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Influence of Mining on Nutrient Cycling in the Tropical Rain Forests of the Colombian Pacific

Harley Quinto Mosquera [1,*], Jhon Jerley Torres-Torres [2] and David Pérez-Abadía [3]

[1] Biology Program, School of Natural Sciences, Universidad Tecnológica del Chocó Diego Luis Córdoba, Quibdó, Chocó 270002, Colombia
[2] Agroforestry Engineering Program, Faculty of Engineering, Universidad Tecnológica del Chocó Diego Luis Córdoba, Quibdó, Chocó 270002, Colombia; i-jhon.torres@utch.edu.co
[3] University Institute for Research in Sustainable Forest Management, Universidad de Valladolid, 47002 Palencia, Spain; davidfernandoperez@gmail.com
* Correspondence: d-harley.quinto@utch.edu.co; Tel.: +57-3218154729

Abstract: Nutrient recycling is a fundamental process for the functioning of tropical forests; however, anthropogenic activities such as mining could affect this process in tropical ecosystems. Given that little is known about the effects of mining on nutrient recycling in tropical forests, the objective was set to evaluate the influence of mining on nutrient cycling in tropical rainforests of the Colombian Pacific. Additionally, the hypothesis that nutrient cycling could be lower in post-mining areas was evaluated. To evaluate the effect of mining on nutrient cycling, permanent plots were established in mature and post-mining forests. In both forests, soil acidity, aluminum (Al), organic matter (OM), total nitrogen (N), available phosphorus (P), magnesium (Mg), potassium (K), calcium (Ca), and effective cation exchange capacity (ECEC) were considered. Likewise, the litter production, decomposition, and accumulation on the ground were determined; additionally, nutrient content and nutrient use efficiency (NUE) were determined. It was observed that mining influenced the nutrient contents of the soil in a different way. It was evident that total N and soil OM were similar in both forests, while the contents of P, K, Ca, Mg, Al, and ECEC available were higher in post-mining. The litterfall production and litter mass accumulation on the ground were greater in post-mining, while litter decomposition was greater in mature forests. In mature forests, there was higher foliar content of N, Ca, and B and, in addition, higher NUE of Ca. However, in post-mining, there was higher leaf content of K, Mg, P, Fe, Cu, Mn, and Zn and, in addition, greater NUE of N, P and K. In conclusion, an increase in post-mining nutrient cycling was noted as a strategy for nutrient conservation, and recovery of the functioning and maintenance of productivity in degraded Pacific ecosystems. Consequently, it is expected that in the future, if mining continues in the region, productivity and nutrient recycling will be altered.

Keywords: calcium; litter decomposition; litterfall production; mining; nitrogen; organic matter; phosphorus; potassium; tropical rainforests

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1. Introduction

Tropical forests are considered the most important terrestrial ecosystems in the world [1], due to their high biodiversity [2,3], rates of endemism [4], and carbon sequestration rates [5], and their role in regulating global climate change [6]. In particular, high sequestration rates and carbon balance are determined by environmental factors such as soil type and nutrient content [7,8]. However, most low-altitude tropical rainforests with high net primary productivity (NPP) have infertile, acidic, and nutrient-poor soils [9]. Consequently, this high NPP is influenced and supported by ecological processes of the ecosystem, such as nutrient uptake and cycling [10,11].

