



Article

Assessment of Mixed Amendments of $\text{CaCO}_3/\text{Na}_2\text{SO}_4$ Ratio on the pH Buffer Capacity and Exchangeable Sodium Percentage of Soils with Contrasting Properties

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Highlights:

- The pH buffering capacity was higher in volcanic than non-volcanic soils.
- The sodium concentration increased exponentially in volcanic soils.
- The sulfate input increased the sulfur mineralization in soils.

Abstract: Reusing the by-products from wood pulp processing can promote the efficient use of resources. In this sense, the objective of this research was to determine the agronomic efficiency of CaCO_3 and Na_2SO_4 by-products from wood pulp processing to establish criteria for their use and avoid undesirable side effects when applying these materials to the soil. Six treatments in proportions of 1; 0.9; 0.75; 0.5; 0.25, and 0, of $\text{CaCO}_3/\text{Na}_2\text{SO}_4$, respectively, were incubated at a constant temperature and humidity for 15 days. The first proportion consisted of 100% CaCO_3 , while M1 mixed 90% CaCO_3 and 10% Na_2SO_4 , M2: 75% CaCO_3 and 25% Na_2SO_4 , M3: 50% CaCO_3 and 50% Na_2SO_4 , M4: 25% CaCO_3 and 75% Na_2SO_4 , with the last proportion comprised of 100% Na_2SO_4 . Samples of 40 g from two soil series, Licantén (Inceptisol) and San José (Andisol), were used. The rates applied for each treatment were 0, 1, 2, 4, and 8 g of material per kg of dry soil. At the end of the incubation period, pH in water, pH in CaCl_2 , exchange bases (Ca^{2+} , Mg^{2+} , K^+ and Na^+) and extractable sulfur were determined. The results showed that the San José soil had a pH buffering capacity three times higher than that of the Licantén soil. The linear increase in pH was thus explained by the soil type in relation to the applied rate of CaCO_3 . The analysis of the increase in the exchangeable Na percentage (ESP) showed that the soils increased up to about 70% of their ESP with the highest added rate of Na_2SO_4 . The application of a mixture of 25% Na_2SO_4 and 75% CaCO_3 resulted in an increase in the ESP close to 15%; therefore, it is not recommended to use mixtures with a Na_2SO_4 content higher than 25% in these soils. Finally, we affirm that for M2 the maximum recommended dose for application should be 4 Mg ha^{-1} , i.e., 3 g of material per kg of soil.

Keywords: soil liming; buffer capacity; sodium saturation; extractable sulfur



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1. Introduction

By 2050, the total waste generation is expected to more than double due to rapidly increasing population growth worldwide [1]. The treatment and management of industrial waste is therefore essential for sustainable development. The pulp industry generates a large impact associated with its emissions of solid, liquid and gaseous waste, resulting from the chemical and physical treatments of wood, which in turn result in potential contaminants of water, air and soils [2]. Globally, Chile is ranked as the tenth country in pulp production [3]. During 2021, around 5200 million tons of pulp were produced,

and exports significantly increased by 20.6% post pandemic, where 45.1% corresponded to chemical pulp [4]. Due to the current increase in demand for products derived from the pulp industry, pulp mills face an interesting challenge regarding the balance between market requirements and economic, environmental and social aspects [5].

A decrease in waste volume and increase in production efficiency has been achieved with the reuse of pulp mill waste through technological innovations [5]. Some examples include the manufacturing of building materials, such as moldings, adhesives and cement [6–8], energy purposes, such as biogas production, the production of fertilizers and liming agents [6,9,10], and also for irrigation water in forest plantations [11].

Particularly, in the production of bleached chemical pulp, there is a recovery system that allows reusing the inputs for the cellulose delignification process [12]. In production, an additive called “white liquor” is used, composed mainly of sodium and sulfur in their active forms as sodium hydroxide (NaOH) and sodium sulfide (Na₂S) [13]. This liquor can be reclaimed through the recovery cycle, reaching an efficiency level of up to 97% [14]. After wood cooking, this additive is converted into “green liquor” containing a large proportion of these elements in the form of sodium carbonate (Na₂CO₃) and sodium sulfate (Na₂SO₄), representing approximately 80% of the total solid waste [14,15]. In the recovery cycle, Na₂CO₃ is converted back to NaOH, using calcium oxide (CaO) obtained from calcination of lime sludge [13]. Finally, impurities, such as calcium carbonate (CaCO₃), Na₂SO₄, some solid remains of the lime sludge, boiler ash, salts and a certain proportion of green liquor are obtained from this process [13,16].

Among the by-products obtained, lime sludge, NaS, Na₂CO₃ and Na₂SO₄ have emerged as substitutes for liming materials, which have been used to neutralize the acidifying effects of soils in Canada and Portugal [10,17]. In addition, it has been evidenced that the use of Na₂SO₄ has modified the uptake and translocation of toxic metals, such as As and Cd in wheat grains [18]. On the contrary, it has been observed that applying by-products or solutions with high levels of sodium (e.g., wastewater) cause the dispersion of micro-aggregates, which affect the soil structure [19,20]. However, the application of these by-products on soils in Chile has been scarcely studied. In this context, the objectives of this research were (i) to investigate the use of these materials, particularly wastes that contain sodium (Na) in their composition, (ii) to determine the agronomic efficiency of pulp by-products, specifically CaCO₃ and Na₂SO₄, and (iii) to establish criteria for their use and avoid undesirable side effects when applying these materials to the soil.

2. Materials and Methods

To carry out this research, two soils of different pedogenesis, but similar acidities, were used. These soils were also chosen based on their proximity to the pulp mill from which the applied amendments were obtained. The soils used were “Licantén”, corresponding to an alluvial soil of the Mataquito River Terrace, composed of andesitic basaltic materials mixed with colluvial deposits of materials with granitic origin (Typic Xerochrepts; Ref. [21]), and the “San José” soil derived from volcanic ashes on alluvial deposit material, corresponding to a deep terrace of the San José River (Aquic Hapludands; Ref. [21]). These soils were characterized according to their initial levels of permanent soil fertility parameters (Table 1).

Table 1. Chemical characterization of the soils.

