Long-Term Effects of Calcium-Based Liming Materials on Soil Fertility Sustainability and Rye Production as Soil Quality Indicators on a Typic Palexerult

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Abstract: Liming is a common practice used to improve acidic soil properties, as is essential for agricultural quality. A long-term field experiment with one lime rate (6000 kg/ha of carbonate calcium equivalent) and three calcium-based liming amendments (gypsum, limestone and sugar foam) was maintained on a Typic Palexerult for 10 years in order to determine changes in soil acidity and to assess the effects on crop (rye) yields. The soil acidity conditions decreased with all the amendments tested, but the sugar foam and limestone was more effective than gypsum over a long-term period. No significant changes in organic soil matter levels between the treatments tested were found. Interestingly, an increase in the leaching of organic soil matter was observed in limed soils. Lime application significantly increased the total rye biomass compared to the control soils during the whole experiment (2002–2011). Yield trends observed in spike and stem biomass were similar to those reported for total rye biomass. In this respect, at the end of the research, gypsum, limestone and sugar foam increased in relation to the total production of rye biomass by 16%, 32% and 38%, respectively, as compared to the control soils. Additionally, a significant and prolonged difference in calcium concentrations in rye stems between unlimed and limed subplots was observed. However, in spite of the results presented here, further investigations are needed to gain a better understanding of the long-term effects of liming on the chemical properties of soil.

Keywords: aluminum toxicity; biomass; leaching; liming; organo-mineral complex; rye; soil acidity

1. Introduction

While it is true that plants can present normal growth in inorganic soil media, and even in liquid cultures containing no organic matter, so long as the essential inorganic nutrients are supplied, there are many benefits derived from the presence of organic matter in soil [1]. Furthermore, the presence of soil organic matter (SOM) affects the soil quality and the types of weathering products that form because of the influences of dissolution and aqueous speciation [2]. Despite its often-minor contribution to the total mass of mineral soils, SOM can have an influence on a wide variety of soil properties, ecosystem functioning, and the magnitude of various obligatory ecosystem processes. In this way, amongst others, the following factors can be mentioned: (i) biological properties (reservoir of metabolic energy, source of macronutrients and ecosystem resilience), (ii) physical properties (stabilization of soil structure, water retention and thermal properties) and (iii) chemical properties (cation exchange capacity (CEC), buffering capacity and pH effects, chelation of metals and interactions with xenobiotics) [3]. In this respect, changes in the soil organic matter...
level is a common indicator of the chemical and biological quality of soil because of its significant effects on biological activity, cation exchange capacity, pH, and nutrient levels across a wide range of soils [4]. However, it has also been suggested that the total soil organic matter may not be a good indicator of soil quality [5], particularly as the total pool contains relatively inert physically and chemically stabilized fractions [5]. Despite this, the role of soil organic matter in sustainable nutrient cycling, and therefore in the sustainability of agronomic environments, is undoubtedly important.

Many agricultural soils are poorly productive as a result of their surface and subsurface soil acidity. Natural soil acidification is favoured in areas with high rainfall, which facilitates the leaching of exchangeable calcium and magnesium, and it exhibits a high saturation of aluminium as it becomes the dominant cation in the exchange complex. These characteristics by themselves impose severe restrictions on the agricultural use of soils in Mediterranean environments [6].

For crop production, soil acidity depends on numerous factors, but aluminium toxicity is considered to be the main limiting factor for plant growth in acid soils [7]. When the pH of the soil is below 5.5, trivalent aluminium can become the major cation in the exchange complex, and can exceed calcium, magnesium and potassium cations [8]. As the pH decreases, the trivalent aluminium species concentration increases when compared to the hydroxylated species, which favours a complete desorption and leaching of the rest of the exchangeable cations [9]. More specifically, in addition to the low activity of beneficial microorganisms, a reduced plant root growth and a low water uptake capacity of root plants [10], and the nutrient/element deficiencies and toxicities that result from soil acidity are other remarkable limiting factors for plants growing in acid soils. Thus, soil acidity affects the biological, chemical and physical properties of soil and affects the sustainability of biomass production in managed ecosystems.

While SOM can provide some buffering capacity against acidification, this only delays the onset of that process and does not solve the fundamental problem [11]. Moreover, SOM is able to both decrease soil pH by releasing hydrogen ions that can be associated with organic anions or by nitrification in an agrosystem, and can result in an increased pH, either by mineralization of organic anions to CO$_2$ and water (thereby removing hydronium anions) or because of the alkaline nature of the organic material [12]. Traditionally, liming is the most effective practice to ameliorate soil acidity constraints in order to achieve optimal crop production [13]. Its primary purpose is to increase the pH of acid soils through hydrolysis of the carbonate anions. This hydrolysis produces hydroxy anions that are able to neutralize the hydronium cations, and to thereby increase the soil’s pH. Additionally, liming has favourable effects on the structure of soil, such as (1) reducing the soil crusting and the power requirements for tillage operations, and (2) playing a significant role in the control of certain plant pathogens [10]. Adequate liming neutralizes soil acidity, and thus eliminates the toxicity produced by aluminium, manganese, iron and hydronium ions. Moreover, it improves the soil structure (aeration) and enhances the bioavailability of calcium, magnesium, phosphorus and molybdenum. However, inadequate liming rates (overliming) can create deficiencies in micronutrients like iron, manganese, zinc, copper and boron [13]. Furthermore, the relative extent and net effect of liming on soil properties, such as SOM, will certainly depend on such important factors as initial soil pH, the liming rate, clay content and mineralogy, soil use, climate, and other factors including amendment solubility. Interestingly, lime applications are usually discontinuous, so different short and long-term effects may exist [14]. As a general rule, the low solubility of the traditional liming materials, such as limestone, could be overcome by replacing them with more soluble liming materials, such as sugar foam and gypsum. Sugar foam results from the purification-flocculation of colloid matter from the liquor extracted from sugar beet [15] and it is a relatively new organic residue that has emerged from the significant growth in the sugar beet industry [16].