Nutrient cycling is a fundamental process for the functioning of tropical forests [11,12], which includes the weathering of rocks, the release of nutrients into the soil solution, mineral leaching, nutrient absorption, translocation of nutrients within plants, herbivory, leaf litterfall, and, finally, the decomposition of organic matter (OM) from the soil [9,11,13]. In summary, nutrient cycling includes the processes of utilization and reuse of mineral nutrients between soil and plants [10,12]. Consequently, environmental and biological factors that regulate nutrient storage processes in the soil, and the litter production and decomposition, also directly determine nutrient cycling [10,14]. For example, Austin and Vitousek [15] and Quinto and Moreno [16] reported that soil nutrient contents tend to decrease with increasing annual precipitation levels. On the other hand, Walker and Syers [17], Guariguata and Ostertag [18], Davidson et al. [19], Walker and del Moral [20], Dalling et al. [21], and Quinto et al. [22] denoted that the contents of nutrients such as P, N, Ca, and Mg change with succession time. In particular, it was observed that the contents of available P tend to decrease until it is a limiting factor [17,21,23]; however, N contents tend to increase over time [19,20,24]. For example, studies carried out by Li et al. [25] show that pH, NH_4+, P, and K concentrations decrease with succession, while Quinto et al. [22] denoted a change in the contents of P, total N, Ca, K, and OM with succession in forests. This shows the influence of succession age on nutrient content [19].

In synthesis, soil nutrient content is determined by the interaction of soil factors, such as climate [15,16], organisms (solubilizing bacteria of P and N fixers) [26], topography, parental material, time (succession) [17,19,25], and land use [10,18,22,27]. Consequently, the magnitude of nutrient content is determined by the action of these factors [28]. For its part, litterfall production is determined by factors such as precipitation [29,30], plant species, age of the forest, successional stage, topography, temperature, and edaphic conditions [31,32]. Nutrient content and soil type are the main drivers of such production in tropical forests [8,32,33]. Particularly, the content of P, N, Ca, Mg, K, and OM in the soil generates greater litterfall production [7,34], and especially, the contents of N, P, and K tend to be the most limiting [33,35–37]. Likewise, different research shows that as well as litterfall production, the foliar nutrient content is related to soil nutrient content in forests [12,21,33,38,39].

For its part, litter decomposition, a fundamental process of nutrient recycling, is determined by factors such as the physical and climatic environment (temperature and humidity), the decomposing microbial community, the quantity and quality of the OM [40–43], soil properties [44], oxygen availability [45,46], nutrient content, cellulose, lignin, ratio C:N, plant species [41,47–49], and type of vegetation cover [50,51]. In particular, soil nutrient content is an important factor controlling decomposition because it influences the activity of decomposers, thereby considerably promoting decomposition [43,52–54]. Consequently, any affectation of the vegetation, and/or the nutrient contents of the soil, can affect litter production and decomposition, and with it, the nutrients cycling of the ecosystem [10,19,48].

In tropical forests, despite the complexity that the nutrient cycling process denotes, since many environmental and biological factors affect each of the processes [11,12,55], it is essential to understand how anthropic disturbances such as deforestation, forest degradation, livestock farming, and open pit mining [27,56] influence the nutrients cycling and recycling [19], even more so if the importance of these processes for the functioning of the ecosystem is considered. In this sense, it has been shown that in recent decades open pit mining has generated the destruction of about 1680 km^2 of natural forests in tropical regions [3,56]. In addition, mining destroys soil horizons [57], reduces vegetation [58], and affects biodiversity [59]; consequently, it possibly alters ecosystem functioning, including nutrient cycling [60].

Specifically, in the Colombian Pacific, mining has generated the degradation of more than 360 hectares of forest annually [59], and, until 2015, licenses had been granted for the exploitation of more than 300 thousand hectares of natural forest, which represents 6.49% of the territory [61]. This shows the impact on the vegetation and soil nutrients of the ecosystem [22]. However, little is known about the effects of mining on ecosystem nutrient cycling in tropical rainforests [60]. Based on the above, the objective was set to evaluate the influence of mining on nutrient cycling in the tropical rainforests of the Colombian Pacific.