		Soils	
Parameter		Licantén	San José
pHw	(1:2.5)	5.20 ± 0.07	5.38 ± 0.05
pHc	(1:2.5)	4.17 ± 0.03	5.06 ± 0.03
Exchangeable Al	cmol kg ^{−1}	1.03 ± 0.02	0.24 ± 0.03
Organic C	g 100 g ^{−1}	1.94 ± 0.03	6.29 ± 0.05
SOM	g 100 g ^{−1}	3.35 ± 0.05	10.81 ± 0.08
Extractable Al	mg 1000 g ^{−1}	78.0 ± 1.9	773.3 ± 20.6
Sum of bases	cmol kg ^{−1}	4.27 ± 0.2	4.08 ± 0.1

Table 1. Cont.

		Soils	
Parameter		Licantén	San José
CEC	cmol kg ⁻¹	5.30	4.32
SatNa	g 100 g ⁻¹	1.30	1.80
SatAl	g 100 g ⁻¹	19.40	5.70
70% WHC	g 100 g ⁻¹	32	80

SOM: soil organic matter; pHw: pH in water; pHc: pH in CaCl₂; SatNa: Na saturation; SatAl: Al saturation; CEC: cation exchange capacity; WHC: water holding capacity.

2.1. Incubation Experiment

For the incubation experiment, CaCO₃ and Na₂SO₄, by-products of the wood pulp industry, were used. These originated from three pulp mills in Chile: Licancel, Nueva Aldea and Valdivia. The CaCO₃ by-products were characterized according to their agricultural quality [22,23] through the parameters' water content (humidity), CaCO₃ equivalent (CaCO₃ eq), relative efficiency and relative power of total neutralization (PRNT). IANSA Lime, which is a low CaCO₃ eq and PRNT amendment, was also included as a control. For Na₂SO₄ by-products, the sodium content in water and acid, and the total sulfur (S) content were also determined (Table 2).

Table 2. Characterization of the materials used for the mixtures.

Lime Materials				
	OM1	OM2	OM3	IANSA
Parameters				
Humidity (%)	26.7	0.1	0.4	20.8
CaCO ₃ eq (%)	101.5	98.5	99.9	88.1
Relative efficiency (%)	99.9	66.2	64.9	76.1
PRNT (%)	101.4	65.2	64.8	67.1
Humidity (%)	0.3	1.4	0.8	-
Relative efficiency (%)	81.9	59.5	67.2	-
Water sodium (%)	15.6	15.9	14.0	-
Acid sodium (%)	23.5	23.9	22.5	-
Total S (%)	17.9	14.4	18.4	-

OM1, OM2 and OM3: Mixtures from the Licancel, Nueva Aldea and Valdivia pulp mills, respectively. PRNT: Relative Power of Total Neutralization. IANSA lime was used as a CaCO₃ control.

To determine the CaCO₃ eq (%), the buffer capacity of each material was measured through an acid–base titration using 1 M HCl and 0.5 N NaOH [24]. For the relative efficiency (%), the fineness of each material was calculated by adding the relative efficiencies of the different particle sizes contained in each material and distributed in different mesh size ranges (10, 20, 60 and 100 mesh). Finally, the PRNT value was obtained by multiplying the CaCO₃ eq by the relative efficiency [22,23]. For Na₂SO₄ materials, the Na content in water was obtained through atomic absorption and emission spectrophotometry. In the case of the Na concentration in acid, a digestion with HNO₃ and HClO₄ was performed before taking the reading [24]. For the sulfur content, a digestion was performed with concentrated HCl; then, 10% BaCl₂ was added to obtain the precipitated sulfur [24].

Six treatments with different proportions of the evaluated materials were used, ranging from 1, 0.9, 0.75, 0.5, 0.25 and 0, understood as the desired CaCO₃/Na₂SO₄ ratios, i.e., 100% CaCO₃, M1: 90% CaCO₃ and 10% Na₂SO₄, M2: 75% CaCO₃ and 25% Na₂SO₄, M3: 50% CaCO₃ and 50% Na₂SO₄, M4: 25% CaCO₃ and 75% Na₂SO₄, and 100% Na₂SO₄. Each of the treatments was mixed with an equivalent of 40 g of dry soil (sieved < 2 mm and air-dried) in three replicates for each applied rate. The rates used for the treatments in equivalent values were 0, 1, 2, 4 and 8 g of material per kg of dry soil (0, 40, 80, 160

and 320 mg of material in 40 g of soil). In this sense, mixtures were made by origin of material (OM), i.e., 6 mixtures were made with the materials CaCO_3 and Na_2SO_4 from the Licancel mill (OM1), 6 mixtures with materials from the Nueva Aldea mill (OM2) and 6 mixtures with materials from the Valdivia mill (OM3). The soils were wetted to 70% of their water holding capacity (WHC) and incubated in plastic bags at a constant temperature of 25 ± 1.5 °C for 15 days. The WHC was determined using a funnel closed off at the bottom with cotton to which 50 g of soil was added. The soil was saturated with distilled water and after allowing for a complete draining after 24 h, the funnel was weighed to measure the amount of water retained in the soil [22]. At the end of the incubation period, the pH was measured in the water, as was the CaCl_2 in a 1:2.5 ratio. The content of exchange bases (Ca^{2+} , Mg^{2+} , K^+ and Na^+) extracted in 1 M of ammonium acetate and measured by atomic absorption and emission spectrophotometry was also assessed. The extractable sulfur (S) was extracted in 0.01 M calcium dihydrogen phosphate and measured by turbidimetry [25]. The sum of the bases was calculated as the sum of exchangeable Ca^{2+} , Mg^{2+} , K^+ and Na^+ . The cation exchangeable capacity was calculated as the sum of the bases, plus exchangeable Al (extracted by 1 M of KCl). SatNa was calculated as the ratio between exchangeable Na and CEC. SatAl was calculated as the ratio between exchangeable Al and CEC.

2.2. Statistical Analysis

The effect of the treatments and applied rates was evaluated with an analysis of variance (ANOVA). Normality of the residuals and homogeneity of variance were determined with the Shapiro–Wilk test ($p \geq 0.05$) and Levene’s test ($p \geq 0.05$), respectively. Considering that there were similarities among the behaviors of the three origins of materials (without statistical differences) from the different wood pulp mills for the same soil (Licantén soil and San José soil), these were evaluated as replicates.