Despite liming being an important practice to achieve optimum yields for all crops grown in acid soils, a number of initiatives that are state of the art in soil acidity fields try
to replace or complement its beneficial effects. These include genotypes within crop species with a greater ability to tolerate toxic levels of aluminum, alternative liming materials like ash products or biosolids from waste treatment plants, tillage systems and crop rotations. Additionally, new efforts are being made in the research of liming effects on phosphorus immobilization, activities of beneficial microorganisms, solubility and leaching of heavy metals, controlling plant diseases and mitigating nitrous oxide emission from soils [10,13]. Further, liming materials like limestone (CaCO$_3$) are being investigated in new areas of research (environmental field), such as the inertization purposes of materials containing asbestos when they are mixed with lime or limestone before the thermal inertization process [17].

Since the main purpose of liming is to modify soil pH and the composition of the exchange complex, most of the scientific studies in this field are focused on soil pH, exchangeable cations or plant productivity. To the best of our knowledge, the long-term effects of liming on SOM have been rarely studied on their own [14]. Consonant with this, the knowledge increases in these long-term effects at the same time of assessing these effects on lime-induced change in the chemical composition of SOM, e.g., the amount and proportional distribution of each type of SOM, could reflect its stability and provide an indication of the long-term carbon sequestration mechanisms [18].

Therefore, the main aim of this research is to assess the long-term effects (10 years) of three calcium-based liming amendments (namely limestone, gypsum and sugar foam) on several soil properties (including SOM) as key indicators of its agronomic quality and rye biomass production in an acid soil under dry, summer oceanic climatic conditions, as well as to make a closer inspection of their temporal changes. This could improve agronomic strategies in acid soil management in two ways: (i) to evaluate whether there may be a better efficiency with the combined application of liming materials than applying them alone, and (ii) to estimate the duration of the residual effect of liming based on the decrease in aluminum saturation, which can be used to determine when additional liming amendments should be applied. In addition to rye yield production, calcium, magnesium and potassium concentrations in rye stem biomass have also been studied. Finally, because long-term experiments are of scientific interest in agriculture, it is hoped that this research will contribute to a deeper understanding of liming on soil fertility conditions.

2. Materials and Methods

2.1. Study Site

The soil under study corresponds to an acid Typic Palexerult [19] located in the village of Camposagrado (municipality of Rioseco de Tapia, León Spain) with Universal Transverse Mercator (UTM) coordinates of 275185E for the X-coordinate and 4734044N for the Y-coordinate (European Terrestrial Reference System 1989/UTM zone 30N), situated at an altitude of 1130 m (Figure 1). The research evaluated a *Secale cereale* L. crop (rye) over a period of ten cropping years (2002–2011). The amount of seed applied was 100 kg/ha. From a bioclimatic point of view, the research area would be classified as a summer dry oceanic climate (Csib), according to the climate classification of Köppen-Geiger [20]. For all the treatments, the following local fertilization scheme was used: 150 kg/ha of background fertilizer in the form of an 8/15/15 complex (12.0 kg/ha N, 22.5 kg/ha P$_2$O$_5$ and 22.5 kg/ha K$_2$O) with top dressing application of 38.0 kg/ha N as 33% calcium ammonium nitrate.
2.2. Characterisation of the Liming Materials and Doses

Table 1 shows the mineral composition of the three liming materials used in this study, as well as its calcium carbonate equivalent (CCE) [21]. The limestone exhibited the highest calcium oxide content, and correspondingly, the higher CCE. A liming rate was calculated for the first 35 cm of the soil, with the aim of decreasing the Al saturation of the effective cation exchange capacity (ECEC) below 20% in order to ensure an adequate degree of base saturation (i.e., 80%) that is, in general, required by most annual and permanent crops [13]. The ECEC can be defined as the total amount of exchangeable cations, which are mostly bases, in non-acidic soils and bases, plus aluminum in acidic soils. In this way, ECEC corresponded to the arithmetic sum of the concentrations of exchangeable calcium, magnesium, potassium and aluminum (sodium concentrations in the soil under study were negligible).

Table 1. Chemical composition of the liming materials expressed as dry matter.

| Treatment        | CaO  a | MgO  a | K$_2$O a | Aluminum b | CCE c  | OM c |
|------------------|--------|--------|----------|------------|--------|------|
| Limestone (L)    | 437    | 20.8   | 3.50     | 7870       | 0.83   | 0.00 |
| Sugar foam (SF)  | 404    | 14.5   | 0.90     | 2470       | 0.76   | 0.08 |
| Gypsum (G)       | 332    | 17.5   | 1.50     | 3350       | 0.64   | 0.00 |

a Calcium, magnesium and potassium oxide (CaO, MgO and K$_2$O respectively) in g/kg; b aluminum in mg/kg; c CCE (calcium carbonate equivalent) and OM (organic matter) in %.

