



## Article

# Multiple Linear and Polynomial Models for Studying the Dynamics of the Soil Solution

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**Abstract:** The objective of the present work was to study the soil solution throughout time in pots under greenhouse conditions. The work consisted of monitoring the solution of calcareous soil and forest soil in the absence of plants, with different types of fertilization: treatment 1: absolute control (irrigation water); treatment 2: Steiner nutrient solution; treatment 3: solid fertilizers; and treatment 4: vermicompost tea (aqueous extract). The samples were collected weekly using lysimeters for 14 weeks. They were analyzed to determine the nitrate content, total nitrogen, calcium, potassium, magnesium, sodium, sulfur, zinc, boron, pH, electrical conductivity, and oxide-reduction potential. To understand the interactions between treatments, soil type, and time over ion behavior and availability, linear and polynomial models were used, selected by a cross-validation method, which resulted in robust models, where it was found that the pH behavior is associated with the type of fertilization and soil type, with the elapsed time being a nonsignificant factor. On the other hand, time influenced the dynamics of the remaining ions and their availability. It was found that the multiple polynomial model fit better for the variables: potassium, calcium, sodium (square degree), electrical conductivity, nitrates, sulfur (cubic degree), zinc, oxidation-reduction potential, nitrogen, magnesium, and boron (quartic degree).

**Keywords:** linear models; multiple models; soil solution; cross-validation; soil chemical processes; Calcisol; calcareous soil; forest soil



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## 1. Introduction

The liquid phase, soil pore water, or soil solution is a nonhomogeneous solution distinguished by marked spatial and temporary variability in concentration and composition [1]. Soil solution is a product of the interaction of several biological and physiochemical processes from different phases that form the edaphic system. The liquid phase of the soil is one of the most variable components within the soil system due to the great diversity of its components and its scattered nature, which allows complex flows of matter and energy [2]. Slight changes in the solid phase of the soil system can lead to extensive modifications in the soil solution, which in turn can be extended by the action of living components in the system [3]. Traditionally, crop nutrition focuses on the nutrient analysis of the solid soil phase, which functions as the nutrient store and provides an indication of a soil's ability to supply nutrients to the plant but does not adequately indicate (and, in some cases, does not indicate at all) the disponibility of nutrients in the soil solution, as well as the changes induced by the roots of plants and by the edaphic microbiome [4]. However, from the perspective of studying the soil system for agricultural purposes, the soil solution is a fundamental system to study and understand due to its close relationship with crop

nutrition, being the primary source from which the roots absorb all elements in their ionic forms, and which are indispensable for their development [1,2].

The soil water (soil solution) composition is dynamic and fluctuates over time, which will be reflected in the dissolved nutrient quantity. The mineral concentration will vary depending on several specific factors, such as climate, the amount of water in soil, content, pore diameter, depth of pores, type, and depth of the edaphic horizon, pH, cationic interchange capacity, redox potential, amount of organic matter in soil and microbiota activity [5]. Human activities, such as fertilization, liming, irrigation, and artificial drainage can also change the solution of the soil. Likewise, excessive tillage profoundly alters the natural structure of the soil, changing the length, connectivity, and distribution of soil pore diameters, characteristics closely related to soil water composition and the synchronization of soil–plant–microorganism interactions [6].

The behavior of ions in soil solution has been extensively described using diffusion and empirical chemical models [7,8]. However, the dynamics of soil solution composition and its relationship with the types of fertilizers used have been shallowly researched. Hernández-Díaz et al. [9] monitored soil solutions in different tomato plant growth phases to obtain nutrition reference levels. Yanai et al. [10] carried out experimentation on pots, examining the solution of four types of soil in pots with and without maize plants; they observed a relation between the decrease in the concentration of the soil solution and the absorption of the plant. Yanai et al. [11] performed a factorial experiment to monitor the soil solution over time in the presence and absence of plants and with or without the application of nitrogen to observe the effects of nitrogen on the initial composition of the soil solution and its impact on the dynamic composition of the soil solution during crop growth, as well as to observe the number of elements absorbed by the plant and its decrease in the soil solution. Yanai et al. [12] studied the effects of slow-release fertilizers on nutrient absorption by plants and the leaching potential of soil nutrients based on soil solution dynamics. They studied the soil solution over time in the presence and absence of a wheat crop under three scenarios of nitrogen supply: soluble fertilizer such as  $\text{Ca}(\text{NO}_3)_2$ , slow-release fertilizer, and without fertilization.

Extending the research on the dynamic behavior of soil solutions makes it convenient to use new tools for modeling, such as linear and polynomial modeling, which makes it possible to forecast qualitative and quantitative response variables from predictive qualitative and quantitative variables. However, this is not the only application that can be given to linear and polynomial models: they also allow the construction of predictive models, selecting the variables with the most significant influence on the response and discarding the variables that do not contribute relevant information or have no significant effects [13]; agronomist can use the data obtained in a growing season to predict what is expected in the following season. This type of analysis has been reported when modeling the absorption response of mineral elements in corn and rice [14], as well as in the prediction of specific soil properties such as pH, Ca, Mg, K, P, Al, and H concentration, the sum of bases, cationic interchange capacity, base saturation and aluminum saturation using spectral data from the soil at different depths [15].

In the present study, soil solution monitoring was carried out over time using suction soil-water extractors (lysimeters), which is a nondestructive method for soil structure [16]. The objective was to analyze the obtained data to build and select linear and polynomial models through methods of leave-one-out cross-validation (LOOCV), which allowed us to develop robust models of the behavior of the soil solution under the different scenarios of fertilization and types of soil.

## 2. Materials and Methods

### 2.1. Location

The study was performed under greenhouse conditions at Universidad Autónoma Agraria Antonio Narro facilities, located in Saltillo, México, from January 2015 to April 2015. Weekly records are available in Supplementary Materials.

## 2.2. Study Material

Two Calcisols [17] were used as study materials: a nonagricultural, non-vegetation covered soil (Calcareous) and a vegetation-covered soil (Forest) from an area with reforestation of 20 years with *Pinus halepensis*. The soil was collected from land belonging to the University, located at 25°21'14.87" N and 101°2'23.25" W for calcareous soil and 25°21'6.81" N and 101°1'27.69" W for forest soil. The soils used in the study have the same origin and are found in the same basin separated by a short distance (1.57 km); the difference lies in the impact of the 20 years of forest plantation. This allows appreciating the change induced by the vegetation on the chemical characteristics of the soil solution. After sampling, the soils were characterized from a physical-chemical point of view according to NOM-021-RECNAT-2000 [18] (Table 1).

**Table 1.** Physical-chemical analysis of the soil.

Physical Properties of Soil													
Soil	pH	Electrical Conductivity (dS m <sup>-1</sup> )	Texture	Saturation Point (%)	Field Capacity (%)	Wilting Point (%)	Bulk Density (%)						
Calcareous	8.08	0.90	Loam	39	20.7	12.3	1.04						
Forest	7.59	0.58	Loam	51	27.2	16.2	0.95						
Soil fertility analysis													
	O.M	P-Olsen	N-NO <sub>3</sub>	K	Ca	Mg	Na	Fe	Zn	Mn	Cu	B	S
Soil	%												
	(mg kg <sup>-1</sup> )												
Calcareous	0.97	19	23.1	296	6536	714	107	1.68	0.19	1.28	0.22	0.09	20.5
Forest	4.9	15	2.72	599	6364	341	101	3.90	1.87	8.17	0.54	0.47	12.2

## 2.3. Experiment Installation

The collected soils were deposited in 12 L plastic pots, and 24 pots per soil type (calcareous and forest) were filled, resulting in 48 pots. For each pot with soil, a lysimeter of 13 inches in length was inserted to a depth of 15 cm in the central part of the pot. Once the lysimeters were installed, pots were watered with previously characterized water (Table 2), until a solution was observed draining freely from the bottom of the pot. It should be mentioned that except for air drying and manual removal of stones and coarse matter, the soils were not brought under any physical or chemical process before the experiment took place so they could reach their natural condition as much as possible.

**Table 2.** General characteristics of salinity/sodicity, cations, anions, and special determinations of irrigation water.

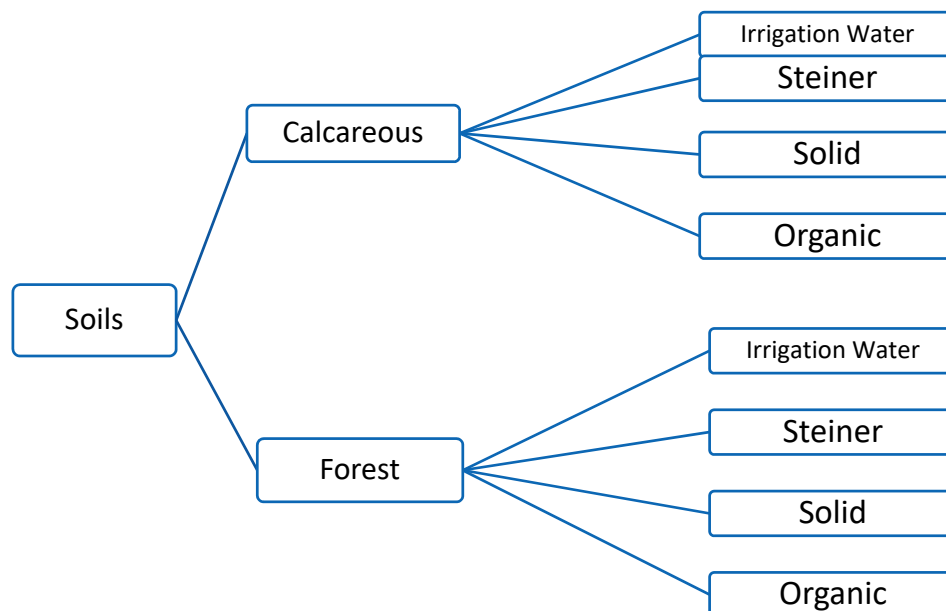
	Salinity/Sodicity	Cations		Anions		Micronutrients	
		(mg L <sup>-1</sup> )		(mg L <sup>-1</sup> )		(mg L <sup>-1</sup> )	
pH	8.06	Ca	95.8	SO <sub>4</sub>	81.7	B	0.01
EC (dS m <sup>-1</sup> )	0.77	Mg	24.1	HCO <sub>3</sub>	256	Fe	ND
ARS	0.48	Na	20.5	Cl	37.1	Mn	ND
ARSaj	0.63	K	6.24	CO <sub>3</sub>	34.2	Cu	ND
				N-NO <sub>3</sub>	1.12	Zn	ND

EC: electrical conductivity; ARS: absorption ratio of sodium; ARSaj: adjusted sodium adsorption ratio; ND: not detected.