Regression analyses were used to evaluate the degree of association between the evaluated variables. All statistical analyses were performed using GraphPad Prism software version 5.0. Plots were made using Rstudio 2023.3.0.386 [26].

3. Results

3.1. Effects of the Addition of Different Proportions of $\text{CaCO}_3/\text{Na}_2\text{SO}_4$ on the Evaluated Soils

The addition of CaCO_3 in different proportions (100%, M1, M2, M3 and M4) resulted in a change in the pH of the water (Figure 1A), as well as in CaCl_2 (Figure 2A). Thus, an increase in the CaCO_3 rate ($p < 0.05$) resulted in an increase in the pH.

The magnitude of the change depended on the soil type and the applied rate. With the application of 1 g of CaCO_3 per kg of soil, the pH_w increased by 0.13 units in the San José soil and 0.37 units in the Licantén soil (Figure 1A). Similar behaviors were observed for IANSA lime in both soils. Moreover, as the percentage of Na_2SO_4 in the mixtures increased, the neutralizing power of the material decreased, which resulted in the application of a higher rate of material to produce the same increase in pH as the 100% CaCO_3 treatment. A slight increase in pH was observed with the application of increasing rates of Na_2SO_4 in both soils, i.e., for every 1 g of Na_2SO_4 applied per kg of soil, the pH increased by 0.03 units. In addition, the results obtained show that there is a clear difference in the buffering capacity of the soils, as reflected in the slopes (Figures 1B and 2B). The San José soil presented a slope of 0.1 and the Licantén soil a slope of 0.33, i.e., the Licantén soil proved to be three times less buffered than the San José soil.

The Ca content increased linearly with the addition of CaCO_3 in its different proportions (Figure 3A). The increase in the Ca content was proportional to the applied rate (linear increase of the slope, $p < 0.05$) and the applied proportion. However, in the mixtures M3 and M4 (50% and 75% Na_2SO_4), for both soils, the increase in Ca was around 0.7 and 0.4 $\text{cmol}_+ \text{ per kg}^{-1}$ of soil per gram of material applied, respectively.

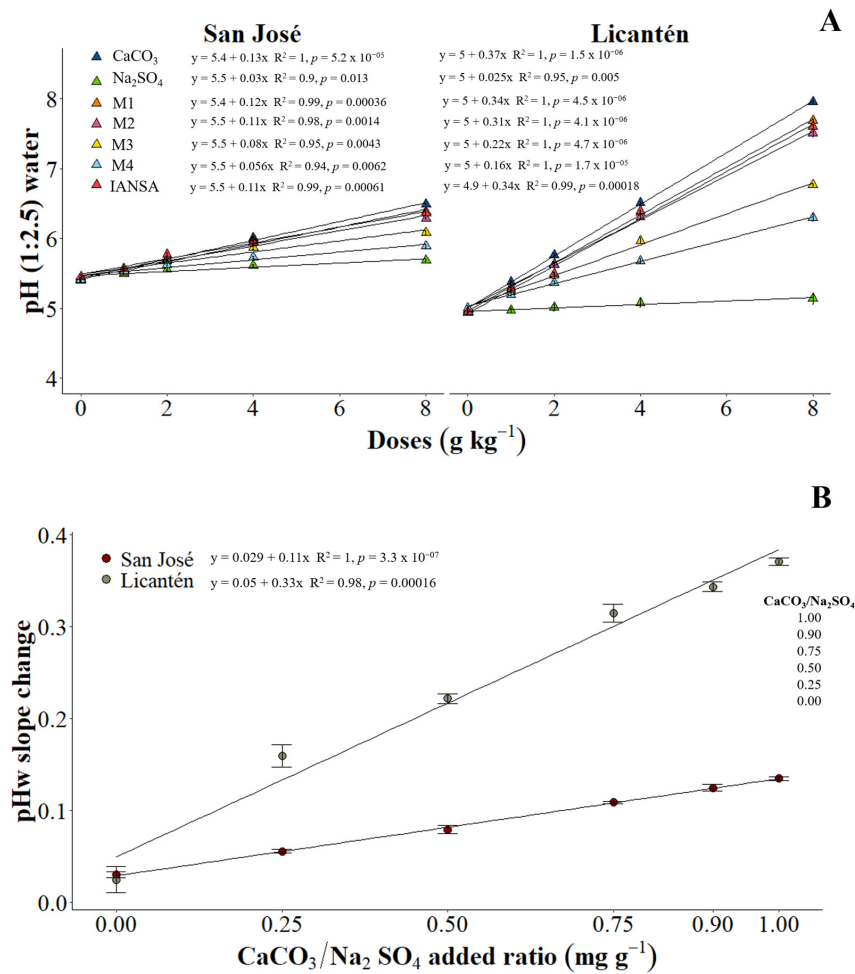
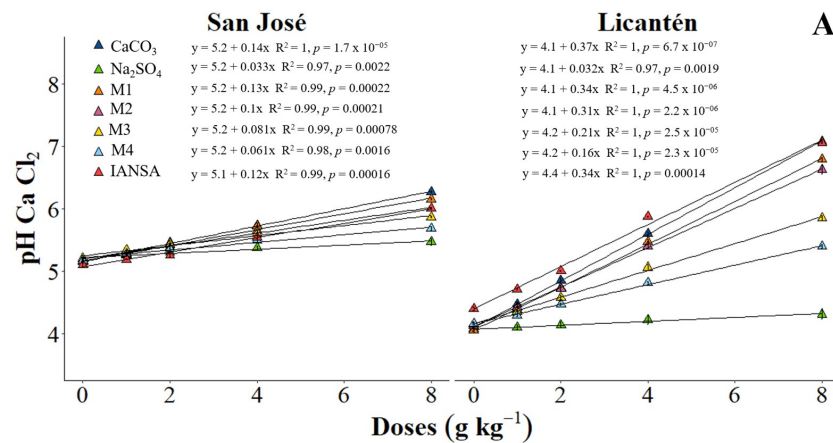


Figure 1. (A) Effect of the applied dose and the $\text{CaCO}_3/\text{Na}_2\text{SO}_4$ mix on the pH in water (pHw) in both soils. **(B)** Variation of the pHw slope as a function of the $\text{CaCO}_3/\text{Na}_2\text{SO}_4$ ratio applied to both soils. 100% CaCO_3 , M1: mix 90/10, M2: mix 75/25, M3: mix 50/50, M4: mix 25/75, and 100% Na_2SO_4 .