2. Materials and Methods

2.1. Study Area

The present study was carried out between 2019 and 2022, in forested areas previously degraded by open-pit gold mining in the town of Jigualito (5°06′01″ N–76°32′44″ W), and the mature tropical rain forests of Opogodó (municipality of Condoto) in the state of Chocó, Colombia. These forests (mature and post-mining) were located less than five kilometers apart; therefore, they presented similar levels of precipitation, altitude, and temperature, which have an average rainfall of 8000 mm per year, and a mean temperature is 26 °C, an altitude of 70 m and flat topography. This locality is part of the North Central Chocó biogeographical region, which includes the upper basins of the Atrato and San Juan rivers, in Piedemonte and Colinas low landscape units with humid terraced soils and with a type of transitional sedimentary rock [62]. The localities are within the geomorphological unit of the Sedimentary Hills of the Tertiary period, which are formed by sedimentary rocks of low altitude, composed of sandy claystone, sandstone, and limestone. The forests are mostly primary, mature, and secondary with different ages of recovery after the impact of mining has been carried out in the area at different times.

In the mature forest, the most abundant tree species were *Wettinia quinaria*, *Mabea occidentalis*, *Eschweilera sclerophylla*, *Vismia* sp., *Inga* sp., *Pourouma chocoana*, *Vismia macrophylla*, *Matisia* sp., *Protium apiculatum*, *Couepia platycalyx*, *Miconia* sp., *Sloanea grandiflora*, *Sloanea fragrans*, *Anaxagorea crassipetala*, *Humiriastrum melanocarpum*, *Faramea jefensis*, *Cespedesia spathulata*, *Chrysochlamys clusiifolia*, and *Brosimum utile* [63,64], while in post-mining forests, the most dominant tree species were *Cecropia peltata*, *Vismia baccifera*, *Cosmibuena macrocarpa*, *Ochroma pyramidalis*, *Welfia regia*, *Pityrogramma calomelanos*, *Cespedesia spathulata*, *Perebea xanthochyma*, *Inga chocoensis*, *Pourouma bicolor*, and *Ocotea cernua* [65]. In these forests, aboveground biomass of 35.17 t ha^{-1} and 178.32 t ha^{-1} was recorded at 30–35 years and mature forest, respectively [66], while a wood net primary productivity of between 6.25 t ha^{-1} $year^{-1}$ and 9.8 t ha^{-1} $year^{-1}$ was recorded at 30–35 years and mature forest, respectively [66]. In post-mining forests of 30–35 years, the fine root biomass was lower, with average values of 2.56 t ha^{-1}. But, in mature forests, the fine root biomass was 5.91 t ha^{-1} [67].

The soils of post-mining forests are ultisols, but due to mining, they are characterized by a lot of rocky material and sand. In addition, they are acidic and have high contents of OM (13.9%), total N (0.58%), available P (32.0 mg kg^{-1}), Al (2.7 $cmol_c$ kg^{-1}), and clay, while the concentrations of Ca (5.8 $cmol_c$ kg^{-1}), K (0.36 $cmol_c$ kg^{-1}), Mg (2.5 $cmol_c$ kg^{-1}), ECEC (11.5 $cmol_c$ kg^{-1}) and silt are very low in areas of recent mining activity, but their content is higher in areas with more recovery time [22]. On the other hand, the soils of the mature forests surrounding the mines present extreme acidity, with high contents of Al (0.12 $cmol_c$ kg^{-1}), OM (11.9%) and total N (0.6%), and low amounts of P (1.3 mg kg^{-1}), Mg (0.2 $cmol_c$ kg^{-1}) and Ca (0.38 $cmol_c$ kg^{-1}), while the K (0.2 $cmol_c$ kg^{-1}) contents are intermediate and ECEC (1.0 $cmol_c$ kg^{-1}) is low [16].

2.2. Methods

2.2.1. Experimental Design

A design stratified by age of succession was used, with two strata for sampling. Stratum 1 corresponded to areas that had a recovery time of 30–35 years post-mining. In this, tree vegetation with greater diameter and species richness was found. Stratum 2 corresponded to primary forests present in the region and was taken as the reference scenario. In mature forests, the blocks consisted of 37 random permanent plots of 10 × 10 m (100 m^2). In post-mining forests, 125 random permanent plots of 10 × 10 m (100 m^2) were established.