## 2.4. Description of the Treatments

The experiment consisted of the continuous application of irrigation under different nutrient supply scenarios for the two soil types: calcareous and forest, without the presence of crops; the irrigation was carried out manually to maintain the most similar possible irrigation volumes applied to different treatments; two irrigations were carried out per week of

1 L each, a sufficient volume to obtain a sufficient humidity level to get soil solution samples. Experimental treatments were treatment 1 (control): irrigation with water only; treatment 2 (Steiner): continuous application of Steiner nutrient solution [19]; treatment 3 (Solid): discontinuous and fractional application of solid fertilizers; and treatment 4 (Organic): organic fertilizer application with vermicompost tea (aqueous extract). These applications were made for the two types of soil (Figure 1).



**Figure 1.** Diagram for the different nutritional contributions of each type of soil.

For the treatments with the application of inorganic fertilizers, the number of nutrients applied to the Steiner and Solid treatments were similar in quantity but different in their form of application; in both cases, the composition of irrigation water was considered (Table 2), and soluble fertilizers were used (Table 3). The total volume of water applied in irrigation for each of the treatments during the entire experiment was 28 L for each pot. For treatments using solid fertilizer irrigation provided with water acidified to ~5.5 pH using sulfuric acid ( $\text{H}_2\text{SO}_4$ ), the application of fertilizers was fractionated three times (28 January, 4 March and 1 April 2015).

Organic treatment with vermicompost tea was obtained from the manure of bovine origin. The aqueous extract was made 24 h before its application. Once the solution was obtained, it was acidified to a final pH of ~5.5 with food-grade citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) and with EC  $\sim 2 \text{ dS cm}^{-1}$  through dilution with irrigation water to avoid phytotoxicity [20,21]. The mineral composition of vermicompost tea is shown in Table 4.

**Table 3.** Fertilizers used in the preparation of the nutrient solution and in the application of the treatment in solid and fractioned form.

Fertilizer	Formula	Fertilization <sup>¥</sup>		Element <sup>&amp;</sup>
		Steiner mg L <sup>-1</sup>	Solid * g pot <sup>-1</sup>	g pot <sup>-1</sup>
Calcium nitrate	Ca (NO <sub>3</sub> ) <sub>2</sub> · 4H <sub>2</sub> O	590	16.52	Ca = 2.8
Potassium nitrate	KNO <sub>3</sub>	710	19.88	K = 7.64
Magnesium sulphate	Mg SO <sub>4</sub> · 7H <sub>2</sub> O	246.4	6.899	Mg = 0.66
Monobasic potassium phosphate	KH <sub>2</sub> PO <sub>4</sub>	136	3.808	N = 4.7
Ultrasol micro (microelements)	Fe EDTA, Mn EDTA, Zn EDTA, Cu EDTA, B and Mo	40	1.12	P = 0.86
				S = 2.68
				Fe = 0.084
				Mn = 0.041
				B = 0.0044
				Zn = 0.006
				Cu = 0.0033
				Mo = 0.0022

<sup>¥</sup> Fertilizer content considering the contribution of irrigation water. \* Amount of total fertilizer applied in the fractional and solid forms treatments. <sup>&</sup> Total amount of elements provided in grams per pot, in the treatments with Steiner and Solid fertilization.

**Table 4.** Chemical characteristics and mineral composition of vermicompost tea applied in organic treatment.

Variable		¥ g pot <sup>-1</sup>	Variable		¥ g pot <sup>-1</sup>
pH *	8.2		Mn (mg L <sup>-1</sup> )	<0.025	
EC (dS cm <sup>-1</sup> )	2.03		Na (mg L <sup>-1</sup> )	186.4	5.21
N-NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	75	2.1	S (mg L <sup>-1</sup> )	154.51	4.32
P (mg L <sup>-1</sup> )	9.33	0.26	Zn (mg L <sup>-1</sup> )	0.046	0.001
Ca (mg L <sup>-1</sup> )	96.53	2.7	B (mg L <sup>-1</sup> )	1.017	0.028
K (mg L <sup>-1</sup> )	440.17	12.32	Cu (mg L <sup>-1</sup> )	<0.005	
Mg (mg L <sup>-1</sup> )	42.75	1.19	Fe (mg L <sup>-1</sup> )	0.28	0.007

\* pH obtained after the preparation of the vermicompost tea before being acidified with citric acid. <sup>¥</sup> Total amount of elements provided in grams per pot, in the vermicompost tea applied in the organic treatment.

### 2.5. Sample Collection and Analysis

For the obtention of soil solution samples, the pots were irrigated the day before. They were allowed to reach 30 kPa measured through Irrrometer tension gauges placed before the application of irrigation. Once the tension of 30 kPa was reached, all the lysimeters that were placed in the 48 pots from the beginning of the experiment and kept in the pots during the whole experiment were vacuumed. The vacuum pressure inside the lysimeters was -60 kPa, which was obtained with a hand pump. The samples were collected from the soil solution 24 h after vacuum.

The soil solution was collected once a week over 14 weeks. Three replicates per sample were obtained and placed in plastic containers for each treatment and soil type. The obtained samples were subjected to in situ analysis to determine pH with a Horiba Brand potentiometer model B-173, electric conductivity (E.C.) with a Horiba brand Spectrum Cardy Twin model; oxidation-reduction potential (ORP) that was measured with an OMEGA brand electrode model PHH-7011 and nitrate concentration (NO<sub>3</sub><sup>-</sup>) that was measured with selective-ion Horiba brand equipment model B-743. Subsequently, soil solution samples were analyzed in the laboratory to determine the total nitrogen content (N) by the micro-Kjeldahl technique [22], as well as potassium concentration (K<sup>+</sup>), calcium (Ca<sup>2+</sup>), magnesium (Mg<sup>2+</sup>), total sulfur (S), sodium (Na<sup>+</sup>) and boron (B) through the wet calcination technique [23] and with a Perkin Elmer ICP-OES equipment optima 8300 model.

## 2.6. Data Analysis

A database of 4032 (336 observations and 12 variables) was built with the data obtained. Furthermore, exploratory and graphic analyses of its dynamics over time were performed, which were used to construct multiple models and their validation (LOOCV).

Data processing for the analysis of multiple models and Leave-one-out cross-validation (LOOCV) were performed with the language and environment for statistical computing R version 3.1.1 (© 2014 The R Foundation, Vienna, Austria).

### 2.6.1. Multiple Polynomial and Linear Regression Analysis

The data obtained in the different soil solution measurements were analyzed with multiple linear and polynomial models using three different predictors: (1) treatments (irrigation water, Steiner, solids, and vermicompost tea); (2) type of soil (calcareous and forest soil); and (3) elapsed time of 14 weeks. The first two were considered categorical, while time was considered a numerical variable that was used under different polynomial degrees. The use of multiple linear regression methods offered the advantage of considering all the available information when building the model and therefore making more accurate estimates [11]. The models used were the following:

Multiple linear model:

$$Y = \beta_0 + \beta_1X_1 + \beta_2X_2 + \beta_3X_3 \dots\dots\dots + \beta_pX_p + \varepsilon$$

Multiple polynomial model:

$$Y = \beta_0 + (\beta_1X_1 + \beta_2X_2) + \beta_3X_3 + \beta_3X^2 + \beta_3X^3 \dots\dots\dots + \beta_pX^P + \varepsilon$$

where:

$B_0$  = the intercept term, the expected value of Y when X = 0

$B_1$  = the slope of the line between the  $X_j$  and the response Y, interpret  $\beta_j$  as the average effect on an increase of one unit in  $X_j$ , keeping fixed all other predictors.

$X_j$  = the j-th predictor

$\varepsilon$  = the error term

One of the objectives of the use of models was to determine if all of the predictors help to rebuild the dependent variable (Y) or only a subset of predictors, which represents the values and concentrations of pH, E, C, ORP,  $\text{NO}_3^-$ , N,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , S,  $\text{Zn}^{2+}$  and B. To verify whether there was a relationship between the variables of response and the predictors, we used a hypothesis test to test the null hypothesis:

$$H_0: \beta_1 = \beta_2 = \dots\dots\dots = \beta_p = 0$$

Versus the alternative hypothesis

$H_\alpha$ : At least one  $\beta_j$  is not zero.