Specifically, the lime requirement (LR) was calculated using the known Cochrane’s formula [22], which alleviates crop aluminum stress and takes the levels of exchangeable aluminum, calcium and magnesium in the soil into account as ECEC, and fixes a required percentage aluminum saturation (RAS) of the ECEC (LR (CCE Mg/ha) = f[Aluminium − RAS (ECEC)/100]), where aluminum and ECEC are in cmol kg$^{-1}$ soil and f is a crop factor. This yielded a value of about 6.4 Mg CCE/ha, which corresponds to about 7.7 Mg/ha of limestone (L), 10 Mg/ha of gypsum (G) and 15 Mg/ha of sugar foam (SF: accordingly to its moisture content). For a complete comparison, a control treatment (C) without the

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Figure 1. Location of the experimental site (scale, north orientation and experimental units within the research area are shown on the right side).
applications was used. The liming materials were uniformly spread onto the entire surface of the plots, and were incorporated into the soil at a depth of approximately 20 cm using a rotovator pass.

2.3. Experimental Design and Statistical Analyses

The experimental design was a randomized block located in the previously commented site and it presented with four replicates. Each experimental unit (subplot) had a size of 3 m × 5 m and was separated from the next subplot by a distance of 2 m. Statistical analyses were performed using R software [23]. Several mixed ANOVAs were carried out to determine whether the differences between liming treatments (T), on the soil chemical properties and the biomass data, were statistically significant and whether they depended on the soil depth (D) and sampling year (Y). To complete the statistical evaluation, the interaction between the three factors was also assessed.

In this mixed design, T (with four levels: control (C), gypsum (G), limestone (L) and sugar foam (SF)) and D (with three levels: Ap1, Ap2 and AB as soil horizons) were the fixed factors because they are interesting in themselves, whereas the Y factor (with ten levels: 2002–2011) was added as a random factor (Table 2). To reveal the overall effect of each of these three main factors and their possible interactions, a hierarchical multilevel model approach was used. In this multilevel approach, the different models were built with one predictor at a time from a baseline with no other predictors than the intercept. Factors in these nested models were added in the following order: no predictors, T, D, Y, and the interaction terms between them. The maximum likelihood ratio (ML ratio) was used to compare the nested models using a variance analysis. From the results evaluated, if the interaction between the factors resulted in a significant effect, we could not assess any main effect because the higher-order interaction superseded it. In that case, the effect of that particular treatment was split independently for D, Y or both, in order to determine the treatments that differed significantly. As mixed ANOVAs are fairly robust in terms of the error rate associated with violations of the assumption of both normality and homogeneity of variance (homoscedasticity) [24], all the sample sizes were the same in this study. In addition to ANOVA studies, an outlier analysis of the data was carried out beforehand.

Table 2. Factors and levels by the factors considered in mixed ANOVAs.

| Factor                  | Levels                                              |
|-------------------------|-----------------------------------------------------|
| Treatments (T)          | Four levels: control (C), gypsum (G), limestone (L) and sugar foam (SF) |
| Soil depth (D)          | Three levels: Ap1, Ap2 and AB                       |
| Sampling year (Y)       | Ten levels: 2002–2011                               |

When the ML ratio of mixed ANOVAs was large enough to be considered statistically significant, post-hoc comparisons were carried out to determine which treatments significantly differed (at the * p < 0.05, ** p < 0.01 or *** p < 0.001 levels). These comparisons were performed through Tukey’s honest significance test with a Holm-Bonferroni adjustment.

2.4. Soil and Biomass Analyses

The soil samples of each horizon (Ap1, Ap2 and AB) were collected using an auger. During the first five years of soil monitoring, the top 5 cm of the soil samples was discarded in order to avoid uncertainties due to the possible presence of undissolved amendment particles. Soil samples were taken at 0–12 cm (Ap1 horizon), 12–25 cm (Ap2 horizon) and 25–35 cm (AB horizon) of soil depth after harvesting (October). They were then sealed in plastic bags, transported to the laboratory and air-dried at room temperature. Next, they were disaggregated, sieved in a 2 mm mesh, and finally, they were analyzed. Textural classes according to the United States Department of Agriculture were determined by the Bouyoucos hydrometer method [25]. Afterwards, analysis methods were applied to determine (i) the SOM by wet oxidation, followed by titration with ferrous ammonium sulphate [24], (ii) the pH in 1 N KCl (pH) [26], (iii) the electrical conductivity at 25 °C (EC) in
soil:water (1:2.5) suspension [25], (iv) the content of exchangeable calcium (Ca), magnesium (Mg) and potassium (K) by extraction with successive aliquots of 1 M ammonium acetate (NH$_4$C$_2$H$_3$O$_2$) [25], followed by analysis of the displaced cations by atomic absorption spectrometry (AAS), and (v) the exchangeable aluminum (Al) determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using 1 M KCl as the extraction solution [27].

At each sampling date (July every year) during the evaluated period, the total rye biomass production (Biomass), spike biomass production (Spike) and stem biomass production (Stem) were measured. Additionally, calcium, magnesium and potassium concentrations in stem biomass production (Ca-Rye, Mg-Rye and K-Rye, respectively) were analyzed by (ICP-AES) after wet digestion.