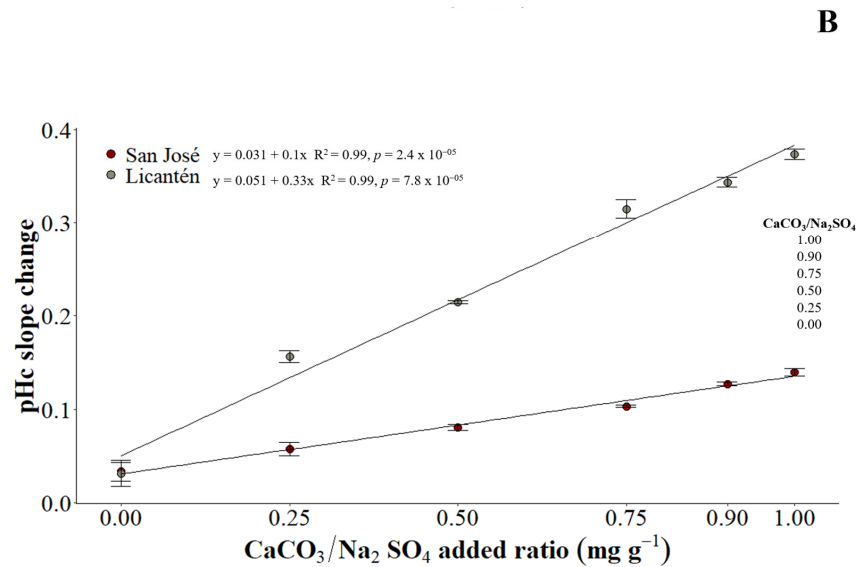


Figure 2. (A) Effect of the applied dose and the CaCO₃/Na₂SO₄ mix on the pH in CaCl₂ (pHc) in both soils. (B) Variation of the pHc slope as a function of the CaCO₃/Na₂SO₄ ratio applied to both soils. 100% CaCO₃, M1: mix 90/10, M2: mix 75/25, M3: mix 50/50, M4: mix 25/75, and 100% NaSO₄.

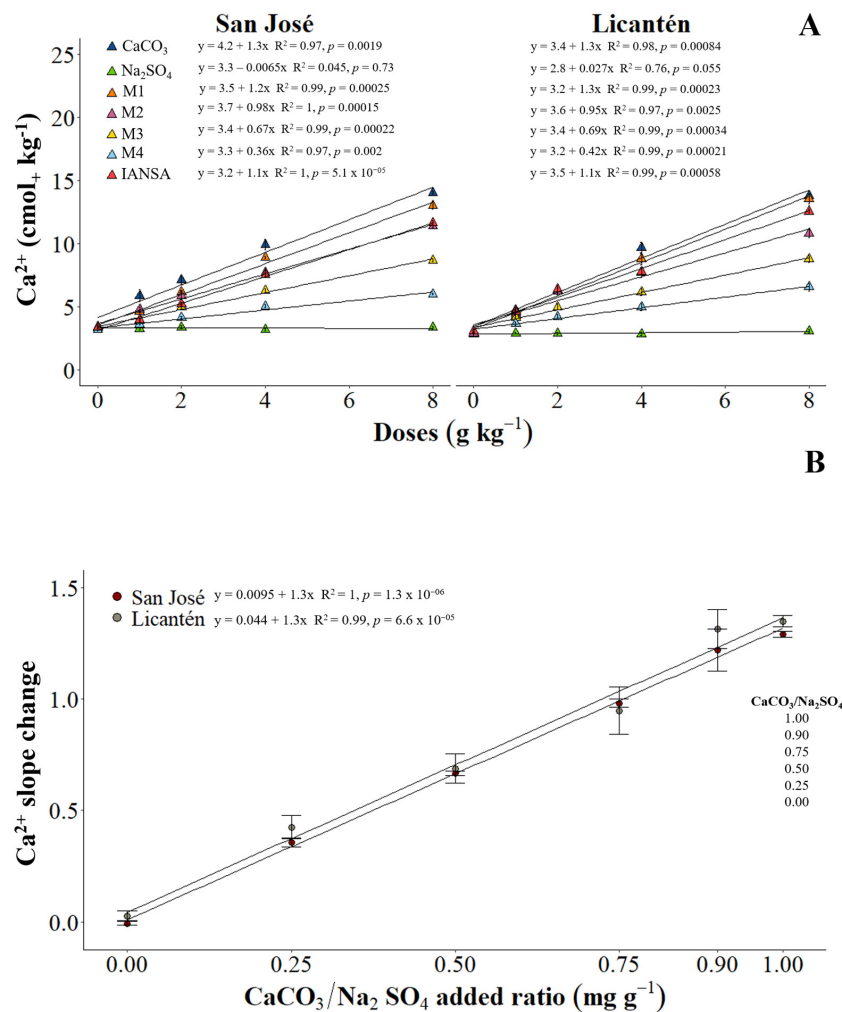


Figure 3. (A) Effect of the applied dose and the CaCO₃/Na₂SO₄ mix on the exchangeable Ca in both soils. (B) Variation of the exchangeable Ca slope as a function of the CaCO₃/Na₂SO₄ ratio applied to both soils. 100% CaCO₃, M1: mix 90/10, M2: mix 75/25, M3: mix 50/50, M4: mix 25/75, and 100% NaSO₄.

Upon analyzing the Ca ratio, which was obtained as a function of the proportion applied in the mixture, the slope ratios were found to be close to the value of 1, this increase being proportional to the applied rate in both soils (Figure 3B). On the contrary, the application of Na_2SO_4 had no significant effect on the variation of Ca^{2+} in either soil ($p \geq 0.05$).

One interesting result was that observed in the case of exchangeable K^+ . It was found that the addition of Na resulted in an increase in exchangeable K^+ of about 7% in the Licantén soil and 9% in the San José soil (Figure 4A).