This hypothesis test is performed by calculating the F statistic. When there is no relationship between the response and the predictors, we would expect the F statistic to assume a value close to 1.

### 2.6.2. Leave-One-Out Cross-Validation

The evaluation and selection of the linear model or polynomial degree to use were carried out through a cross-validation method, considered a technique of resampling and an important tool in the practical application of many statistical learning procedures; this method estimates the test error associated with a given statistical learning method to evaluate its performance or to select the appropriate level of flexibility [13]. The test error is the average error that results from using a statistical learning method to predict the response in a new observation, meaning a measure that was not used in the formation of the method. Given a data set, the use of a particular statistical learning method is guaranteed if it results in a low-test error. The test error can be easily calculated if a designated set of

tests is available. In contrast, training error can be easily calculated using the method of statistical learning for the observations used in its formation. The training error will be lower as more variables or polynomial grades are incorporated into the model, leading to an over-adjustment of the model, but with a poor performance for the prediction of new results. The error rate of training is often very different from the test error rate, and in particular, the first may dramatically underestimate the last [13].

Leave-one-out cross-validation (LOOCV) involves splitting the set of observations into two parts. Instead of creating two subsets of comparable size, a single observation ( $X_1, Y_1$ ) is used for the validation set, and the remaining observations ( $(X_2, Y_2), \dots, (X_n, Y_n)$ ) constitute the training set. For this validation method, many interactions are made as samples ( $n$ ) are in the set of data [13,24]. Thus, for each of the ( $n$ ) interactions, an error calculation is performed. The final result is obtained with the arithmetic mean of the  $n$  error values obtained according to the formula:

$$CV_{(n)} = \frac{1}{n} \sum_{i=1}^n MSE_i.$$

where the sum of the  $n$  error values is divided by the value of  $n$ .

### 3. Results

#### 3.1. Selection of Multiple Models Using Cross-Validation

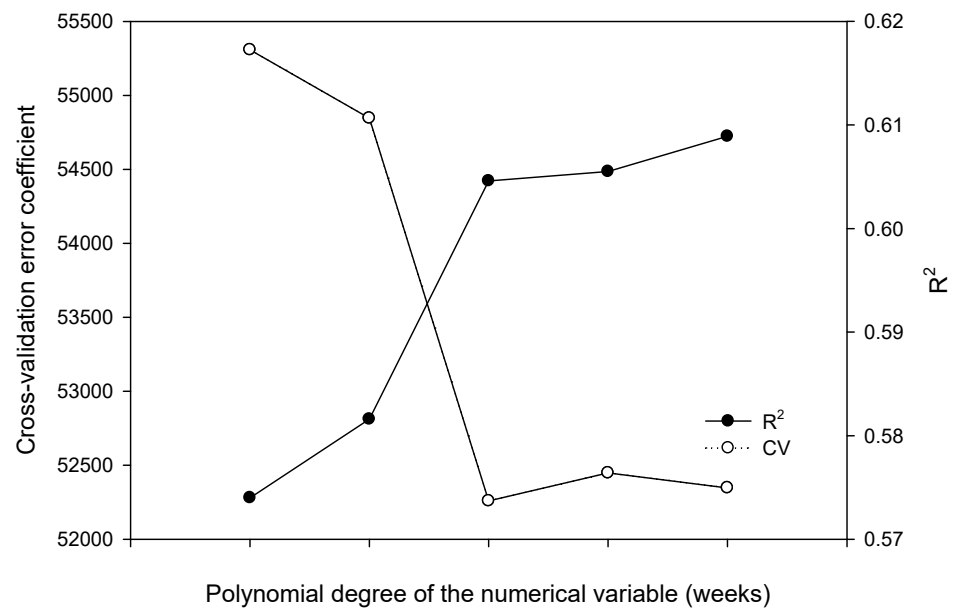
To find the most robust models, the predictive variables (treatments, soil type, and time in weeks) were subjected to multiple model analysis, wherefrom their significant effect and through cross-validation analysis, the error was estimated. Finally, the model that presented the smallest error was chosen (Table 5).

**Table 5.** Error coefficients obtained by a cross-validation method for the different subsets of the explanatory variables as well as for the different polynomial grades performed in the numerical variable.

Y	Predictive Explanatory Variables				
	Linear Models		Polynomial Models		
	T + S	T + S + W	T + S + (W) <sup>2</sup>	T + S + (W) <sup>2</sup> + (W) <sup>3</sup>	T + S + (W) <sup>2</sup> + (W) <sup>3</sup> (W) <sup>4</sup>
pH	0.04270 *	0.04279	0.04307	0.04293	0.04303
E.C	0.8843	0.8822	0.8765	0.8741 *	0.8746
ORP	658.4	660.4	661.2	654.1	632.6 *
NO <sub>3</sub> <sup>-</sup>	192,534.9	192,534.9	191,012.7	188,569.1 *	189,259.0
N	1456.8	1461.8	1412.6	1382.9	1333.6 *
K <sup>+</sup>	1253.2	1205.4	1192.6 *	1192.7	1199.7
Ca <sup>2+</sup>	55,308.0	54,845.5	52,259.2 *	52,447.9	52,347.7
Mg <sup>2+</sup>	3372.5	3401.9	3324.3	3335.1	3315.5 *
Na <sup>+</sup>	416.4	305.1	293.6 *	295.8	294.8
S	795.1	758.3	755.4	739.8 *	744.8
Zn <sup>2+</sup>	0.1474	0.1408	0.1410	0.1381 *	0.1388
B	0.57	0.57	0.58	0.56	0.46 *

Y: Response variables; T: treatment; S: soil; W: weeks; W<sup>2</sup>: quadratic degree weeks; W<sup>3</sup>: cubic degree weeks; W<sup>4</sup>: quartic grade weeks. \* Lowest coefficient obtained by the cross-validation method.

The cross-validation procedure has an advantage concerning the setting of the traditional models using R<sup>2</sup>. It provides a direct estimate of the test error and makes fewer assumptions about the accurate underlying model. In Figure 2, we see an example of the coefficients for the R<sup>2</sup> and the coefficient of cross-validation to estimate the most robust model for prediction, in this case, the Ca<sup>2+</sup> content in the soil solution.



**Figure 2.** For the data set of the  $\text{Ca}^{2+}$  concentration in the soil solution, the  $R^2$  and the cross-validation error coefficient (CV) for the different polynomial grades of the numerical variable (weeks). In all polynomial grades, the two categorical variables are considered.

If we examine only the  $R^2$ , it could be concluded erroneously that the model with the higher number of variables is better, ending with a model that involves all the variables. A high  $R^2$  value indicates a model with a low training error, but in addition to a high  $R^2$  value, it is desired to choose a model with a lower test error. According to the cross-validation method, the most robust model involves the variables treatment, soil type, and weeks (Table 5) with the quadratic order as indicated in Figure 2 and not necessarily the highest polynomial degree as deduced by  $R^2$ .

### 3.2. Multiple Linear Models in the Study of the Soil Solution

According to the coefficients obtained by the cross-validation method (Table 5) for all the variables measured in the soil solution, pH was the only variable that was adjusted to the linear model, where the categorical variables predictive: treatments (irrigation water, Steiner, solid and organic) and the soil types (calcareous and forest soil types) obtained the lowest coefficient of validation error (Table 5). Therefore, the linear model indicated that the time variable did not influence the behavior and dynamics of the pH.

#### Multiple Linear Model with Two Predictor Variables for pH

In Table 6, we present the results of the analysis of the linear model of the pH of the soil solution and the following variables: treatments (irrigation water, Steiner, solid and organic) and soil types (calcareous and forest). According to the multiple linear model (Table 6), the reference treatment was irrigation water within the categorical variable treatments. When compared with the treatments with fertilization, significant differences were observed between the control and treatments with the application of inorganic fertilizers (Steiner and solid) ( $p \leq 0.01$ ). In contrast, the organic treatment did not show significant differences. For the categorical variable of soils, the reference variable was the forest soil, which presented significant differences when compared with the calcareous soil. Significant effects point to the existence of a relationship between the predictors and the predictor; when we observed the coefficients obtained in the model for the treatments (Table 6), we found negative coefficients, which indicated that the treatments that significantly decreased the pH of the soil solution to a greater extent by the effect of fertilizers in solid form. On the other hand, the coefficient obtained for the calcareous soil was positive, suggesting that the pH levels in