3. Results
3.1. Initial Soil Characterisation before Liming

Table 2 shows the initial analytical data of the three soil depths subsequently sampled in the research. From the data reported, the Al was found to be very high for all horizons at the start of the investigation. In a similar way to other Typic Palexerults, the Al concentration in the Ap and AB horizons was very similar, with the low pH values being very remarkable [28] and showing the extremely acidic conditions of the soil studied. The Al saturation of the effective cation exchange capacity (AlECEC) was 84.1% for the Ap1 horizon (0–12 cm), 84.6% for the Ap2 horizon (12–25 cm) and 78.6% for the AB horizon (25–35 cm). In addition, low levels of the exchangeable Ca and Mg, and therefore low base saturation, were evident. Moreover, the available exchangeable K contents were in the low availability range.

Table 3 also shows the initial SOM levels. As can be seen, the first 25 cm of the soil profile (horizons Ap1 and Ap2) showed an average level of 2%, which can be regarded as very appropriate according to local conditions.

Table 3. Baseline soil horizons characteristics before liming for Ap1 (0–12 cm), Ap2 (12–25 cm) and AB (25–35 cm).

| Soil Depth | Textural Class | pH   | EC b | SOM c | Ca d | Mg d | K d | Al d | AlECEC e |
|------------|---------------|------|------|-------|------|------|-----|------|----------|
| Ap1        | Sandy loam    | 3.99 | 0.05 | 2.27  | 0.10 | 0.06 | 0.09| 1.30 | 84.1     |
| Ap2        | Sandy loam    | 4.03 | 0.04 | 2.06  | 0.13 | 0.04 | 0.06| 1.29 | 84.6     |
| AB         | Sandy clay loam | 4.13 | 0.03 | 1.03  | 0.30 | 0.04 | 0.04| 1.33 | 78.6     |

a Textural class from the United States Department of Agriculture Textural Classification System; b EC in dS/m; c SOM in %; d Ca, Mg, K and Al in cmol(+)/kg; e AlECEC in %.

3.2. Temporal Evolution of Soil Parameters

The temporal evolution of pH in all the study depths (Ap1, Ap2 and AB) is shown in Figure 2. It could be remarkable that SF was the most effective liming treatment to increase the soil pH. At the Ap1 depth, liming with L increased the soil pH by nearly 1.5 units for the first five years, as compared to the unlimed control, whereas SF increased the soil pH by nearly 2.5 pH units. The increase in the pH of Ap2 was related to the presence of L and SF. On closer inspection, it can be observed that this trend was more important from the sixth year onwards. Finally, at depth AB, only a marked increase in soil pH in the seventh year could be observed. While the application of G can decrease, increase or have no effect on the soil pH [29], as a result of our research, it is clear that the effect of G on soil pH was negligible.

Similarly, the temporal evolution of SOM and the exchangeable content of Ca, Mg and Al throughout the ten years of monitoring using the liming treatments and control subplots in all study depths are shown in Figures 3–5, respectively. As is displayed in the corresponding Figures, SF and L were the most effective amendments in increasing soil Ca bioavailability, as well as in decreasing soil Al levels. The higher solubility of the G amendment relative to the others might be behind the pattern of its lesser effect on both Ca and Al levels in the Ap1 horizon from the second year of monitoring onwards. However,
the in-depth lime effect of the amendments L and SF, on the one hand, and the amendment G on the other hand, did not seem important enough until 2004 (third year of the study) in the case of the Ap2 horizon, and 2008 (seventh year) in the case of the AB horizon.

Figure 2. Temporal evolution of pH in the three horizons (Ap1, Ap2 and AB) studied throughout the ten years of soil monitoring (2002–2011).

Figure 3. Temporal evolution of SOM, Ca, Mg and Al in the Ap1 horizon throughout the ten years of soil monitoring (2002–2011).
The results obtained from the mixed ANOVAs are presented in Table 4. From these results, there was a significant effect of T on all the soil properties studied (pH, Ca, Mg, K and Al), with the exception of SOM. Moreover, the effect of D on each of the soil properties was significant; indeed, the effect of T significantly changed with both D and Y in all the soil properties studied, as revealed by the significant interaction between these factors (T × D × Y). With the aim of evaluating where significant differences between T means lie out, a further comparison between all possible variable pairs must be carried out through post-hoc methods (see Table 4), for both D and Y separately (because the significant interaction of T × D × Y was previously mentioned).

Table 4. Analysis of variance performed on soil parameters (pH, SOM, Ca, Mg, K and Al). The variability in the soil parameters was evaluated using the hierarchical multilevel model (maximum likelihood (ML) ratio). The results were significant at *p* < 0.05 and ***p*** < 0.001.

| Soil Parameter | ML Ratio (T) | ML Ratio (D) | ML Ratio (Y) | ML Ratio (T × D × Y) |
|----------------|--------------|--------------|--------------|-----------------------|
| pH             | 195 (***)    | 151 (***)    | 16.9 (0.05)  | 636 (***              |
| SOM            | 5.49 (0.14)  | 681 (***)    | 33.3 (***)   | 172 (***              |
| Ca             | 182 (***)    | 203 (***)    | 10.5 (0.31)  | 494 (***              |
| Mg             | 9.61 (*)     | 10.5 (***)   | 45.7 (***)   | 191 (***              |
| K              | 34.0 (***)   | 46.5 (***)   | 52.1 (***)   | 149 (***              |
| Al             | 93.6 (***)   | 98.0 (***)   | 37.1 (***)   | 265 (***              |

From the results reported in Table S1, at the Ap1 depth, liming with L significantly increased Ca levels and soil pH starting in 2002, whereas liming with SF significantly increased these ones starting in 2003 (one-year post-treatment). Both liming materials maintained this effect until the end of the research (2011). The magnitude of the difference in Ca levels between liming with both L and SF and C treatments increased most notably.
The results obtained from the mixed ANOVAs are presented in Table 4. From these results, there was a significant effect of T on all the soil properties studied (pH, Ca, Mg, K and Al), with the exception of SOM. Moreover, the effect of D on each of the soil properties was significant; indeed, the effect of T significantly changed with both D and Y in all the soil properties studied, as revealed by the significant interaction between these factors (T × D × Y). With the aim of evaluating where significant differences between T means lie out, a further comparison between all possible variable pairs must be carried out through post-hoc methods (see Table 4), for both D and Y separately (because the significant interaction of T × D × Y was previously mentioned).

