again through a cellulose membrane with a 0.45 μm pore diameter, which, according to Chow et al. (2005), is the standard diameter for collecting soluble C fractions from the soil liquid phase. Taking into account that the HM pore is designed to retain some microorganisms, it should be investigated if this selectiveness is also followed by some restriction to free or complexed organic compounds found in the soil solution.

The SIC concentrations in the LHd and CXbd solutions changed only slightly over time, although significant increases in solution analytes were verified in the last sampling time. In the RQ samples, the SIC concentrations in solution decreased over the sampling period. The SOC concentrations and TSC remained stable in the LHd solutions over the sampling period; SOC and TSC in the RQ solutions decreased compared to the levels measured from the third to fourth sampling time. Levels of SOC and TSC in the LHd and CXbd samples were much higher than those observed in the RQ solutions. Such results are not uncommon, since the soluble C content in the soil depends on its OM content (Pinheiro et al., 2014). Thus, high contents of C in the LHd (6.5 %) and CXbd (3 %) may explain the higher soluble C content found in the solution of these soils compared to the levels measured in the RQ solutions. The soluble C concentrations are directly related to the amounts of C stored in the soil as a whole (Ciotta et al., 2004).

The solution pH changed over the sampling period, ranging from 5.8 to 7.2 in the LHd. Over the sampling period, the lowest pH value in the LHd solutions was verified at the beginning of soil incubation. In the RQ samples, the solution pH ranged from 5.7 to 7, with a slight increase in pH in samples collected at the second sampling time and a