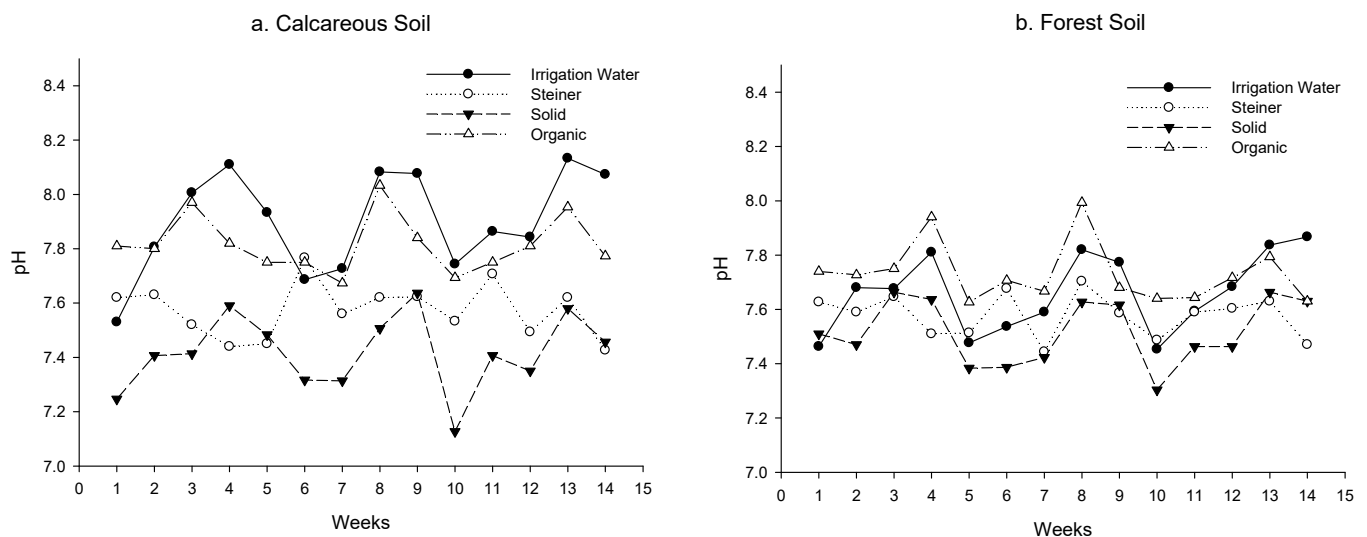


the calcareous soil were higher than those in the forest soil, and the pH of the soil solution did not fluctuate by more than one unit for all treatments (Figure 3a,b).

**Table 6.** Multiple linear model between pH and two explanatory variables (treatment and soil type). The reference treatment for the comparison of the different nutrient contribution scenarios was irrigation water, while the forest soil was used as a reference to compare it against the calcareous soil.

Variables	Coefficient	Std. Error	p Value
<b>pH</b>			
Steiner	−0.206786	0.031651	$2.43 \times 10^{-10}$ **
Solid	−0.314405	0.031651	$<2 \times 10^{-16}$ **
Organic	−0.007024	0.031651	0.8245
Calcareous soil	0.054583	0.022380	0.0153 *

\*\* = significant at  $p \leq 0.01$ ; \* = significant at  $p \leq 0.05$ .



**Figure 3.** pH dynamics, determined in soil solution samples for calcareous (a) and forest soils (b), under pot and greenhouse conditions under different nutrient supply scenarios, using inorganic fertilizers: nutrient solution (Steiner) and fertilizers in fractional form (solid) and organic fertilizer with vermicompost tea (aqueous extract).

### 3.3. Multiple Polynomial Models in the Study of the Soil Solution

According to the coefficients obtained by the method of cross-validation (Table 5), in the variables measured in the soil solution except for the pH, it was found that the multiple polynomial models were the best adjusted to explain the response variables. Obtaining models with different polynomial grades, wherein in the case of potassium, calcium, and sodium, the suitable model was of quadratic degree; for electrical conductivity, nitrates, sulfur, and zinc were of cubic degree; and for the potential of reduction oxide, nitrogen, magnesium, and boron were of quartic degree. All the polynomial models implied the categorical variables (treatments and soil types).

#### 3.3.1. Multiple Polynomial Models of Second Order with Three Predictive Variables for Potassium, Calcium, and Sodium

Table 7 shows the results of the polynomial models for the variables of potassium, calcium, and sodium response with categorical variables: treatments (irrigation water, Steiner, solid, and organic), soil types (calcareous and forest); and the numerical variable of time in weeks. The potassium and calcium contents showed similar behavior according to the polynomial model. In both cases, there were significant differences between the control and treatments with inorganic fertilizers ( $p \leq 0.01$ ) based on a Steiner nutrient

solution and fertilizers in solid form (Table 7). However, the organic treatment had no significant influence on the concentration of potassium or calcium in the soil solution. The categorical variable of soil types showed significant differences between calcareous and forest soil, with the latter used as the reference. According to the polynomial model, potassium and calcium showed positive coefficients for the treatment variables (Table 7), which suggests that the inorganic treatments increased the levels of these ions in the soil solution compared to the control treatment, with the Solid treatment showing the best results. For the calcareous soil variable, the coefficients obtained for both potassium and calcium were negative (Table 7), indicating that the average levels of potassium and calcium in the calcareous soil were below the levels of the forest soil at average concentrations of 45 and 295.5 mg L<sup>-1</sup>, respectively.

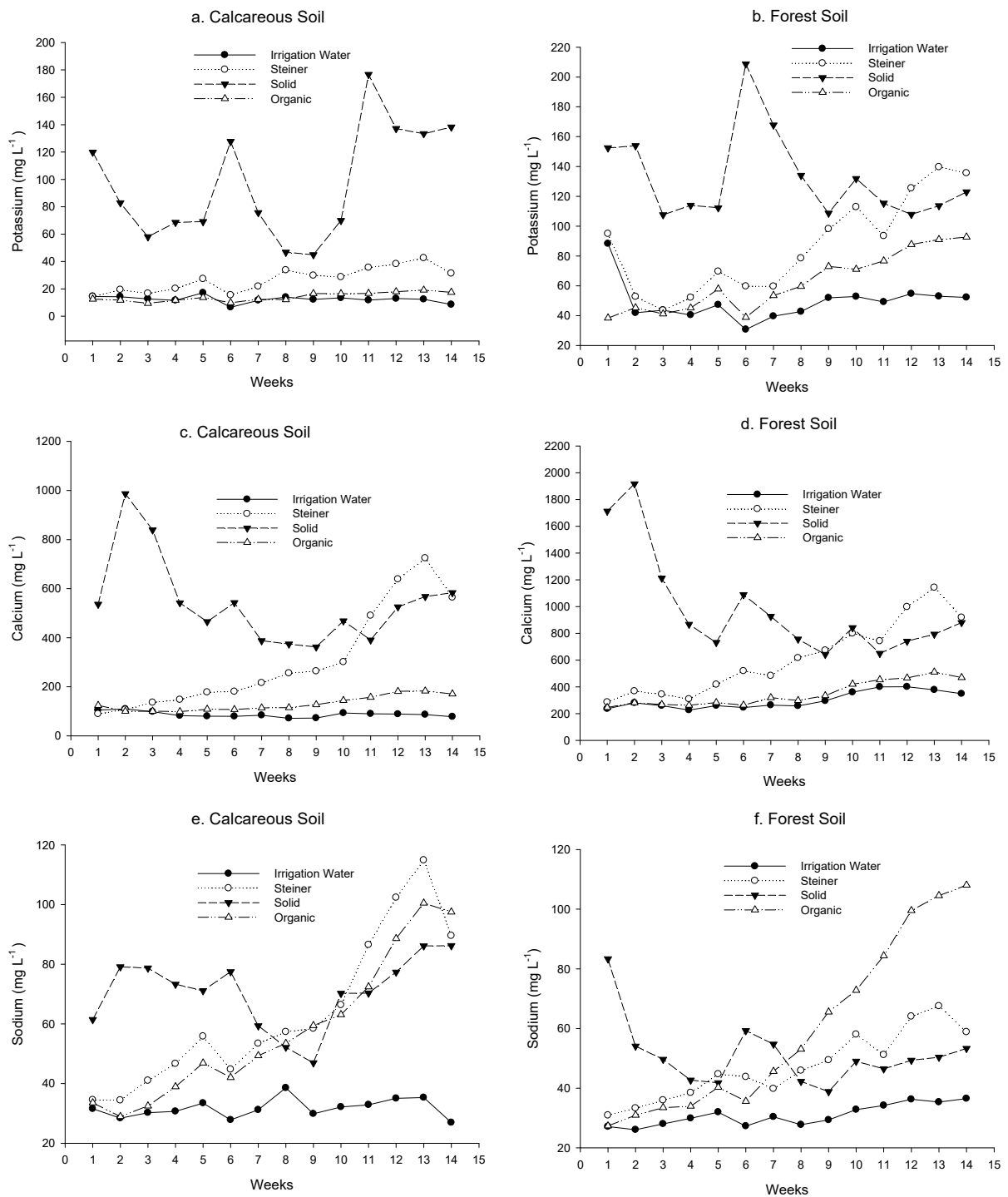
**Table 7.** Multiple polynomial model between the content of potassium, calcium, sodium, and three variables: two explanatory variables (treatment and soil type) and one numerical variable (weeks) of quadratic degree. The reference treatment for the comparison of the different nutrient contribution scenarios was irrigation water, while the forest soil was used as a reference to compare it against the calcareous soil.

Variables	Coefficient	Std. Error	p Value
Potassium			
Steiner	26.029	5.2579	$1.18 \times 10^{-6}$ **
Solid	83.4773	5.2579	$<2 \times 10^{-16}$ **
Organic	7.397	5.2579	0.160
Calcareous soil	-45.2445	3.7179	$<2 \times 10^{-16}$ **
Weeks	-3.1489	1.9876	0.114
Weeks <sup>2</sup>	0.3339	0.1289	0.010 *
Calcium			
Steiner	267.0032	34.8054	$1.95 \times 10^{-13}$ **
Solid	567.6242	34.8054	$<2 \times 10^{-16}$ **
Organic	45.4315	34.8054	0.192702
Calcareous soil	-295.5239	24.6111	$<2 \times 10^{-16}$ **
Weeks	-48.2493	13.1576	0.000286 **
Weeks <sup>2</sup>	3.7295	0.8532	$1.66 \times 10^{-5}$ **
Sodium			
Steiner	23.96214	2.60988	$<2 \times 10^{-16}$ **
Solid	29.55917	2.60988	$<2 \times 10^{-16}$ **
Organic	27.32929	2.60988	$<2 \times 10^{-16}$ **
Calcareous soil	8.59827	1.84546	$4.62 \times 10^{-6}$ **
Weeks	-1.19594	0.98662	0.226
Weeks <sup>2</sup>	0.25367	0.06398	$9.01 \times 10^{-5}$ **

\*\* = significant at  $p \leq 0.01$ ; \* = significant at  $p \leq 0.05$ .