Table 4. Analysis of variance performed on soil parameters (pH, SOM, Ca, Mg, K and Al). The variability in the soil parameters was evaluated using the hierarchical multilevel model (maximum likelihood (ML) ratio). The results were significant at *p < 0.05 and ***p < 0.001.

| Soil Parameter | ML Ratio (T) | ML Ratio (D) | ML Ratio (Y) | ML Ratio (T × D × Y) |
|----------------|--------------|--------------|--------------|-----------------------|
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| SOM            | 5.49 (0.14)  | 681 (***     | 33.3 (***    | 172 (***              |
| Ca             | 182.5 (***   | 203 (***     | 10.5 (0.31)  | 494 (***              |
| Mg             | 9.61 (*)     | 10.5 (***    | 45.7 (***    | 191 (***              |
| K              | 34.0 (***    | 46.5 (***    | 52.1 (***    | 149 (***              |
| Al             | 93.6 (***    | 98.0 (***    | 37.1 (***    | 265 (***              |

From the results reported in Table S1, at the Ap1 depth, liming with L significantly increased Ca levels and soil pH starting in 2002, whereas liming with SF significantly increased these ones starting in 2003 (one-year post-treatment). Both liming materials maintained this effect until the end of the research (2011). The magnitude of the difference in Ca levels between liming with both L and SF and C treatments increased most notably during the first five years (2002–2006), when exchangeable Ca at the Ap1 depth was, excluding 2004, almost 20 and 75 times higher when compared to untreated plots. In this sense, at the beginning of the research, Ca levels in L and SF treatments were higher than C by 47 and 20 times, respectively, while at the end of the research, they were 17 and 18 times higher, respectively. Conversely, G only significantly increased Ca levels at the beginning of the research (40 times higher than C in 2002), and surprisingly, in 2009 and 2010, at the end of the research, it was only 5 times higher. On closer analysis of Table S1, it can be observed that exchangeable Al in this soil layer decreased dramatically in response to liming in 2002 for both L and SF (Al levels in C were 26 and 8 times higher than L and SF, respectively), and this reduction was maintained throughout 2011. However, G did not show significant differences from C subplots in Al levels throughout the research. Finally, no significant differences were found, in practical terms, for SOM, Mg and K soil levels (the most remarkable feature is only an apparent stable trend of SOM levels in G treatment during a five-year period (2004–2008)).

At the Ap2 depth (Table S1), liming with L and SF significantly increased soil Ca levels and soil pH from the beginning of the research (this was also found in the AB horizon). More specifically, a higher overall increase was observed for SF. Interestingly, Ca levels at this study depth were 7 and 5 times higher than C in 2002 for L and SF treatments, respectively. With the exception of a few single years, the significant and prolonged impact from liming with L in soil pH ended in 2008, but this significant effect of SF on this soil parameter continued until the end of the research (2011). However, both liming materials significantly increased soil Ca levels throughout the research period. As opposed to the results reported at the Ap1 depth, G significantly increased soil Ca levels, not only at the beginning of the research (7 times higher than C), but also throughout the entire research period. However, exchangeable Al at this soil depth significantly decreased in response to liming with L and SF from 2002 (Al levels in C were twice higher than those for L and SF treatments), as well as with G from 2005. This reduction pattern was sustained throughout 2011, with the exception of a few single years. As was observed at the Ap1 depth, a few
significant differences in SOM, Mg and K soil levels between liming treatments were found at this study depth, but they are not worth mentioning.

At the AB depth (Table S1), liming with L and SF significantly increased soil pH, starting in 2003 (one-year post-treatment), but after this year, only SF showed a significant effect on this soil parameter in 2004, 2006 and 2008. However, both L and SF significantly increased soil Ca levels throughout the research period (from the years 2002 and 2003 onwards for L and SF, respectively), while G only showed a significant effect from 2002 to 2004, and surprisingly, in 2010. However, exchangeable Al only significantly decreased in response to liming with SF at the end of the research (2011). Similarly, to depths Ap1 and Ap2, there are a few significant differences in SOM, Mg and K soil levels between liming treatments, so there was no evidence that liming materials could have an influence on these soil parameters at this study depth. In this regard, it should be noted that, for both soil horizons (Ap2 and AB), in the seventh year of the investigation (2008), there was a slight increase in the SOM levels, which was more marked for all liming treatments (G, L and SF) at both depths.