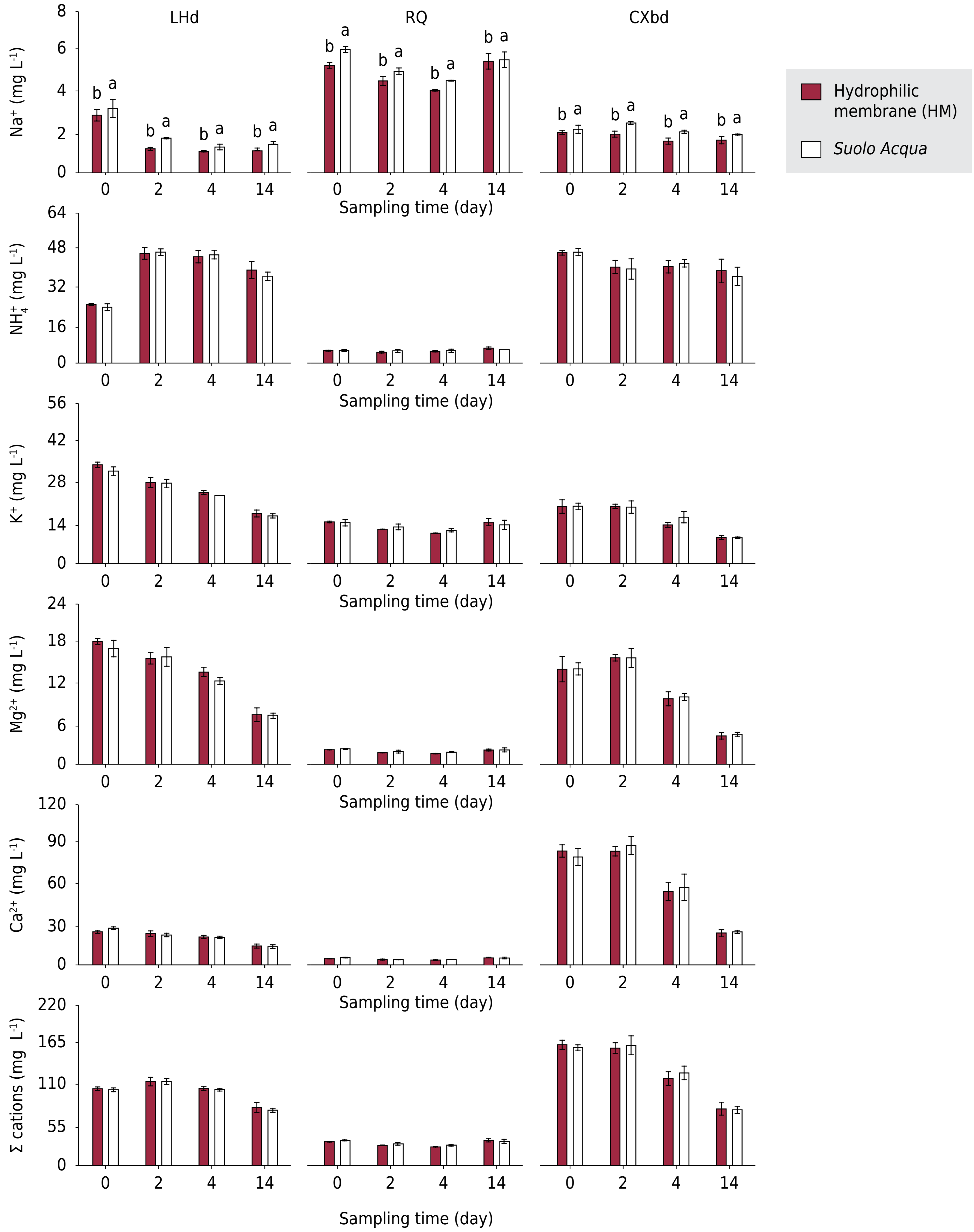


Figure 3. Cation concentrations over the sampling period in solutions of the studied soils. Soil solutions were collected by the Suolo Acqua and hydrophilic membrane (HM) samplers. Na$^+$ = exchangeable sodium; NH$_4^+$ = ammonium; K$^+$ = exchangeable potassium; Mg^{2+} = exchangeable magnesium; Ca^{2+} = exchangeable calcium. LHd - *Latossolo Húmico Distrófico*, RQ - *Neossolo Quartzarênico* and CXbd - *Cambissolo Háplico Tb Distrófico*. Mean values followed by the same letter do not differ statistically by the F test ($p<0.05$).