For the sodium levels in the soil solution, significant differences were found between the treatments ( $p \leq 0.01$ ) and soil types (Table 7). The coefficients obtained by the polynomial model for both the treatments and for the calcareous soil were positive, which means that all treatments contributed to increasing sodium levels in the soil solution by a general average of 26.9 mg L<sup>-1</sup>. Furthermore, it was observed that the sodium concentration was higher in calcareous soil at an average of 8.5 mg L<sup>-1</sup> compared to the forest soil.

The significant effects found by the polynomial model of quadratic order indicate the existence of a relationship between the predictor variables and the predictor (Table 7). Within the dynamics of the cations, the dynamics were found to increase similarly but at different intensities for all treatments except for the treatment with the application of solid fertilizer, and its behavior departed from the general pattern (Figure 4).



**Figure 4.** Potassium, calcium, and sodium dynamics, determined in soil solution samples for calcareous and forest soils under pot and greenhouse conditions under different nutrient supply scenarios, using inorganic fertilizers: nutrient solution (Steiner) and fertilizers in fractional (solid) form and organic fertilizer with vermicompost tea (aqueous extract).

### 3.3.2. Multiple Polynomial Models of Third Order with Three Predictive Variables for Electrical Conductivity, Nitrates, Sulfur, and Zinc

Table 8 shows the results of the polynomial models for the response variables electrical conductivity, nitrates, sulfur, and zinc and the categorical predictive variables treatments (irrigation water, Steiner, solid and organic), soil types (calcareous and forest), and the numerical predictive variable (time in weeks) of cubic degree.

**Table 8.** Multiple polynomial model between electrical conductivity, nitrates, sulfur, zinc, and three variables: two explanatory variables (treatment and soil type) and one numerical variable (weeks) of cubic degree. The reference treatment for the comparison of the different nutrient contribution scenarios was irrigation water, while the forest soil was used as a reference to compare it against the calcareous soil.

Variables	Coefficient	Std. Error	p Value
Electric Conductivity			
Steiner	1.395000	0.142609	$<2 \times 10^{-16}$ **
Solid	2.916071	0.142609	$<2 \times 10^{-16}$ **
Organic	0.369881	0.142609	0.00992 **
Calcareous soil	−0.667857	0.100840	$1.44 \times 10^{-10}$ **
Weeks	0.377170	0.150824	0.01288 *
Weeks <sup>2</sup>	−0.047783	0.022955	0.03815 *
Weeks <sup>3</sup>	0.001814	0.001008	0.07286
Nitrates			
Steiner	913.0952	65.9477	$<2 \times 10^{-16}$ **
Solid	1618.5714	65.9477	$<2 \times 10^{-16}$ **
Organic	−29.9286	65.9477	0.65026
Calcareous soil	−361.7500	46.6321	$1.11 \times 10^{-13}$ **
Weeks	153.7308	69.7468	0.02821 *
Weeks <sup>2</sup>	−23.4050	10.6151	0.02816 *
Weeks <sup>3</sup>	1.2104	0.4663	0.00986 **
Sulfur			
Steiner	13.04131	4.13602	0.001765 **
Solid	13.38048	4.13602	0.001340 **
Organic	24.95929	4.13602	$4.30 \times 10^{-9}$ **
Calcareous soil	−18.24827	2.92461	$1.35 \times 10^{-9}$ **
Weeks	−13.89950	4.37429	0.001627 **
Weeks <sup>2</sup>	2.21597	0.66574	0.000972 **
Weeks <sup>3</sup>	−0.08965	0.02924	0.002351 **
Zinc			
Steiner	0.0764286	0.0566417	0.17816
Solid	0.4747619	0.0566417	$1.55 \times 10^{-15}$ **
Organic	−0.0027976	0.0566417	0.96064
Calcareous soil	−0.2030655	0.0400517	$6.66 \times 10^{-7}$ **
Weeks	0.1781132	0.0599047	0.00316 **
Weeks <sup>2</sup>	−0.0294383	0.0091172	0.00137 **
Weeks <sup>3</sup>	0.0012264	0.0004005	0.00238 **

\*\* = significant at  $p \leq 0.01$ ; \* = significant at  $p \leq 0.05$ .

For the response variables such as electrical conductivity and sulfur, significant differences were found between treatments and soil types ( $p \leq 0.01$ ) (Table 8), which indicates the existence of a relationship between the predictor variables and the predictor. The coefficients obtained in the polynomial model for the different treatments showed positive trends. The treatment with the application of solid fertilizers showed the highest levels of electrical conductivity in the soil solution, exceeding the control by an average of 2.9 dS  $\text{cm}^{-1}$ . On the other hand, the concentration of sulfur was favored mainly by applying the organic treatment. Comparing the levels of electrical conductivity and sulfur among soil types, lower levels were observed in the calcareous soil, as seen in the negative coefficients obtained by the polynomial model (Table 8). For the average weekly data of the electrical conductivity, it was observed that within its dynamics, treatments (irrigation water and organic) were very similar over time, while treatments with inorganic fertilizer showed a decoupling, moving in opposite directions (Figure 5a,b). Peaks of increase in the EC dynamics were observed for the treatment with solid fertilizers, which coincided with the dates of application (Figure 5a,b).

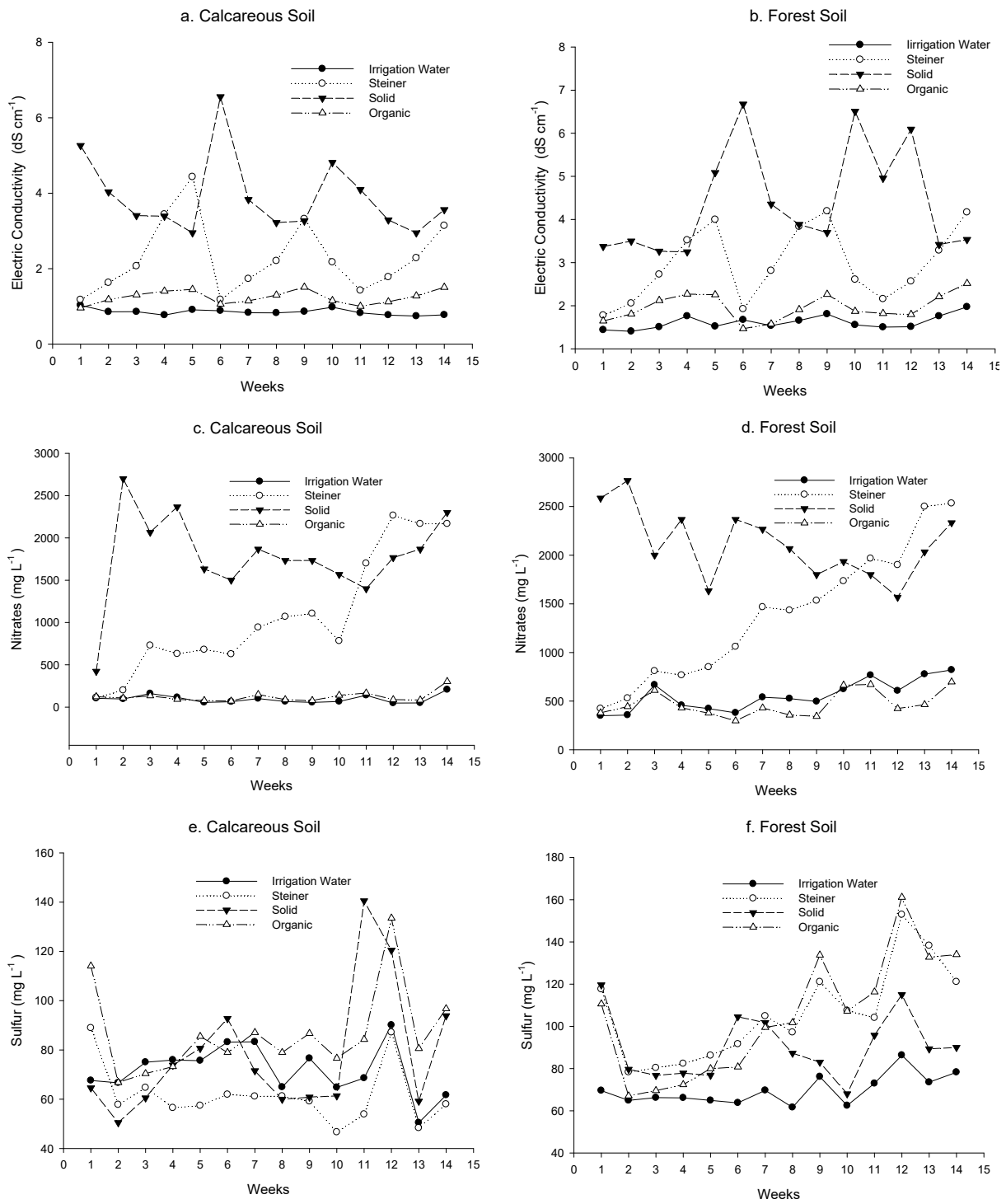
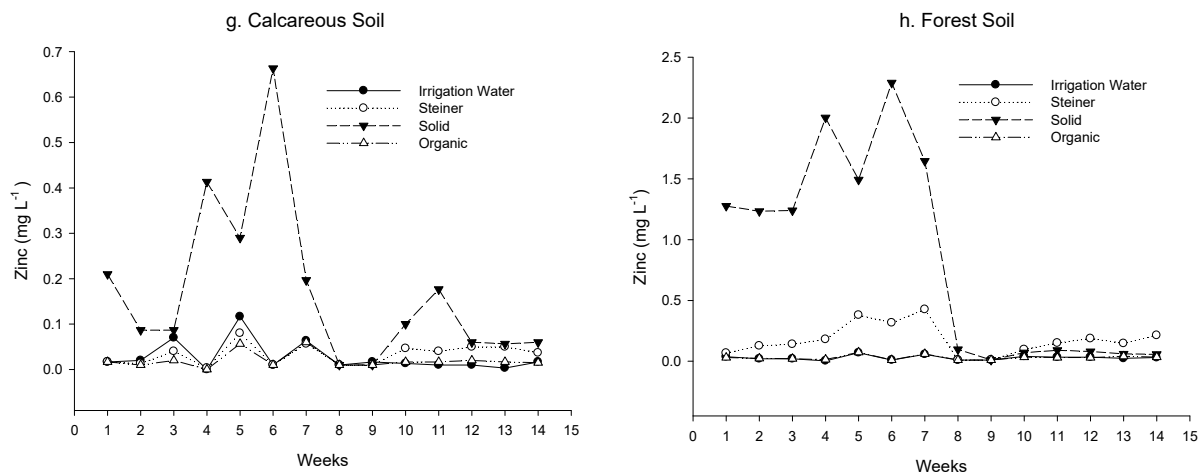