3.3. Temporal Evolution Biomass

In the same way as for soil parameters, the temporal evolution throughout the ten years of monitoring of spike, stem and total rye biomass are shown in Figure 6. From this figure, a slight increase can be seen in the total biomass in both spike and stem biomass in those subplots limed with L and SF, as compared to the controls, and even with those subplots limed with G. Thus, the biomass production results seemed to show, as was reported in some soil parameters, that it was significantly conditioned by the type of liming material used. During 2007, there was a great decrease in biomass production. The main reasons were the low rainfall and the low average annual temperature for that year in the research area (which has a yearly average temperature and precipitation of 9.4 °C and 600–850 mm, respectively [20]). Interestingly, the effect of L and SF, as compared to G and C on biomass production, was remarkably observed.

![Figure 6](image-url)

**Figure 6.** Temporal evolution of spike, stem and total biomass throughout the ten years of biomass monitoring (2002–2011).
Due to the high trivalent Al concentration being associated with important growth reduction and because it is a yield limiting factor for crops in acid soils (pH ≤ 5.5), as a result of it being the most recognized toxic chemical specie of Al for plants observed in their root systems [30], the relationship between total biomass, soil pH and exchangeable Al percentage (defined it by the ratio between the Al content and the effective cationic exchange capacity (ECEC), obtained as the sum of Ca, Mg, K and Al), was evaluated in Figure 7. In light of this figure, it can be observed that lower total biomass productions are mainly presented in areas of the graph belonging to higher AlECECs and lower soil pHs.

Figure 7. Relationship between soil pH, Al saturation of the effective cation exchange capacity (AlECEC) and total rye biomass.

For the sake of completeness, the temporal evolution of Ca-Rye, Mg-Rye and K-Rye levels are shown in Figure 8. More specifically, Figure 8 allowed us to hypothesise that all liming materials (G, L and SF) have influenced the Ca concentration in rye stems. However, only L and SF seem to have influenced the Mg concentration, while none of the liming materials seem to have modulated the K concentration in rye stems. Specifically, in unlimed plots (C), Mg-Rye showed a general trend of decreasing cation concentrations with the increasing research year.

Figure 8. Temporal evolution of Ca, Mg and K levels in stem throughout the ten years of cation content in stem monitoring (2002–2011).
According to the mixed ANOVA results presented in Table 5, there was a significant effect of T on all the biomass parameters studied (spike, stem and total biomass, as well as Ca, Mg and K content in stems). Moreover, the effect of Y on each of the soil properties was found to be significant. Similarly, as was previously reported in soil properties, the effect of T significantly changed with Y, as revealed by the significant interaction between both factors (T × Y) (see Table 5). As previously mentioned, in order to evaluate where significant differences between T are, a comparison between all parameter pairs was performed using post-hoc methods (biomass data and cation content in stems data presented in Tables S2 and S3, respectively), but was done for Y separately (because significant interaction of T × Y).

Table 5. Analysis of variance performed on biomass parameters (spike, stem and total biomass; Ca, Mg and K content in stems) at the harvest stage. The variability in the biomass parameters was evaluated using the hierarchical multilevel model (maximum likelihood (ML) ratio). The results were significant at *** p < 0.001.

| Biomass Parameter | ML Ratio (T) | ML Ratio (Y) | ML Ratio (T × Y) |
|-------------------|--------------|--------------|------------------|
| Spike             | 135 (***     | 53.2 (***)   | 92.9 (***)       |
| Stem              | 110 (***     | 51.0 (***)   | 96.8 (***)       |
| Total             | 130 (***     | 52.9 (***)   | 105 (***)        |
| Ca-Rye            | 50.8 (***)   | 26.9 (***)   | 59.3 (***)       |
| Mg-Rye            | 96.2 (***)   | 35.1 (***)   | 115 (***)        |
| K-Rye             | 25.6 (***)   | 39.6 (***)   | 77.9 (***)       |

Liming with any of the liming materials tested significantly increased the total and spike biomass levels, starting from 2002, while stem biomass only presented a significant increase from the beginning of the research when liming with L and SF. Interestingly, biomass levels (all total, spike and stem biomass) were consistently higher throughout the research in L and SF, as compared to G and C (especially in the low rainfall year (2007), where biomass levels in L and SF were approximately 5 times higher than both G and C treatments). Thus, it can be concluded that, although in 2003 the G results showed a significantly increase in the total, spike and stem biomasses were only sustained by L and SF (see Table S2).

However, with the exception of 2005, from 2004 until one year before the end of the research (2010), a significant and prolonged difference of Ca-Rye between unlimed and limed subplots with G, L and SF was observed. This finding was particularly important when L and SF were used (Ca levels from 2006 to 2010 were significant and twice as high as C treatments). However, by contrast to that reported in the soil horizons, there were more differences in the rye levels of magnesium (Mg-Rye) and potassium (K-Rye) between limed and unlimed soils (principally between L and SF with C) (see Figure 8 and Table S3).

4. Discussion

As the pH of the soil affects the bioavailability of plant nutrients, and thus indirectly affects crop plant growth [31], SF could be considered to be the most effective liming treatment in terms of plant nutrition in ameliorating this master parameter of soil in agricultural production. For the sake of clarity, this idea is presented in Figure 9, in terms of soil pH and base saturation levels (the latter is represented as the percentage of ECEC occupied by soil bases (Ca, Mg and K)), for the three soil horizons studied. It is very likely that the difference between SF and L in its effectiveness to increase the soil pH and the base saturation levels is based on its reactivity (rate of dissolution), which depends on both particle size and hardness [31].
The effect of G on the soil pH is the result of the opposing reactions of Al\(^{3+}\) and H\(^+\) exchange by Ca\(^{2+}\), and the ligand exchange of OH\(^-\) by SO\(_4^{2-}\) [32]. Consequently, no significant differences in pH were found between G and C in the soil profile. However, when L and SF were used, the soil pH decreased as the soil depth increased. This finding is consistent with other studies found in the literature that have reported that liming material application can be slow, or in some cases, even ineffective in increasing subsoil pH [33]. Specifically, this lower impact was observed to be more pronounced in L than in SF (perhaps due to a greater restriction on L dissolution).