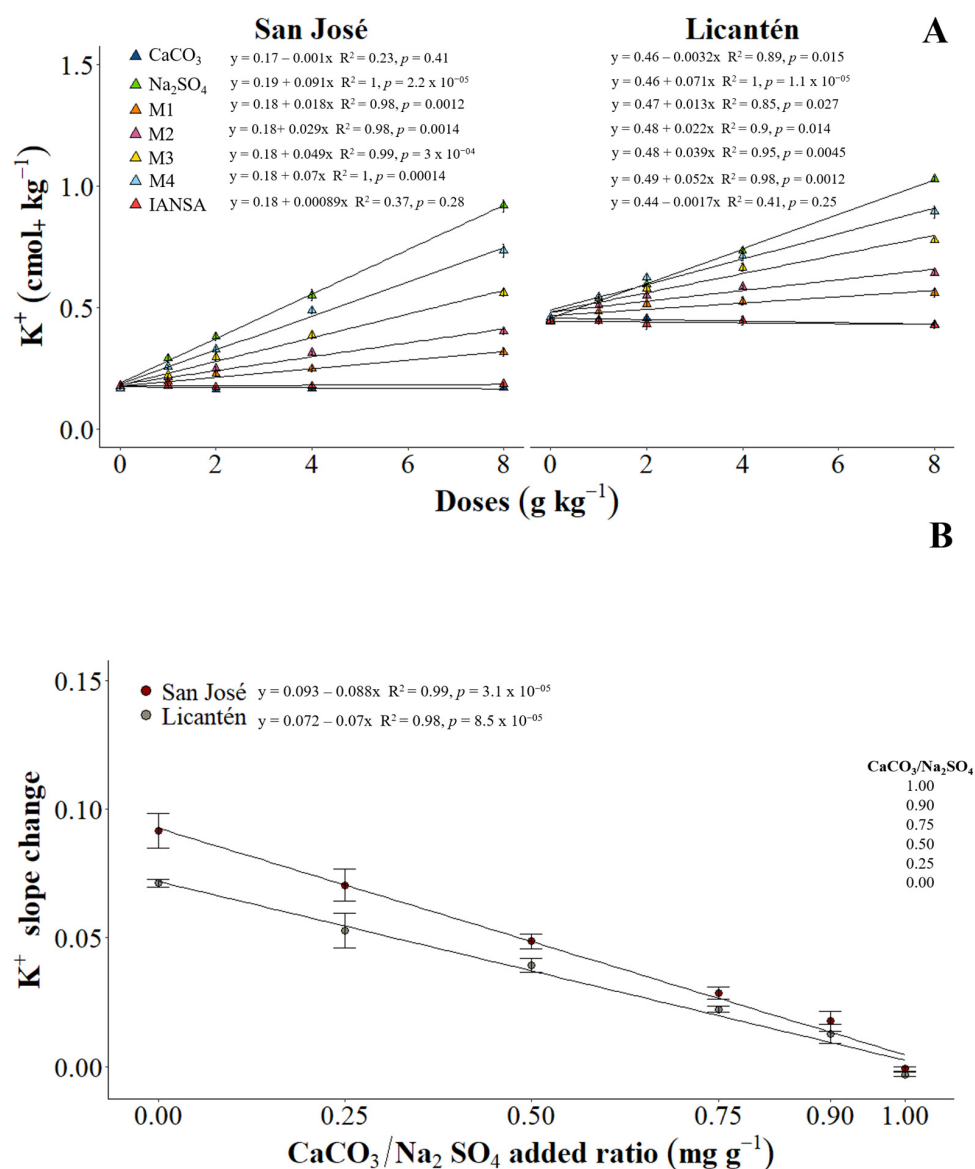


Figure 4. (A) Effect of the applied dose and the $\text{CaCO}_3/\text{Na}_2\text{SO}_4$ mix on the exchangeable K values in both soils. (B) Variation of the exchangeable K slope as a function of the $\text{CaCO}_3/\text{Na}_2\text{SO}_4$ ratio applied to both soils. 100% CaCO_3 , M1: mix 90/10, M2: mix 75/25, M3: mix 50/50, M4: mix 25/75, and 100% Na_2SO_4 .

As shown in Figure 4B, the increase observed in exchangeable K^+ with increasing doses of Na_2SO_4 also depended on the soil type. This is reflected in the slope (0.09 and 0.07 in San José and Licantén soils, respectively).

All treatments that received different proportions of Na_2SO_4 showed a linear relationship between the level of added S and the extractable S in the soil (Figure 5A). With the

addition of 1 g of 100% Na_2SO_4 , the extractable S increased by 110 mg per kg of soil in San José and 160 mg in Licantén. Although an increase was observed in the other treatments, this increase was dependent on the proportion of Na_2SO_4 incorporated into the mixture ($\text{M4} > \text{M3} > \text{M2} > \text{M1}$).