Figure 5. Cont.



**Figure 5.** Dynamics of electrical conductivity, nitrates, sulfur, and zinc, determined in samples of soil solution for calcareous and forest soils under pot and greenhouse conditions under different nutrient supply scenarios, using the Inorganic: nutrient solution (Steiner) fertilizers and fertilizers in fractional form (solid) and organic fertilizer with vermicompost tea (aqueous extract).

Significant differences were found for the response variable nitrates between the control treatment and the treatments by applying inorganic fertilizers ( $p \leq 0.01$ ). In contrast, while the organic treatment did not induce changes in the soil solution. However, despite not having significant effects of organic treatment,  $\text{NO}_3^-$  levels in the soil solution were lower than the control evaluated for the forest soil. In contrast, in calcareous soil, its behavior was very similar (Figure 5c,d). The nitrate dynamics for inorganic treatments showed opposite patterns; while Steiner solution treatment was ascending, treatment with solid application decreased (Figure 5c,d). Comparing soil types (calcareous and forest) were found to be significantly different. Fertilizer treatment in solid form showed the highest positive coefficient (Table 8), which indicates that the treatment was the most effective at maintaining a high concentration of nitrate in the soil solution; when comparing soil types, the coefficient obtained by the polynomial model (Table 8) indicated that the calcareous soil presented average nitrate levels of  $361.7 \text{ mg L}^{-1}$  below the forest soil.

The treatments did not show significant effects on the zinc content in the soil solution except for the treatment where fertilizers were applied in solid form ( $p \leq 0.01$ ), exceeding the control treatment according to the coefficient obtained in an average of  $0.47 \text{ mg L}^{-1}$  (Table 8). Zn increases because solid fertilizer occurred in the first half of the study, showing a similar pattern in their dynamics for both soil types (Figure 5g,h). Significant differences were found between the soil types. According to their negative coefficient recorded by the calcareous soil (Table 8), greater Zn availability was deduced in the black forest soil solution.

### 3.3.3. Multiple Polynomial Models of Fourth Order with Three Predictive Variables for the Oxide-Reduction Potential, Nitrogen, Magnesium, and Boron

For these last four response variables, the multiple polynomial model that was best adjusted according to the cross-validation error coefficient (Table 5) included the two categorical variables (treatment and soil type) and the numerical variable in the quartic degree.

For the response variables ORP and magnesium, the results of the multiple polynomial models are shown in Table 9, with significant differences between the inorganic and organic treatments compared to the control treatment, and between soil types (calcareous and forest). The coefficients obtained through the multiple polynomial model indicate that for both ORP and  $\text{Mg}^{2+}$ , the treatment with the greatest impact on the mentioned variables was the application of fertilizers in solid form, surpassing the control in an average value of  $19.53 \text{ mV}$  and  $130 \text{ mg L}^{-1}$ , respectively. In contrast, when comparing soil types, the soil of calcareous origin surpassed forest soil at ORP levels and  $\text{Mg}^{2+}$  concentration according to the coefficients of the model (Table 9). Furthermore, the ORP dynamics for both soil types

showed a temporal pattern with fluctuations over time (Figure 6a,b) with oscillations of 160 to 260 mV. On the other hand,  $Mg^{2+}$  exhibited a trend toward increasing the two soil types for all treatments except for the treatment with solid fertilizer application, observing that its behavior departs from the general pattern (Figure 6e,f).

**Table 9.** Multiple linear model between the potential oxidation-reduction, nitrogen, boron, and three variables: two explanatory variables (treatment and soil type) and one numerical variable (weeks) of quartic degree. The reference treatment for the comparison of the different nutrient contribution scenarios was irrigation water, while the forest soil was used as a reference to compare it against the calcareous soil.

Variables	Coefficient	Std. Error	p Value
Oxidation–reduction potential			
Steiner	12.520238	3.831539	0.001200 **
Solid	19.535714	3.831539	$5.80 \times 10^{-7}$ **
Organic	8.607143	3.831539	0.025346 *
Calcareous soil	6.620833	2.709308	0.015064 *
Weeks	41.980100	9.494133	$1.33 \times 10^{-5}$ **
Weeks <sup>2</sup>	−10.093597	2.454188	$4.95 \times 10^{-5}$ **
Weeks <sup>3</sup>	0.925696	0.241927	0.000156 **
Weeks <sup>4</sup>	−0.028663	0.008014	0.000400 **
Nitrogen			
Steiner	−5.57000	5.56991	0.318042
Solid	−1.50262	5.56991	0.787504
Organic	0.79643	5.56991	0.886388
Calcareous soil	−1.72417	3.93852	0.661842
Weeks	22.17789	13.80163	0.109041
Weeks <sup>2</sup>	−9.54002	3.56766	0.007871 **
Weeks <sup>3</sup>	1.16756	0.35169	0.001002 **
Weeks <sup>4</sup>	−0.04282	0.01165	0.000277 **
Magnesium			
Steiner	60.67560	8.75297	$2.22 \times 10^{-11}$ **
Solid	130.17726	8.75297	$<2 \times 10^{-16}$ **
Organic	17.89310	8.75297	0.0417 *
Calcareous soil	65.49940	6.18929	$<2 \times 10^{-16}$ **
Weeks	37.33322	21.68890	0.0861
Weeks <sup>2</sup>	−11.57603	5.60648	0.0397 *
Weeks <sup>3</sup>	1.17324	0.55267	0.0345 *
Weeks <sup>4</sup>	−0.03737	0.01831	0.0420 *
Boron			
Steiner	−0.0594881	0.1044116	0.569
Solid	0.0957619	0.1044116	0.360
Organic	−0.0295017	0.1044116	0.778
Calcareous soil	0.3802925	0.0738301	$4.49 \times 10^{-7}$ **
Weeks	1.5860830	0.2587204	$2.52 \times 10^{-9}$ **
Weeks <sup>2</sup>	−0.4885648	0.0668780	$2.13 \times 10^{-12}$ **
Weeks <sup>3</sup>	0.0528210	0.0065926	$2.01 \times 10^{-14}$ **
Weeks <sup>4</sup>	−0.0018441	0.0002184	$1.01 \times 10^{-15}$ **

\*\* = significant at  $p \leq 0.01$ ; \* = significant at  $p \leq 0.05$ .