The overall effect of the liming treatments on the exchange complex is also consistent with other previously reported results [6,30,32–34]. These effects have mainly involved a decrease in soil Al levels, and therefore, a decrease in an effective Al saturation in the exchange complex, as well as an increase in the proportion of Ca in the exchange complex for all the horizons studied.

As expected, Al was markedly reduced and Ca was notably increased in those subplots limed throughout the study. Due to the surface-application of amendments, soil acidity was reduced, especially in the top 12 cm (Ap1). The acidity in the Ap2 was gradually reduced over time (mainly from 2007 onwards). A factor that can be attributed to the effect of surface liming in the subsoil is the ions movement [35], which indicates that the downward movement of exchangeable Ca could occur after exchangeable sites in the top 12 cm are saturated by Ca ions [36].

Globally, SF and L were clearly the most effective treatments in raising pH and Ca levels at the same time as reducing the Al level in the Ap1 horizon. At this depth, pH and Ca tended to decrease significantly following the sequence: sugar foam (SF) ~ limestone (L) > gypsum (G) > control (C). Moreover, these amendments were also the most effective treatments in decreasing subsoil acidity. The higher efficiency of SF and L over G as liming materials was more evident two years after the amendments were applied. Perhaps these results show that a more suitable liming strategy with G could be to apply the amendments more frequently, such as once a year (because it moves readily down the soil profile). The soil acidity reduction in the Ap2 and AB horizons was reflected by the downward movement of Ca and the concomitant decrease of Al in the exchange complex. In addition, the comparison of the distribution of Al in the soil between the different treatments showed that the liming residual efficacy was higher in SF than in L, which were both higher than G. Thus, this long-term experiment shows that the use of G only once in the research did not limit the negative effects of soil acidity in the same way as L and SF because of its lower residual effects (in Ap1, Ap2 and AB horizons). Moreover, in the short, medium
and long-term, the combined application of L or SF with G could be more effective than applying these alone in managing subsoil Al constraints for crop production [33]. However, although the relationships between available Ca, Mg and K contents in this research were not evident, it is possible that our results support the hypothesis that, after intensive liming, the Mg and K contents available in soil may decrease, which is in accordance with the long-term fertilization experiment reported in Reference [37].

As liming improves the soil conditions of plant growth, an increase in plant productivity is expected with higher organic matter inputs [14]. Moreover, because liming can cause a large increase in root and top growths, and a higher carbon return to the soil in the form of dying roots and decaying crop residues [38], an increase in SOM in the long-term might be expected. However, liming has short-term stimulating effects on soil biological activity, hence favoring organic matter mineralization and very likely accelerating organic matter turnover rates in soil [14]. Nevertheless, although none of the liming materials tested showed a significant effect on SOM levels throughout the soil profile, an increase in the leaching of SOM in the deepest soil horizons (Ap2 and AB) was observed. Perhaps contrary to expectations, liming may not have increased the soil microbial activity over the control soil. Moreover, the addition of large amounts of Ca and the concomitant precipitation of exchangeable Al caused by liming could produce a reduction in the potential bioavailability of SOM constituents. The apparent stability of the SOM in the studied soil may be attributed to the predominance of stable organo-mineral complexes formed between Al and humified organic components, which in the long-term are not affected by changes in the A1 saturation of the cation exchange complex [39].

Nevertheless, the findings reported regarding the SOM levels are consistent with those in Reference [40], where it was found that SOM was not affected by several liming rates. However, the findings by these authors in the soil organic matter fractions showed that liming decreased the carbon content in the humic acid fraction, but did not affect the carbon contents in the fulvic acid fraction. However, Reference [16] reported a significantly increase in SOM by using SF as a liming material. However, in our research the use of SF had little effect on SOM in the three depths. In contrast to our results, several authors reported decreases or increases in soil organic carbon (SOC) levels (and consequently in SOM levels) after liming. In such a way, Reference [41] reported a decrease in the SOC content in an Oxic Paleustalf after a soil pH elevation and a concomitant increase in microbial activity (which in turn reduces the stock of SOC). Reference [42] also reported a 25% decrease in SOC levels in the third year following lime application in the soil surface layer of a clayey Oxisol cropped with a rotation of cereals. As opposed to the previous authors, Reference [35] suggested that SOC accumulation in the long-term is related to a greater biomass production per area because of soil fertility improvement. In accordance with the previous authors, Reference [43] reported an increase in the total SOC content in the liming of a Brazilian Oxisol, which was related to a greater biomass production (including roots, whose development was improved by soil liming). The latter authors also reported a reduction in the fulvic and humic acid rates over total SOC because of liming. Finally, the research in Reference [44] suggested that liming had differing effects on SOC mineralization over time in the short-term, although they proposed that changes in SOC availability and mineralization were likely to be predominantly controlled via physiochemical rather than biological processes.