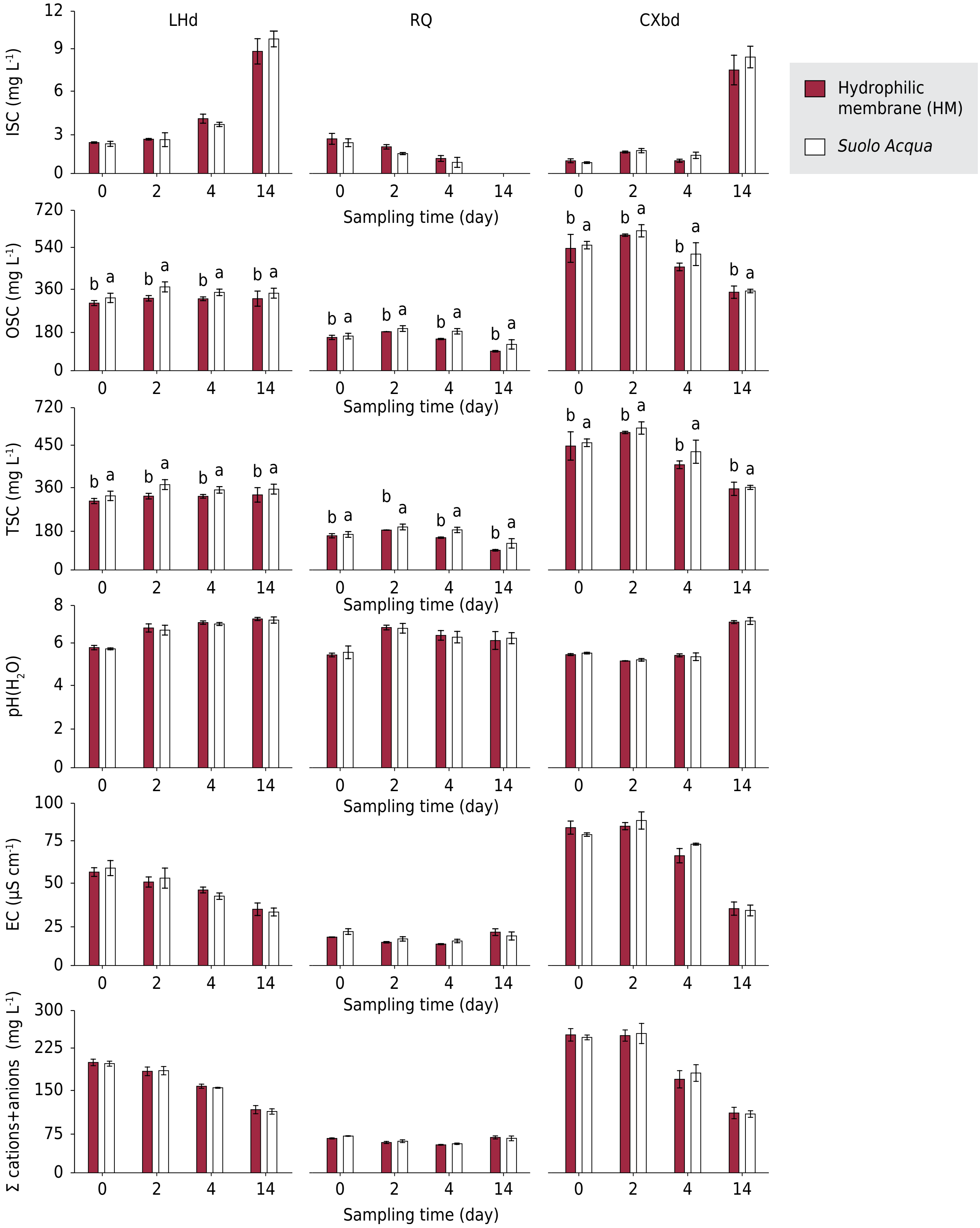


Figure 4. Soluble inorganic C (SIC), soluble organic C (SOC), and total soluble C (TSC) concentrations, pH values, and electrical conductivity (EC) of solutions of the studied soils. Variables were measured in solutions extracted in four sampling times by the Suolo Acqua and hydrophilic membrane (HM) samplers. *LHd - Latossolo Húmico Distrófico, RQ - Neossolo Quartzarênico and CXbd - Cambissolo Háplico Tb Distrófico.* Mean values followed by the same letter in each sampling time and soil investigated did not differ statistically by the F test ($p<0.05$).

small decrease in pH in solutions from the third and fourth sampling times. In the CXbd samples, the solution pH ranged from 5.4 to 5.7 in the three initial sampling times, but a sharp increase in pH (7.3) was verified in the solution of soils incubated for 14 days. Increase in solution pH may be explained by mineralization of N during soil incubation, and denitrification and decarboxylation of organic acids (Silva and Mendonça, 2007), among other processes naturally reported in soils. A decrease in solution pH occurs mainly due to the oxidation of NH_4^+ to NO_3^- and mineralization of soil OM, followed by the release of two H^+ atoms in the soil solution for each organic-derived ammonium molecule oxidized (Tisdale et al., 1993). Soil pH is one of the most important properties that affects the composition of the solution since it controls solubility and concentration, determines the intensity of the reactions in the soil, affects the ionic form of the nutrients in the soil solution, and modulates the intensity of sorption processes. Since pH is a conditioning factor of all processes mentioned before, it regulates the availability of nutrients and other chemical elements to plants (Mcbride and Błasiak, 1979).

Solution EC is directly associated with salt and ion concentrations found in soils. Solution EC ranged ranged from 34 and 59 µS cm^{-1} in the LHd samples, with successive reductions over the sampling period. In the RQ solutions, EC values ranged from 15 to 19 µS cm^{-1}, with minor fluctuations over time. The solution EC of the CXbd samples were higher than values already described for the other soil samples, since values ranged from 83 to 87 µS cm^{-1} in the first and second sampling times; however, EC values decreased sharply, reaching values of 34 and 70 µS cm^{-1} for the third and fourth sampling times, respectively. Values of Σions (cations + anions) showed the same EC behavior for the extracted solutions of the three soils at different sampling times. Changes in solution EC are due to variations in the availability of ions in the soil solution, as verified by Sahrawat and Narteh (2002). The EC fluctuations are inversely correlated to solution pH over the sampling period in the three soils. The EC values decrease as the pH increases and *vice versa*, indicating that the solubilization and precipitation of ions in the solution also rely on the H^+ concentrations in the liquid phase (McBride and Błasiak, 1979; Sousa et al., 2007). Solution EC values of the RQ samples over time were much lower than the values reported for solutions of LHd and CXbd. Such results may be explained by the lower concentrations of anions, cations, and C in the solutions of the RQ, the soil with low clay and organic matter contents. High EC values observed for the LHd and CXbd solutions are due to the high CEC of these soils, which increases their capacity to retain ions, especially cations, such as K^+, Ca^{2+}, Mg^{2+}, and NH_4^+. The increased capacity of soils rich in clay and organic matter in retaining nutrients may explain higher concentrations of salts and ions in the solution and, consequently, the higher solution EC values verified in the LHd and CXbd samples compared to the RQ samples.