2.2.2. Measurement of Physical and Chemical Parameters of Soil

In each plot (37 and 125 in post-mining and mature forest, respectively), composite samples of soil were taken at a depth of 20 cm, to which the parameters of acidity (pH), Al, OM, total N, available P, Ca, K, Mg, ECEC, and texture (percentages of sand, silt, and clay), according to the following laboratory techniques: Bouyoucos for textural fractions, potentiometric in water solution (1:2) for pH, Walkley and Black with the respective coefficient to determine OM, Micro-Kjeldahl for total N, ascorbic acid in an UV-VIS spectrophotometer after extraction with the Bray II method for available P, atomic absorption for Ca, Mg, and K extracted with ammonium acetate, described in Quinto et al. [22]. Soil sampling was carried out in the years 2020 and 2021.

2.2.3. Measurement of the Litterfall Production

The litterfall production was determined with litter collectors (75 in mature forests, and 60 in post-mining) of 1.0 m × 0.5 m of the area of collection for a year [31]; these litter collectors were distributed according to the established treatments. The collected material was dried and weighed; this material was not separated, and the total values stored in each collector were taken biweekly. The quantities collected were expressed in tons per hectare per year (t ha^{-1} $year^{-1}$) [31].

2.2.4. Measurement of Litter Decomposition

To measure this variable, the decomposition bag method was used, which has been used in different previous studies [47,51,68,69]; for this, initially, the leaves of the dominant tree species in the post-mining and primary forests were collected. The selected leaves were the recently fallen ones that were yellow and without signs of decomposition. Said collected material was taken to the Botany and Ecology Laboratory of Universidad Tecnológica de Chocó, where it was dried in ovens for 48 h until it reached a constant dry weight.

Then, 100 g of dry-weight leaf litter was introduced into each decomposition bag, and, subsequently, the material was taken to each forest from which it was collected, following what was indicated in the experimental design. Subsequently, for 32 days, each week, 10 bags of decomposition were randomly collected, which were taken to the laboratory, and there they were dried and weighed again, and with this information, the quantity of dry weight lost was determined. Using the weight loss data over time, the percentage of remaining mass, the percentage of weight loss, and the decomposition rate (k) were determined in each of the established strata or treatments.

2.2.5. Litter Decomposition Equations

The decomposition rate (k) of litter was determined with the simple exponential model [46,70] of the form as follows:

(1) $\mathrm{Ln}(X0/X1) = k \times T$;
(2) $k = \mathrm{Ln}(X0/X1)/T$.

Where Ln is the natural logarithm, k is the decomposition rate in years, X0 is the initial mass (dry weight of the litter), X1 is the mass (dry weight of the litter) remaining at time T, and T is the time in years [9,12,70].

2.2.6. Measurement of the Litter Mass Accumulation on the Ground

The soil litter was determined with the Olson [70] model based on the production and decomposition values of litter of each ecosystem evaluated, in the following way:

(3) Litter mass accumulation = Litterfall production/k

Where k is the decomposition rate in years determined in each of the plots established in mature and post-mining forests. The litter mass accumulation reflects the relationship between litterfall and decomposition [9,10]. Litter mass accumulation on the ground values were presented in tons per hectare (t ha^{-1}).

2.2.7. Measurement of Leaf Nutrient Content

In each plot (37 and 125 in post-mining and mature forest, respectively), composite samples of leaf were taken at a litterfall in the collectors, the collected material was dried and weighed (1.5 kg), to which the parameters of N, P, Ca, K, and Mg, according to the laboratory techniques, were as follows: Micro-Kjeldahl for total N, ascorbic acid in an UV-VIS spectrophotometer after extraction with the Bray II method for available P, and atomic absorption for Ca, Mg, and K extracted with ammonium acetate, described in Osorio [71]. Foliar sampling was carried out in the years 2020 and 2021.