No significant changes in SOM between treatments in the deepest horizon (AB) were found (although since the year 2005, SOM tended to decrease in the sequence limed subplots > unlimed subplots in this soil horizon). There is little information available on the effect of liming materials on SOC mineralization [45] that shows an overall reduction in SOC mineralization with an increasing soil depth. Reference [18] reported that SOC at the first 10 cm decreased or remained unchanged in a long-term liming experiment on soils with variable clay contents (range between 6% and 36%), whereas Reference [14] in discussing the net effect of liming on soil organic carbon stocks reported reductions, increments and no significant effects of liming on SOC and SOC leaching (increased leaching of
SOC from limed soils because of enhanced of physical, chemical and microbiological processes were found in References [46–48]), in long-term field experiments. The latter is an important study area in agronomy because it reports that dissolved organic compounds can significantly affect the transport of both inorganic and organic chemical compounds dissolved in water. Hence, an increase in the leaching of SOC from limed soil can lead to a lower organic carbon content in soil from the point of view of plant nutrition and environmental effects [47]. Nevertheless, liming is known to ameliorate soil structure, as high Ca concentrations in the soil solution enhance the flocculation of clay minerals, and thus, the formation of stable aggregates, which in turn reduce mineralization due to a better physical protection of SOC [14].

In our research, liming significantly increased total rye biomass from the first year (2002) of liming material application (trends observed in spike and stem biomasses were similar to those reported for total rye biomass). SF and L maintained this effect in the biomass during the whole experiment, while this was not observed in G subplots. The reason for the biomass production improvement might be attributed to the enhancement in the rye growth environment that resulted from the reduction in Al levels, the increase in pH and the supply of Ca [35], thereby upgrading the growth of rye roots [36]. Overcoming the effects of subsurface Al toxicity is highly important because it leads to improved deep rooting so that crops can take up water and nutrients from subsoil layers which, concurrently, could greatly increase the supply of water and nutrients to crops. This is especially important in the dry season in arid areas [49] because more significant crop production responses emerge when water stress happens during the growing season [33].

We note in passing that our findings in Ca content in rye tissues are consistent with that found in Reference [33], which showed that shoot Ca concentration in wheat increased significantly after liming a soil with a pH CaCl$_2$ of 4.6 in its first 10 cm, with 8000 kg ha$^{-1}$ of limestone. It is possible to hypothesize that both greater biomass yield (including total, spike and stem biomass) and Ca-Rye biomass levels responses were more influenced by a lower soil acidity than by the increase in Ca supply. This finding agrees with that reported by Reference [50], which showed that liming could remove Al toxicity, and therefore, it could increase the ability of wheat roots to uptake nutrients like phosphorus. This is of great importance because a low efficiency in the use of soil nutrients in crop production is undesirable, from both an economic and environmental point of view [13]. Another potential reason for the increase in biomass production could be attributed to better soil physical conditions because of liming, which emerges as one of the main reasons for the availability, distribution and uptake of nutrients in the soil [51]. The differences shown in K-Rye and Mg-Rye, between limed and unlimed soils, could be explained because of the antagonism between soil ions and the MgO content of liming materials (the very low Mg content of the studied soil could explain the plant response, despite the low MgO content of the liming materials).

Finally, because the soil under study had a very low Mg content, it can thus be suggested that liming with a Ca- and Mg-based liming material could improve soil fertility and rye production results, thus avoiding a potential increase in the competition in uptake with Mg for rye plants [34]. From this study, we also conclude that further studies are required to assess not only the long-term impact of liming on several agrochemical soil properties, but also the effects on crop yield responses because of liming application. Further, despite the positive effects of liming on soil acidity, inappropriate liming rates may result in a reduction in the availability of some nutrients in the soil—particularly micronutrients [13], like manganese [51,52] and phosphorus [34]—with a very negative impact on crop production. However, the effect of too high soil pH levels and problems with micronutrient uptake could be counteracted by spraying complex micronutrient fertilizers in the form of chelates.
5. Conclusions

The results reported in this manuscript show that the liming treatment of an acid soil with calcium-based materials not only helps to maintain an adequate calcium/aluminum ratio in the soil exchange complex, but also improves rye yields. On the basis of our results, it is remarkable that limestone and sugar foam had the most important effects on the soil fertility improvement and the rye biomass production in the long-term. In contrast, the use of gypsum was only found to be appropriate in the short-term. As a result, the combined application of limestone and sugar foam with gypsum could be more effective than applying the first two liming materials alone in managing acidity subsoil constraints for rye production in the short and long-term.

While an increase in the mineralization coupled to a soil pH increment because liming is expected, soil organic matter levels showed no significant differences throughout the study period. However, it is true that a leaching increase of soil organic matter in limed soils was observed. This finding implied that a yield increase not only depends on the reduction of soil acidity, but also on the improvement of soil quality by liming.

Our study offers some important insights into soil acidity management because this knowledge can be integrated into agriculture production systems with low-environmental impacts. However, more information on the long-term effects of lime application on soil properties as soil organic levels is needed in order to establish a greater degree of accuracy on this matter.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/pr9071181/s1. Table S1: Means and standard deviations of soil properties pH, SOM, Ca, Mg, K and Al during ten years (2002–2011), Table S2: Means and standard deviations of biomass (Biomass: total rye biomass; Spike: spike rye biomass; Stem: stem rye biomass) during ten years (2002–2011). Table S3: Means and standard deviations (SD) of calcium, magnesium and potassium content in rye biomass (Ca-Rye, Mg-Rye and K-Rye respectively; all of them in %) during ten years (2002–2011).

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