Variations in the chemistry of solutions are dependent on the soil investigated and are dependent on the sampling time. Overall, it is necessary to check if the levels of analytes in the solution verified in this study are below or above the levels considered critical for adequate plant growth or environmental analysis. Critical nutrient levels or ranges for the purpose of suitable plant growth in formulated substrates are described in Abad et al. (2001) as follows: pH(H_2O) 5.3 to 6.5; EC 0.75 to 3.49 dS m^{-1}; Nitrate-N 100-199 mg L^{-1}; S-sulfate <960 mg L^{-1}; K 15-249 mg L^{-1}; and Na <115 mg L^{-1}. Critical levels of nutrients in hydroponic solutions are also a reference for evaluating the levels of nutrients in the soil solution. In the hydroponic solutions proposed by Hoagland, Arnon, Hewitt, and Cooper and presented in a comprehensive review of Trejo-Téllez and Gómez-Merino (2012), the nutrient levels for high plant growth are as follows: N 168-236 mg L^{-1}; P 31-60 mg L^{-1}; K 156-300 mg L^{-1}; Ca 160-185 mg L^{-1}; Mg 34-50 mg L^{-1}; and S 48-68 mg L^{-1}. A comprehensive review of nutrient levels and their critical levels in the soil solution for optimum plant growth are shown in Smethurst (2000). By using the aforementioned critical nutrient levels, it is possible to assess the limitations or excesses of nutrients in the soil solutions investigated.

The Na^+ levels are below those considered toxic to plants since they are less than 8 mg L^{-1}. N-ammonium levels are too low because when they are totaled with the N-nitrate levels, they are lower than the range considered adequate for N in hydroponic solutions. The K^+ availability is already low in the first solution collected, and it decreases further in subsequent solution sampling times, which are below the range considered optimal. The solution S contents are less than 30 mg L^{-1}; therefore, levels of S available in the solutions are also a factor limiting plant growth. Although no critical Cl^- level is cited in the literature reviewed, the Cl^- levels determined in this study are relatively high. The contents of Br and F are very low; thus, no toxicity problems for plant growth are expected for these two chemical elements. Solution P levels are extremely limiting to plants in all the soil solutions investigated since the levels are below the low quantification limit of this nutrient by the ion chromatography technique used. The Ca^{2+} and Mg^{2+} concentrations are also below the critical range already mentioned, which means that these cations present serious nutritional limitations to proper crop growth. The pH values were within the range considered appropriate in the initial solution sampling times, but they reach values in the alkaline range in subsequent solution sampling. Thus, multiple nutritional deficiencies are expected in these alkaline soils. As a whole, solution EC values are considered low, since they are lower than 0.1 dS m^{-1}; this may be a reflection of low nutrient availability in the soils and in the solutions investigated.

Electrical conductivity and solution analytes

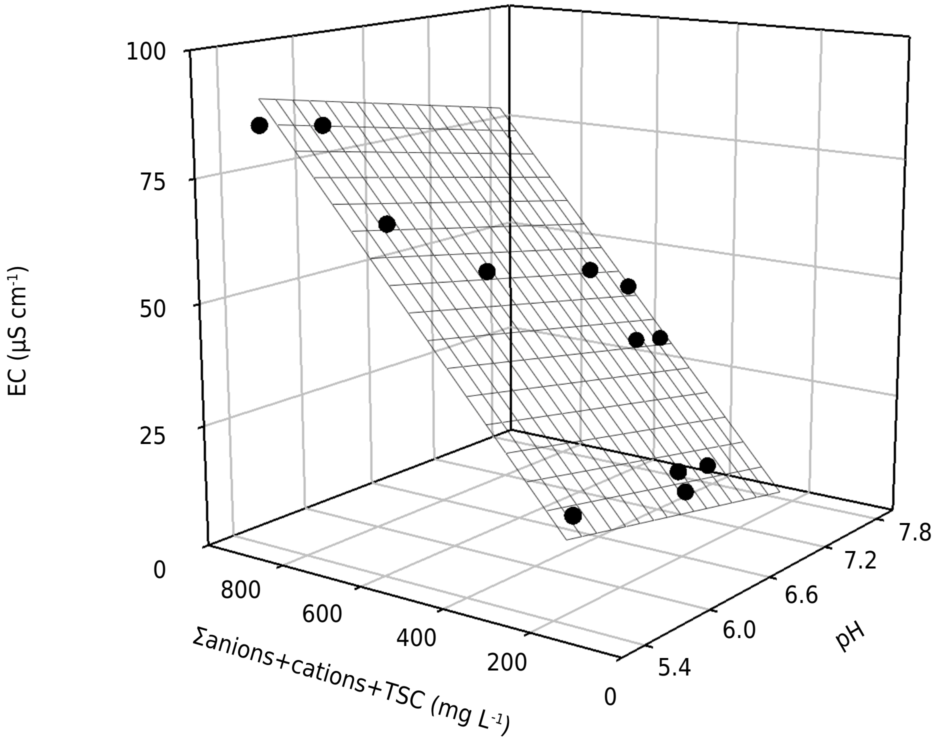
Multiple regressions were performed to correlate solution EC with pH and Σ(cations + anions) + TSC of the solutions obtained by the HM and *Suolo Acqua* at four sampling times (Figure 5). Significant multiple correlation ($p<0.05$) was verified among the properties mentioned above since EC is pH dependent and Σ(cations + anions) + STC dependent for both solutions collected by the *Suolo Acqua* and HM samplers. This result demonstrates that the EC in the soil solution increases as the pH decreases and as the concentrations of anions, cations, and total C in the solution increase, making the EC in the solution a complex and dynamic property which reflects the effects of several properties of the solution acting together. In a study performed by Miranda et al. (2006), the soil solution in coffee fields had higher EC values, higher concentrations of soluble C, Ca^{2+}, Mg^{2+}, and K^+, and lower pH values than the values observed for solutions from pasture areas; pasture solutions had lower EC values and concentrations of Ca^{2+}, Mg^{2+}, K^+, and nitric-N and higher pH values over time, at three soil depths, compared to the soil solution of coffee fields.