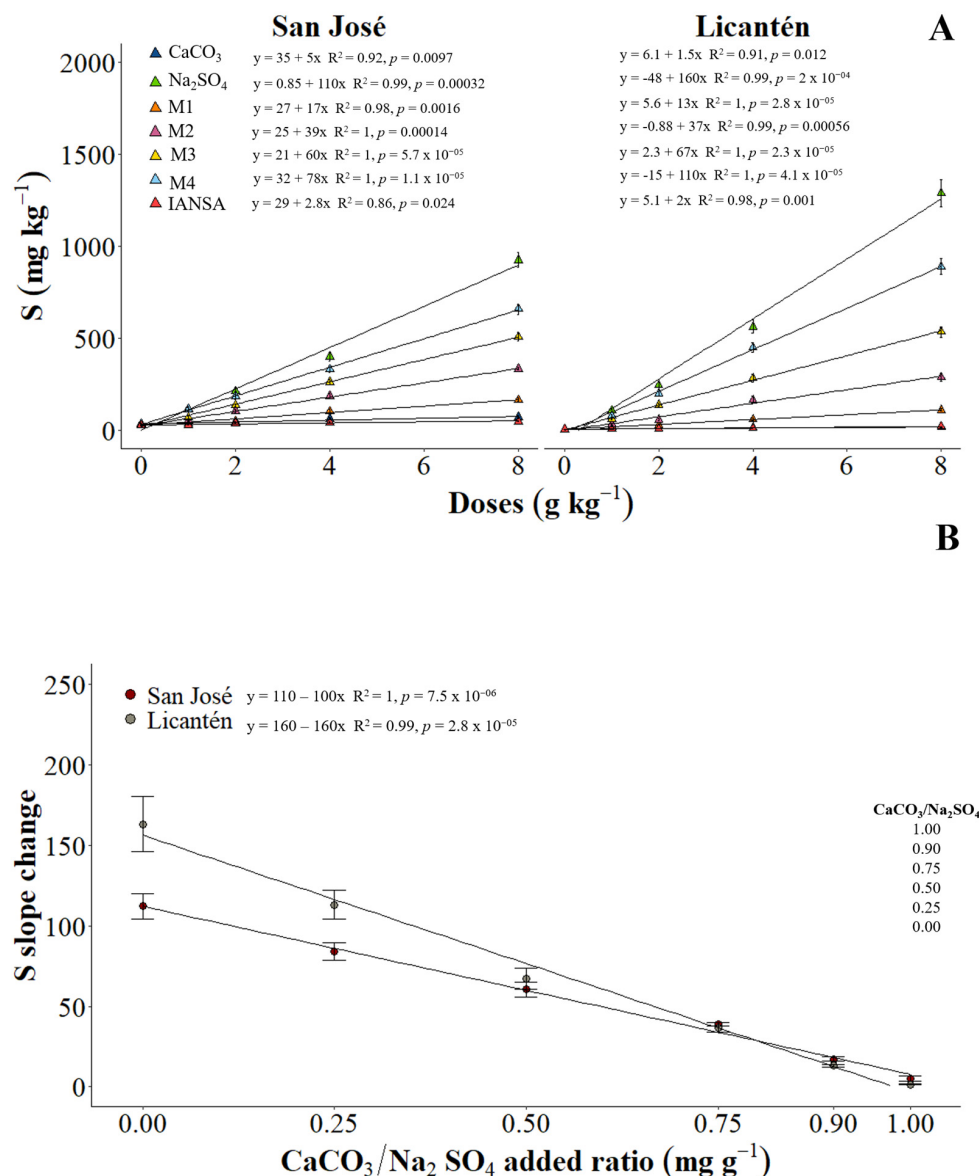


Figure 5. (A) Effect of the applied dose and the $\text{CaCO}_3/\text{Na}_2\text{SO}_4$ mix on the extractable S values in both soils. (B) Variation of the exchangeable S slope as a function of the $\text{CaCO}_3/\text{Na}_2\text{SO}_4$ ratio applied to both soils. 100% CaCO_3 , M1: mix 90/10, M2: mix 75/25, M3: mix 50/50, M4: mix 25/75, and 100% Na_2SO_4 .

The difference between soil types, considering their reactive fractions (e.g., clay and colloidal fractions), was observed in the slope variation of the ratio of added S versus the amount of extracted S (Figure 5B). The latter indicates that changes in the applied rates of S had the greatest effect on the soil, showing a linear reaction. Licantén was, on average, one third less reactive (32%) than the San José soil.

The slope of the exchangeable Na values of both soils corresponded to values very close to 1 (1.2 San José soils and 0.96 Licantén soil; Figure 6A), demonstrating that a similar proportion of the applied Na_2SO_4 was recovered from the added amount in each treatment.

As expected, for IANSA lime, no increase in exchangeable Na was observed in the soil ($p > 0.05$).