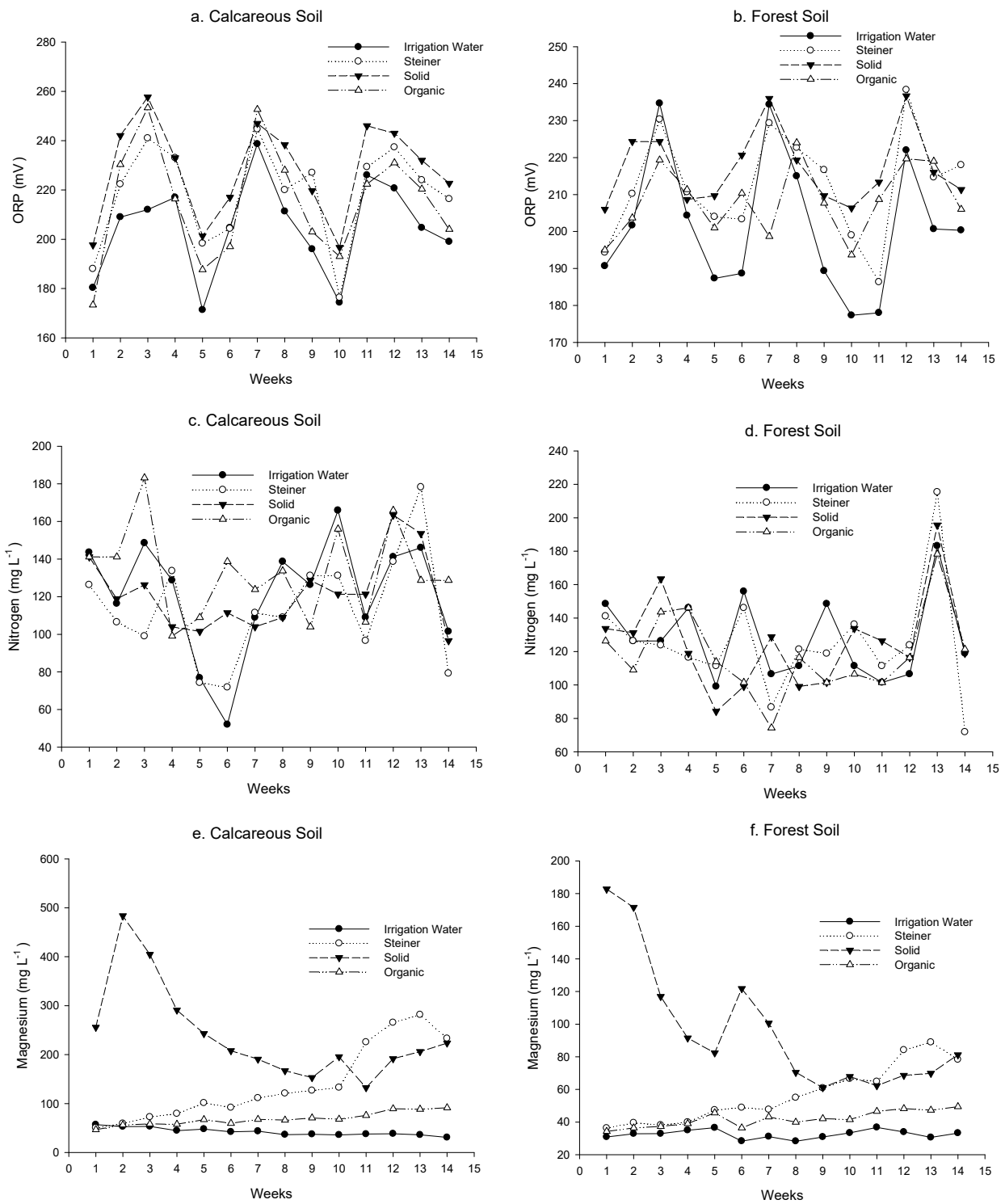
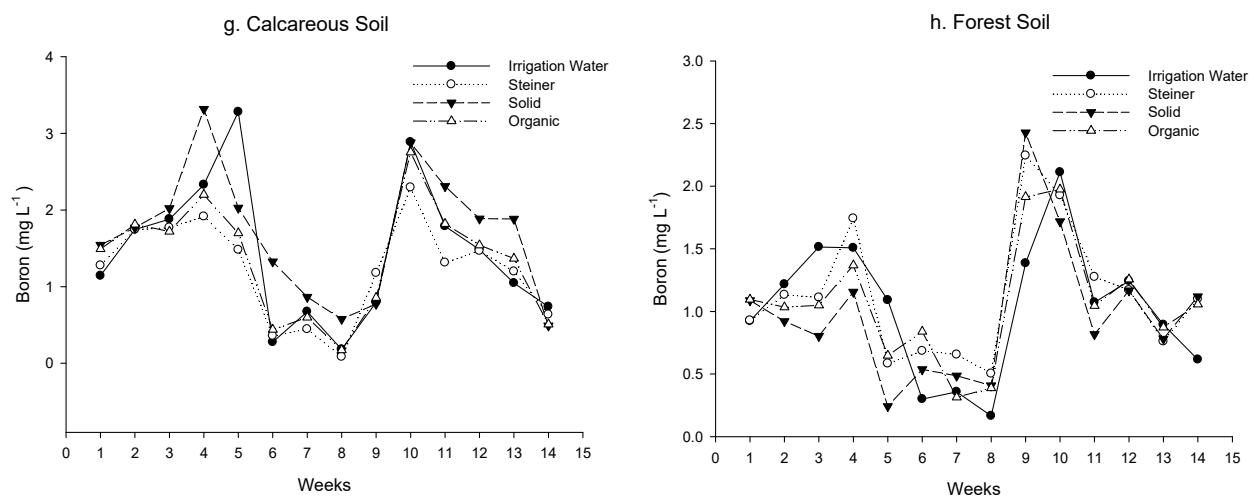


Figure 6. Cont.





**Figure 6.** Dynamics of the oxide reduction potential (ORP), total nitrogen, magnesium, and boron, determined in soil solution samples for a calcareous and forest soil, under pot and greenhouse conditions, submitted to different contribution scenarios of nutrients, through inorganic fertilizers: nutrient solution (Steiner) and fertilizers in fractional form (solid) and organic fertilizer with vermicompost tea (aqueous extract).

The application of the different fertilization scenarios (organic and inorganic) did not show significant effects on the nitrogen and boron contents in the soil solution (Table 9). However, in the case of nitrogen, a slight decrease was observed in treatments with inorganic fertilizers. For boron, negative coefficients were observed for the treatment with Steiner solution and organic treatment, which indicates that the boron concentration for these two treatments was below the control treatment (Table 9). When comparing the calcareous soil against the forest soil, statistical significance was only found for the boron response variable in the soil solution. Based on the coefficient obtained for the calcareous soil in the multiple polynomial analysis, the calcareous soil with an average concentration of  $0.38 \text{ mg L}^{-1}$  of boron was higher than the forest soil.

The dynamics of nitrogen showed variations over time without showing a recognizable pattern in its behavior (Figure 6c,d), while the dynamic behavior of boron fluctuated over time, and a very similar pattern was observed between the two soil types, where a drop in their levels can be noted in the intermediate stage of the experiment (Figure 6g,h).

The presence of significant effects on the response variables through the polynomial models of quadratic degree is a sign of the existence of the relationship between the predictors and the predictor.

#### 4. Discussion

The application of the different types of fertilization in the calcareous soil and the black forest soil showed different effects on the concentration of the elements in the soil solution. The treatments of application of inorganic fertilizers showed superiority in the content of the various variables measured in the solution of the soil in comparison with the rest of the treatments, except for sulfur. The treatment with the fertilizer application in solid form showed the highest concentration of ions, followed by the treatment with the application of the Steiner nutrient solution, and finally, the organic treatment with vermicompost tea. It should be mentioned that the organic treatment did not show significant effects on the concentrations of the different ions measured in the soil solution, except for sulfur, sodium, and manganese.

From an agricultural point of view, the application of nutrient solutions presents dosage advantages, greater efficiency, and localized applications. Still, despite this, the treatment with the application of solid fertilizers showed higher levels of dissolved ions in

the soils (calcareous and forest), possibly due to the nutrient supply in a controlled way over time, although the fertilizers used were water-soluble and not slow release.

Water in soil pores is intimately linked to the physical and chemical properties of the solid phase, and their impact on the volume of water and the presence of elements in the soil solution will depend on the amount of water applied to the soil [25], either as irrigation water or nutrient solutions: organic and inorganic. Soil solution, according to the results obtained for the control, Steiner, and organic treatments, presented very similar patterns in their dynamics with tendencies toward the increase as time progressed, a different situation than that presented the treatment in solid form, where their dynamics showed patterns that deviated from the general behavior of other treatments.

Solid fertilization is not homogeneous, but it is instead placed at specific points for later dissolution. Therefore, it is a point source of chemical elements, causing significant variations in the EC and the concentration of ions at particular points where the fertilizer was applied [26]. Once the irrigation water comes in contact with the solid fertilizers, the heterogeneity of their distribution will create temporal, substantial concentration gradients, as presented in the case of  $K^+$ ,  $Ca^{2+}$ ,  $Na^+$ ,  $NO_3^-$ , and  $Zn^{2+}$ .

#### 4.1. pH, Oxide-Reduction Potential, and Electrical Conductivity in Soil Solution

The pH was lower in the soil solution for the treatment with solid fertilizer application. The decrease in pH was possibly a critical factor in the availability of elements such as  $Mg^{2+}$ ,  $NO_3^-$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Na^+$ , and  $Zn$ , with their higher concentrations for the treatment mentioned. Most likely, the main factor that led to the decrease in pH was the application of sulfuric acid ( $H_2SO_4$ ) and citric acid for the acidification of irrigation water. This phenomenon was observed in calcareous soil for all treatments; a contrary situation was found in the forest soil for organic treatment, where the effect of citric acid on the soil solution was not reflected. This may be related to the greater buffering power of the soil associated with both organic matter present in the soil and for which it is being contributed by vermicompost tea [27], thus neutralizing the acidifying power of citric acid and causing the pH to increase because of organic treatment. In general terms, when comparing soil types, the pH of the forest soil presented a minor variation in its dynamics compared to the calcareous soil. It is possible that the lower variability depended on the organic matter content, which increased the soil buffer power and allowed the maintenance of the pH values within ranges shorter than those shown by the calcareous soil [28]. The presence of  $CaCO_3$  must also be considered, which is the primary buffering substance for acidity [29].