Increase in the solution pH may occur due to neutralization of H^+ and Al^{3+} and complexation of Al by organic ligands (Franchini et al., 2001; Pavinato and Rosolem, 2008; Hue, 2011). It may also be explained by $CaCO_3$ precipitation (Pocknee and Sumner, 1997), which decreases the solubility of Ca^{2+} and C in the soil solution (Franchini et al., 2001). When solution pH is increased to levels above 6.5, several nutrients, such as N, P, Ca, Mg, S, Fe, Cu, Mn, Zn, and B may be co-precipitated with other ions, which makes them less available in the soil solution (Braccini et al., 1999; Sousa et al., 2007), with subsequent reduction in solution EC. A decrease in solution pH with a concomitant increase in EC is only valid for pH values in the range of 5.3 to 7.5. For the three soils investigated, where the pH values were below or above the range mentioned, further studies are necessary to track changes in solution EC related to changes in the presence of salt in the solutions under the effect of sharp changes in pH in acidic and alkaline soils.

In this study, the soluble C contents conditioned the solution EC values. The influence of the soluble C concentration on the EC in the solution is possibly related to the anionic character of soluble organic acids, which makes them strong competitors for anion adsorption sites on the surface of soil colloids, enhancing the availability of inorganic anions in the soil solution (Pavinato and Rosolem, 2008). Fractions of soluble C found in the soil are predominantly composed of a range of carboxylic functional groups whose

(a) Hydrophilic membrane (HM)