2.2.8. Determination of Nutrient Use Efficiency (NUE)

To determine the NUE, the Vitousek [33] model was used, through the following equation:

$$\text{NUE} = \text{Leaf nutrient content} \times \text{litterfall production} \tag{1}$$

The NUE was determined for N, P, Ca, and K nutrients in mature and post-mining forests. High NUE values indicate high nutrient use efficiency due to high litter production or high foliar availability of nutrients, while low NUE values indicate the opposite, with oligotrophic conditions in the ecosystem [12,33].

2.3. Data Analysis

To evaluate the influence of mining on the physicochemical parameters (acidity, Al, MO, total N, available P, Mg, K, Ca, and ECEC) of the soil, litter production, decomposition of litter, litter on the ground, litter nutrient content, and NUE, the non-parametric Mann–Whitney (MW) test was used when the assumptions of normality and homogeneity of data variances and its residuals were not met, and evaluated with the statistical tests of Shapiro–Wilk, Bartlett, Hartley, and Kurtosis (between +2.0 and −2.0), while, when the assumptions were met, the T-Student Test was used. All statistical analyses were performed in the Rstudio version 3.0.0 [72].

3. Results

3.1. Soil Nutrient Content

Mining had a different influence on soil nutrient content in the forests of the Colombian Pacific (Figure 1). In this sense, it was observed that the total soil N was, on average, (±standard error) 0.61 ± 0.02% in mature forests and 0.57 ± 0.04% in post-mining, and it was noted that there were no significant differences between the two forests (MW = −1.24; *p*-value = 0.214) (Figure 1A) hile the available P was 1.32 ± 0.06 ppm in mature forests and 29.52 ± 3.8 ppm in post-mining and a statistically significant difference was noted between the forests (MW = −7.17; *p*-value = 0.00007) (Figure 1B). Likewise, soil K was 0.23 ± 0.01 meq/100 g in mature forests and 0.36 ± 0.02 meq/100 g in post-mining forests, and it was noted that there were significant differences between the forests (MW = −5.43; *p*-value = 0.00005) (Figure 1C). In addition, soil Ca was significantly higher in post-mining forests with 5.8 ± 0.81 meq/100 g, compared to the content of mature forests of 0.38 ± 0.02 meq/100 g (MW = −8.5; *p*-value = 0.00001) (Figure 1D). Also, Mg and ECEC contents were significantly higher in post-mining forests (Figure 1E). For its part, the Al content of the soil was 0.127 ± 0.006 meq/100 g in mature forests and 2.78 ± 0.21 meq/100 g in post-mining, and it was confirmed that there were significant differences between the forests (MW = −9.15; *p*-value = 0.00005).