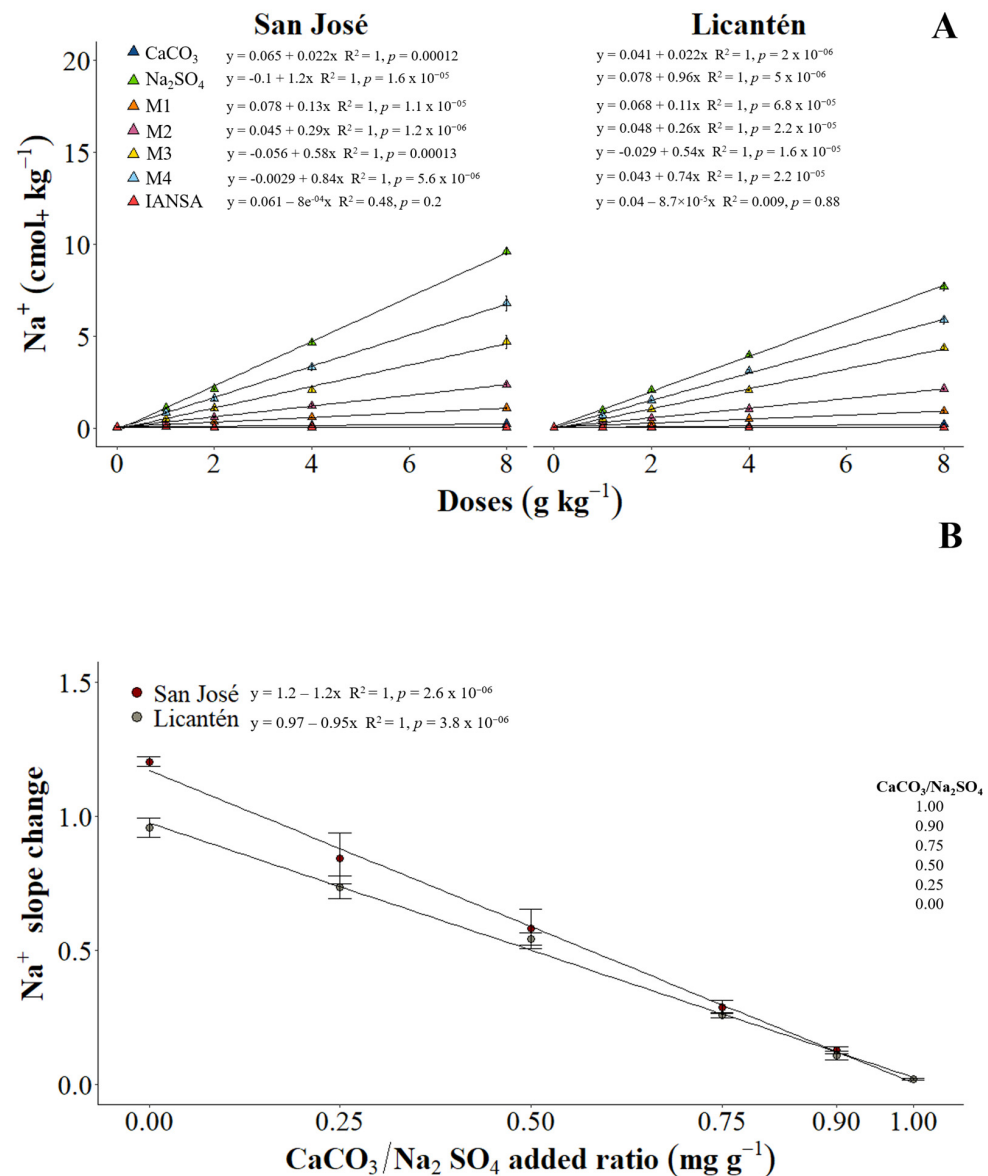


Figure 6. (A) Effect of the applied dose and the $\text{CaCO}_3/\text{Na}_2\text{SO}_4$ mix on the exchangeable Na values in both soils. (B) Variation of the exchangeable Na slope as a function of the $\text{CaCO}_3/\text{Na}_2\text{SO}_4$ ratios applied to both soils. 100% CaCO_3 , M1: mix 90/10, M2: mix 75/25, M3: mix 50/50, M4: mix 25/75, and 100% Na_2SO_4 .

The observed differences corresponded to the soil type and the applied rates (Figure 6B). In the case of the San José soil, the increase in slope (1.2) was greater than that of the Licantén soil (0.95), with the change in exchangeable Na^+ content being 20% greater for each unit of Na applied in the San José soil when Na_2SO_4 was added.

3.2. Effect of Applied Rates on Na Saturation

The data regarding the rates of mixtures applied to each soil were adjusted to determine the increase in the exchangeable sodium percentage (ESP; Figure 7A). The values of the fitted linear equation showed a slight variation in the maximum ESP values reached, depending on the soil type up to the maximum rate added ($8 \text{ g mixture kg}^{-1} \text{ soil}$). The

Licantén soil showed a value of 63% ESP, which was lower than the 71% value found for the San José soil ($p < 0.05$).

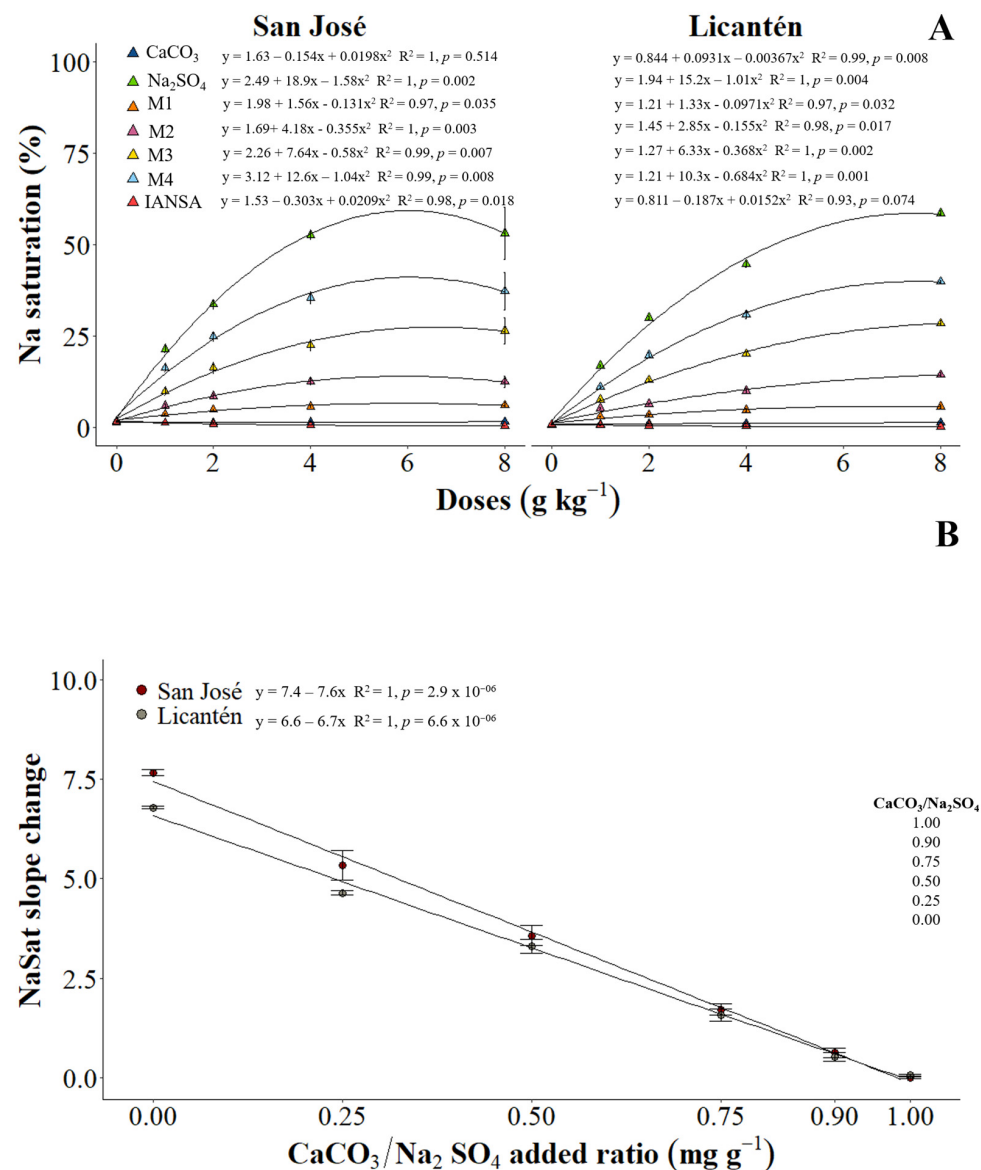


Figure 7. (A) Effect of the applied dose and the $\text{CaCO}_3/\text{Na}_2\text{SO}_4$ mix on the sodium saturation (NaSat) in both soils. (B) Variation of the NaSat slope as a function of the $\text{CaCO}_3/\text{Na}_2\text{SO}_4$ ratio applied to both soils. 100% CaCO_3 , M1: mix 90/10, M2: mix 75/25, M3: mix 50/50, M4: mix 25/75, and 100% Na_2SO_4 .

Although the values are statistically different, from an engineering point of view it can be assumed that they are similar and that the soils tend to reach values of about 70% Na saturation with an increasing Na rate (Figure 7B).