EC = 29.0475*** - 5.2089***pH + 0.1029** ΣIons+TSC $R^2 = 0.95$



(b) *Suolo Acqua*

EC = 46.3552* - 7.8587*pH + 0.0991** ΣIons+TSC $R^2 = 0.98$

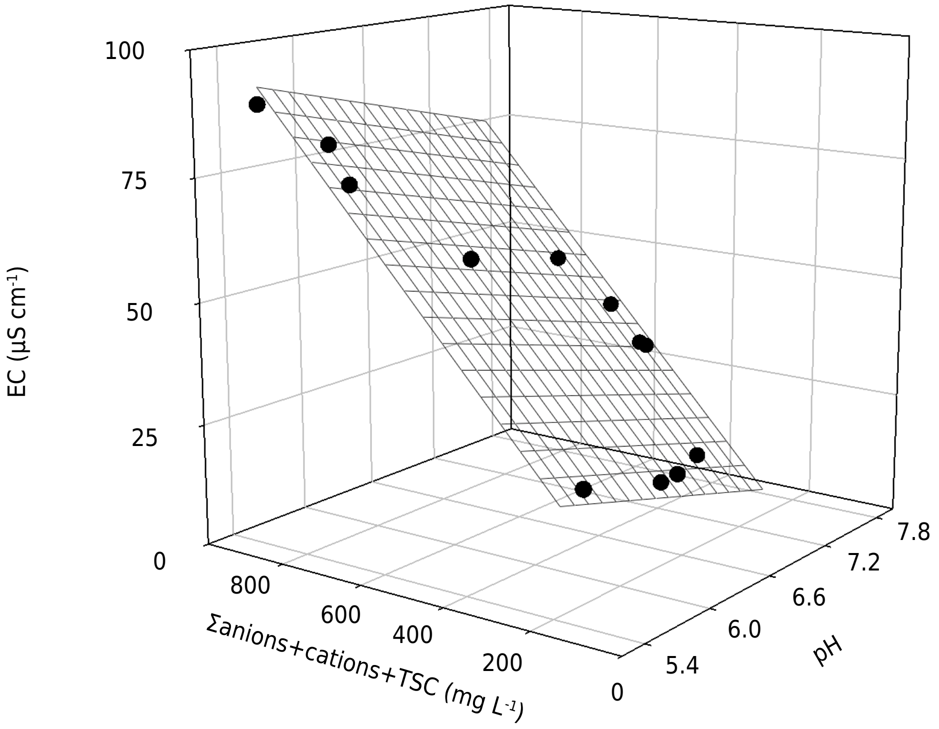


Figure 5. Solution electrical conductivity (EC) as a function of pH and Σ(anions+cations)+total soluble C (TSC), considering the data set of the three soils and four solution sampling times. (a) Hydrophilic membrane (HM) and (b) *Suolo Acqua*. Anions = F^-, Cl^-, NO_3^-, Br^-, SO_4^{2-}; and cations = Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}. *, **, and ***: significant at the 1, 5, and 10 %, respectively, by the F test.

dissociation rate depends on the pH and solution ionic strength. Thus, soluble organic compounds behave like anionic species currently found in soils (Guppy et al., 2005). According to the results found in this study, the pH values and soluble C concentrations act as EC regulators in the soil solution, controlling the availability of ions. Electrical conductivity changes are controlled by the magnitude of adsorption and desorption of ions in mineral and organic colloids, the intensity of precipitation reactions and ion dissociation, and soil organic matter mineralization (Ferreira and Martinez, 1997; Novais and Mello, 2007), whose rates are known to be controlled by soil pH.

The smaller pore diameter of HM, which is selective for some C soluble fractions during solution collection, could explain the lower accuracy of multiple regression for data obtained from the HM compared to *Suolo Acqua* results (Figure 5a). Furthermore, the time demanded to collect 15 mL of soil solution with the HM is higher than that recorded for *Suolo Acqua*. A high sampling time for collecting the soil solution with the HM sampler was also verified by Spangenberg et al. (1997). To avoid changes in the chemical composition, the soil solution should be extracted as quickly as possible (Zambrosi et al., 2008; Meurer and Anghinoni, 2012). Depending on the soil type, the time required to extract 15 mL of solution by the *Suolo Acqua* ranged from 2 to 4 h, a much smaller time than that required to extract the same volume of solution by the hydrophilic membrane. Technically, the *Suolo Acqua* was considered an acceptable method for sampling the soil solution since it recovered equivalent amounts of cations and anions measured by the HM sampler solutions. The contents of Na^+ and soluble C found in solutions extracted by the HM are lower than those recovered by the *Suolo Acqua*, which may be explained by the pores of HM being selective for some large organic molecules regularly found in the soil solution. Thus, *Suolo Acqua* extracted the true amounts of soluble organic compounds found in the soil solution in an effective way. Considering all the solution analytes investigated in this study, the *Suolo Acqua* sampler is a fast, nondestructive, simple, and economical method for extraction of the soil solution, which does not clog the pores of the sampler. It may be used in successive samplings without affecting the chemical status of solutions from contrasting soils over different incubation periods. Thus, *Suolo Acqua* is an alternative to the expensive, imported samplers of the soil solution currently used in Brazilian crop fields.

CONCLUSIONS

The samplers tested do not differ in relation to the chemical composition of the soil solution, except for the fact that *Suolo Acqua* recovered more Na^+ and soluble organic C than the hydrophilic membrane.

Cation+anion concentrations, C-soluble content, and electrical conductivity in the *Latossolo Húmico* and *Cambissolo Háplico* solutions are higher than the levels reported for the low organic matter sandy soil.

The chemical composition of the solution changes over time, with sharp modifications in pH, electrical conductivity, and cation and anion contents. Thus, analysis of the soil solution on only one occasion does not reflect the dynamics of its chemical composition, and may, according to the sampling time chosen, underestimate or overestimate the concentration of nutrients in the soil liquid phase.

Solution electrical conductivity is regulated by pH, sum of cation and anion concentrations, and water-soluble C contents.

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