The ORP showed an inverse pattern in its behavior compared to pH. This behavior is characteristic of the redox reactions that originate in the soil, where the oxidative processes produce  $H^+$  and cause acidification, and the reductive processes consume  $H^+$  and raise the pH [30]. The treatment with solid fertilizers presented higher values of ORP, which can be interpreted as an increase in the level of oxidation of the soil solution; treatment with Steiner solution resulted in lower ORP values, and organic treatment resulted in lower (reduced) values for ORP. However, when comparing the soil types, no adjustment was observed to the expected relationship, since the calcareous soil presented higher values of pH and ORP. In the forest soil, the opposite was true. One possible explanation is that ORP values can vary widely at the same pH value depending on the profile of oxidizing compounds present [31]. Another possibility is that the response of pH and ORP in the case of forest soil could be associated with the presence of organic matter and organic compounds such as sugars or other organic substances soluble in the soil solution, which give reductive power to the environment, amending several changes in the soil solution chemistry [30,32]. ORP often varies greatly in short times, as it was for all treatments. This variation is due to the heterogeneity of soils and microsites with different concentrations of  $O_2$  resulting from different sizes of soil pores, the content of water and microbial metabolism, and the prevailing chemical reactions [4,33]. It has been reported that the temporal variability of the redox potential at a single point in the soil can vary by 1000 mV or more if the soil is periodically saturated or flooded and by periodic drainage as the system changes from

aerobic to anaerobic and vice versa [34], a situation presented for calcareous soil, which presented a higher bulk density and therefore a lower porosity and lower drainage (Table 1). In the case of forest soil, variability is associated with a more significant amount of organic matter and the microbial metabolism associated with it [35–37].

The EC increase in the soil solution was the result of the use of inorganic fertilizers, especially the treatment where fertilizers were added in solid form, which contributed to the increase in  $Mg^{2+}$ ,  $K^+$ ,  $Ca^{2+}$ , and  $Na^+$  and  $NO_3^-$ , the cations, and anions, the cations generally associated with the increase in EC [1,38,39]. The high EC levels of up to  $7 \text{ dS cm}^{-1}$  exhibited by the treatment in solid form could not be considered adequate since they could decrease the water availability to the plants [40]. As the soil salt content increases, specific ion toxicity limits plant growth [41]. In nutrient solutions, it has been observed that many crop plant species are negatively affected by  $EC > 4 \text{ dS cm}^{-1}$  [42]. However, the effects of salinity in soils also depend on soil texture, water content, and salt composition [4]. It is worth mentioning that EC in forest soil was superior, possibly due to the action of the organic matter that acts by retaining and releasing ions, modifying physical, chemical, and biological properties associated with soil sorption capacity, soil water retention, and soil density and possibly preventing leaching [43,44].

#### 4.2. Concentrations of the Different Ions in the Soil Solution

The concentration of ions in the soil solution was favored by applying inorganic fertilizers and, to a greater extent, by treatment with the application of solid fertilizers. Similar results were found by [45], where the application of fertilizer led to a significant increase in the content of K in the soil in three chestnut orchards that were fertilized during two vegetative periods compared to the previous nonfertilized year. The increases in  $Ca^{2+}$ ,  $NO_3^-$ , Zn, and  $K^+$  in the soil solution were higher for black forest soil in conjunction with solid fertilizers. The direct effect on the availability of these elements could be given by the water content in the soil, which is a limiting factor in the availability and supply of nutrients [4], highlighting that the forest soil has a higher bulk density (expected greater porosity) and a greater capacity of retention of humidity. Similarly, high levels of organic matter could increase the availability of nutrients [46]. The  $K^+$  concentration in forest soil solution compared to the calcareous soil was higher in all treatments, probably due to the moderately high levels of this  $K^+$  in the solid phase of the soil. The results indicated a significant increase in  $NO_3^-$  in the soil solution by the effect of the fertilizers. It was observed that the application of irrigation water and vermicompost tea increased the concentration of  $NO_3^-$  in the solution of the forest soil compared to that of the calcareous soil, possibly due to the mineralization processes of organic matter present in the forest soil, where commonly more than 90% of organic nitrogen is found [1]. The decomposition of organic nitrogen that eventually leads to nitrate formation is associated with the production of a strong acid (nitric acid) [1], probably involved in the lower pH values found in the soil solution of the forest soil. Although there were differences in the  $NO_3^-$  content in the soil solution due to the treatments, it would be expected to find the same behavior for the total nitrogen content, which did not occur. The nonexistence of these differences could be due to the presence of other forms of nitrogen in the soil solution, such as organic compounds of low molecular weight and  $NH_4^+$ . However, a slight increase in this nitrogen was observed with the application of vermicompost tea. It has been reported that the application of liquid manure may lead to a transient increase of soluble  $NH_4^+$  [47,48].

The pH influenced the availability of elements, as is the case for  $Ca^{2+}$ , which is positively related to high pH values [49]. The reduction of pH and the ORP would be the probable cause by which the availability of Zn is increased for forest soil [50–52] compared to the calcareous soil. The concentration of Zn in the soil solution is determined by the adsorption and desorption processes that occur in the soil matrix; therefore, the concentration not only of Zn but also several elements at a given pH of the soil can also depend on other components of the solute as well as the organic matter content of the soil and the microbial activity [53]. The presence of organic matter in forest soil could influence

the content of low molecular weight organic substances acting as chelates for Zn and  $\text{Ca}^{2+}$  [1], reducing its sorption to minerals [54]. The low concentration of Zn in calcareous soil was probably due to the slow diffusion of the element, with diffusion coefficients 50-fold lower in soils with high pH compared to low pH soils [55]. In alkaline soils, Zn complexes with  $\text{CaCO}_3$  [56], and reactions with oxides through adsorption, strongly bind Zn and regulate the amount of Zn in the soil solution [56–58]. The levels of the  $\text{Ca}^{2+}$  present in the soil solution were adequate for all treatments and soil types if we take as a reference the concentration that contains a nutrient solution for the development of crops. These levels in the soil solution are explained by the high  $\text{Ca}^{2+}$  content naturally present in soils and irrigation water. The concentration of  $\text{Ca}^{2+}$  was even more favored by fertilizer applications, to a greater extent by fertilizers in solid form.

When comparing soil types, black forest soil had a higher  $\text{Ca}^{2+}$  concentration than calcareous soil. It is known that the availability of calcium in calcareous soil is due to the reactions of calcium carbonates with  $\text{CO}_2$  and  $\text{H}^+$  forming  $\text{Ca}(\text{HCO}_3)_2$ , which is more soluble in water [59,60] releasing  $\text{Ca}^{2+}$  to the liquid phase. These reactions, to some extent, may explain why the presence of organic matter in the forest soil favored the availability of  $\text{Ca}^{2+}$  [1].

The increase in  $\text{Na}^+$  and  $\text{Mg}^{2+}$  in the soil solution is attributed to the contribution of the fertilizer in solid form, with a more apparent effect on the calcareous soil, which can be explained by the high levels of  $\text{Mg}^{2+}$  and  $\text{Na}^+$  interchangeable in the soil. The lower availability of  $\text{Mg}^{2+}$  in forest soil was possibly due to the presence of high concentrations of  $\text{Ca}^{2+}$  and  $\text{K}^+$  in this soil and, in some cases,  $\text{NH}_4^+$ . In addition, the interaction of Mg and soil organic matter can promote clay flocculation, limiting the availability of Mg [61–63]. The lower porosity presented in the calcareous soil could have influenced the greater presence of B due to the difficulty in its drainage, which caused the accumulation of this element [64]; In addition, a more significant amount of boron specifically adsorbed bound to oxide, residual and total have been found in soils with a high  $\text{CaCO}_3$  content [65,66], based on this fact, it is more probable that the solubility of the B decrease, but its concentration can be compensated for by the lower leaching mentioned above and/or by the supply of B in the irrigation water [4]. Although the forest soil presented more organic matter content, which is closely associated with the accumulation and availability of B in the soil, the power of fixing this element by the organic content could increase over time, decreasing its concentration in the soil solution [67]. Clay particles have a similar power of fixing on boron, causing them to be relatively inaccessible for plant absorption [68].

The increase in S in the soil solution is attributed to the presence of organic matter in the forest soil and the incorporation of the S-rich vermicompost tea treatment (Table 4). Similarly, the S in the soil solution results from the decomposition processes of the organic matter by the microorganisms, which release sulfates, contributing to increasing the levels of this element in the soil solution [1].

## 5. Conclusions

It was found that the model that best predicts pH behavior in soil solution was the multiple linear model using categorical variables (treatments and types of soil). The multiple polynomial models were best adjusted for the variables: potassium, calcium, sodium (quadratic grade), electrical conductivity, nitrates, sulfur (cubic degree), zinc, oxidation-reduction potential, nitrogen, magnesium, and boron (quartic grade).

The treatments application with fertilizers (organic and inorganic) increased the mineral contents in both soil types.

The concentrations of  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , S,  $\text{Zn}^{2+}$ , N, and C.E increased in the soil solution of forest soil. While the values of pH,  $\text{Na}^+$ , ORP,  $\text{Mg}^{2+}$ , and B increased for the calcareous soil. The minerals content in the soil solution increased by the contribution of fertilizers as follows: solid fertilizers > Steiner > vermicompost tea > irrigation water. The treatments dynamics in the two soil types were similar, but the variation was less for the forest soil.

The cations, such as  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and anions, such as nitrates, showed an increasing dynamic with the Steiner application; and a dynamic to decrease with the application of the solid fertilizer.

The Steiner application treatment showed adequate levels of ions in the solution of both soils. Unique temporal patterns were found for the dynamics of treatment behavior through the application of solid fertilizers.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/soilsystems6020042/s1>, Table S1. Weekly means and error standard for the variables in the two soil types.

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