4. Discussion

4.1. Effect of the Treatments on the Evaluated Soils

The application of CaCO_3 has been shown to increase the pH in water and CaCl_2 in Chilean soils [22]. The effectiveness and quality of the liming material depends on its dissolution rate, particle size and neutralizing power [27,28]. In this research, the mixture of by-products with different neutralizing capacities due to their $\text{CaCO}_3/\text{Na}_2\text{SO}_4$ ratios caused a gradual increase of the pH in soils (Figures 1 and 2). In this context, the addition of

Na_2SO_4 to soils should not cause an increase in the soil pH, but rather result in a decrease in the soil pH (0.12 g of Na sulfate per kg of soil decreases 0.17 pH units; Ref. [18]). However, it is possible to obtain different types of alkaline residues in the white liquor recovery process from the cellulose treatment, which increases the compositional chemical variation of the by-products [13]. Therefore, we considered that a pH increase in the 100% Na_2SO_4 treatment at the highest rate (8 g Na sulfate per kg of soil increased 0.2 pH units) indicated that the added Na sulfate presented a “contaminant” proportion of liming material (e.g., Na carbonate, Na hydroxide or Na oxide) during its production.

The variation in the slopes of pHw (Figure 1) evidences the difference in the buffer capacities of the two evaluated soils. The Licantén soil showed a buffer capacity similar to those determined for granitic soils (Inceptisols; Ref. [29]), while the San José soil resembled the “trumao” soils of southern Chile (Andisols; Ref. [29]) due to their organic matter contents and textures [30]. The soil organic matter (SOM) was directly related to the pH buffering capacity and increased exchangeable Ca. It has been shown that a decrease in SOM can substantially decrease pH buffering, by up to 24% in the upper 7.5 cm of the soil [31]. Additionally, allophanic soils have non-crystalline clays of varying charge that can contribute, to a greater extent, to pH buffering [31]. In this research, the increase in exchangeable Ca was similar in both soils, i.e., 1 g of CaCO_3 per kg of soil produced an increase of $1.3 \text{ cmol}_+ \text{ per kg}^{-1}$ of soil [32]; thus, the type of colloids present in the evaluated soils was not a significant factor. In this context, a study including a wider range of soil types with a more diverse ratified mineralogy is required to confirm whether a change in the exchangeable Ca content occurs with the addition of CaCO_3 . Regardless of this, it was observed that the applied CaCO_3 was more effective in increasing the pH and exchangeable Ca compared to IANSA lime.

The rise in exchangeable K with treatments of increasing rates of Na_2SO_4 could be explained by Na generating a displacement of K in the exchange complex of the soils. Although the surfaces of soil colloids retain ions with a great hydration radius, such as Na^+ [33], the application of Na^+ proved to decrease the concentration of the K^+ ion below the preferential adsorption point. In both cases, the displacement ratio was in agreement with the expected reaction of the exchange complex. In this sense, soils dominated by 2:1 parts clay are more susceptible to K^+ adsorption [34], which predominate in soils belonging to the Licantén series [35].

The S incorporation showed that the soil type was more relevant in the sulfate retention than the materials used (Figure 5). It is likely that the lower proportion of available S present in the San José soil is due to the type of colloidal material. In that sense, it has been indicated that non-silicate Fe and Al compounds, allophanes and imogolite have higher sulfate adsorption capacities compared to other components of the soil solid phase [36]. On the other hand, it is possible that the addition of CaCO_3 may have generated sulfur mineralization attributable to an increase in the pH, facilitating the activity of microorganisms that mineralize organic sources [37].

4.2. Increased Na Saturation in Soils

Finally, it has been established as a general rule that a value above 15% ESP (exchangeable Na percentage) generates a loss in soil structure accompanied by a decrease in hydraulic conductivity and air conductivity [38,39]. In this study, it was observed that the application of M2 (25% Na_2SO_4 and 75% CaCO_3) in both soils resulted in an increase in ESP of approximately 15% (Figure 7); it is, therefore, not recommended to use mixtures with a Na_2SO_4 content greater than 25%. In this regard, Almeida et al. [40] indicated that high Na concentrations generate an increase in the adsorption of the ion and a subsequent expansion of the diffuse double layer, causing an increase in the electrical conductivity and favoring the dispersion of clays. This effect on the clay fraction and soil microaggregation has also been reported in other research where the consequences of wastewater irrigation on soil structure have been evaluated in long-term experiments [19,20]. While it is true that the application of high Na amendment mixtures (43% CaCO_3 and 56% sodium silicate)

has been shown to improve the nutrient availability and reduce Ca^{2+} and NO_3^- losses by leaching [41], increases in ESP (>30%) reaching exchangeable Na values of $\sim 4 \text{ cmol}_+ \text{ per kg}^{-1}$ of soil have also been observed. Therefore, it is essential to consider the positive and negative effects of the application of high sodium amendments on the soil.

The analysis of the rise in ESP showed that soils increased up to about 70% of their ESP with the highest rate added. This increase in ESP was not linear, but polynomial because Na is part of the denominator and numerator of the equation, so the tendency at higher rates was to lessen the increase in ESP. All the effects mentioned above generate direct consequences on crops because they reduce the roots' access to water and oxygen [42], in addition to the osmotic stress generated by the concentration of the ion in the soil [43].

Chemical additions can either aid or impede soil health depending on the amendments used. In this way, the addition of Ca can improve the soil aggregation [44] as, on the other hand, Na can deteriorate soil aggregation if it is added in excess in relation to other exchangeable bases. This study also emphasizes the importance that the soil buffer capacity plays in relation to the soil bases.

5. Conclusions

The variations observed in this research in relation to soil acidity and exchangeable cation parameters depended mainly on the type of soil evaluated. The variation in the slope of the linear relationship between the amount applied and the parameter measured proved to be more affected by the characteristics of the soil than the proportion of the mixtures added. The results obtained in relation to the rise in the exchangeable K content with an increasing rate of Na_2SO_4 applied in the mixtures, and an increase in the S mineralization with a rise in the pH of the soils due to the addition of CaCO_3 are interesting to evaluate in greater detail in the future. The latter is relevant because the addition of this mixture could have additional positive effects on the soil, i.e., the increase in sulfates present in the solution could form Al-sulfate complexes with Al^{3+} , which is toxic to plants.

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