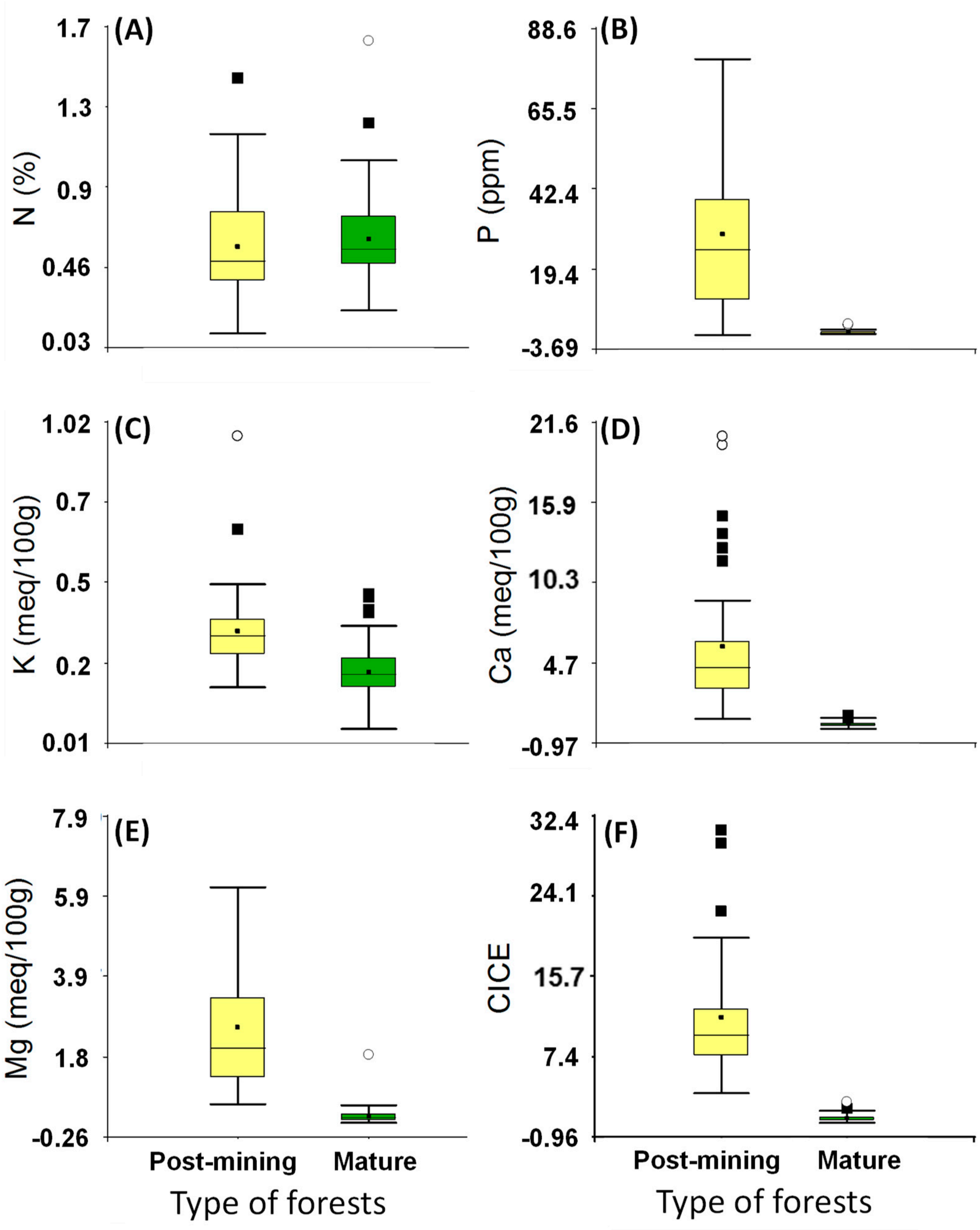

Figure 1. Effects of mining on soil nutrient content in rainforests of the Colombian Pacific. (**A**) nitrogen content—N, (**B**) phosphorus content—P, (**C**) potassium content—K, (**D**) calcium content—Ca, (**E**) magnesium content—Mg, and (**F**) cation exchange capacity—CECC. Post-mining: post-mining forest and Mature: mature forest without significant anthropogenic intervention.

3.2. Litter Dynamics

Litterfall production was 4.29 ± 0.24 t ha^{-1} year^{-1} in mature forests and 9.67 ± 0.28 t ha^{-1} year^{-1} in post-mining forests, and significant differences were evident between forest types (T-student = 14.41; *p* < value= 0.000001) (Figure 2A), while the litter decomposition rate was higher in mature forests (k = 6.71 ± 1.43 year^{-1}) compared to that recorded in post-mining (k = 2.08 ± 0.5 year^{-1}) (MW = −4.5; *p*-value = 0.00006) (Figure 2B). Consequently, litter mass accumulation was lower in mature forests (0.63 ± 0.03 t ha^{-1}) compared to that of post-mining forests (4.62 ± 0.13 t ha^{-1}) (T-Student = 27.6; *p*-value < 0.00001) (Figure 2C). Contrary to this, it was observed that the OM was 11.94 ± 0.4% in mature forests and 13.9 ± 1.24% in post-mining, and it was noted that there were no significant differences between the forests (MW = −0.31; *p*-value = 0.75) (Figure 2D).

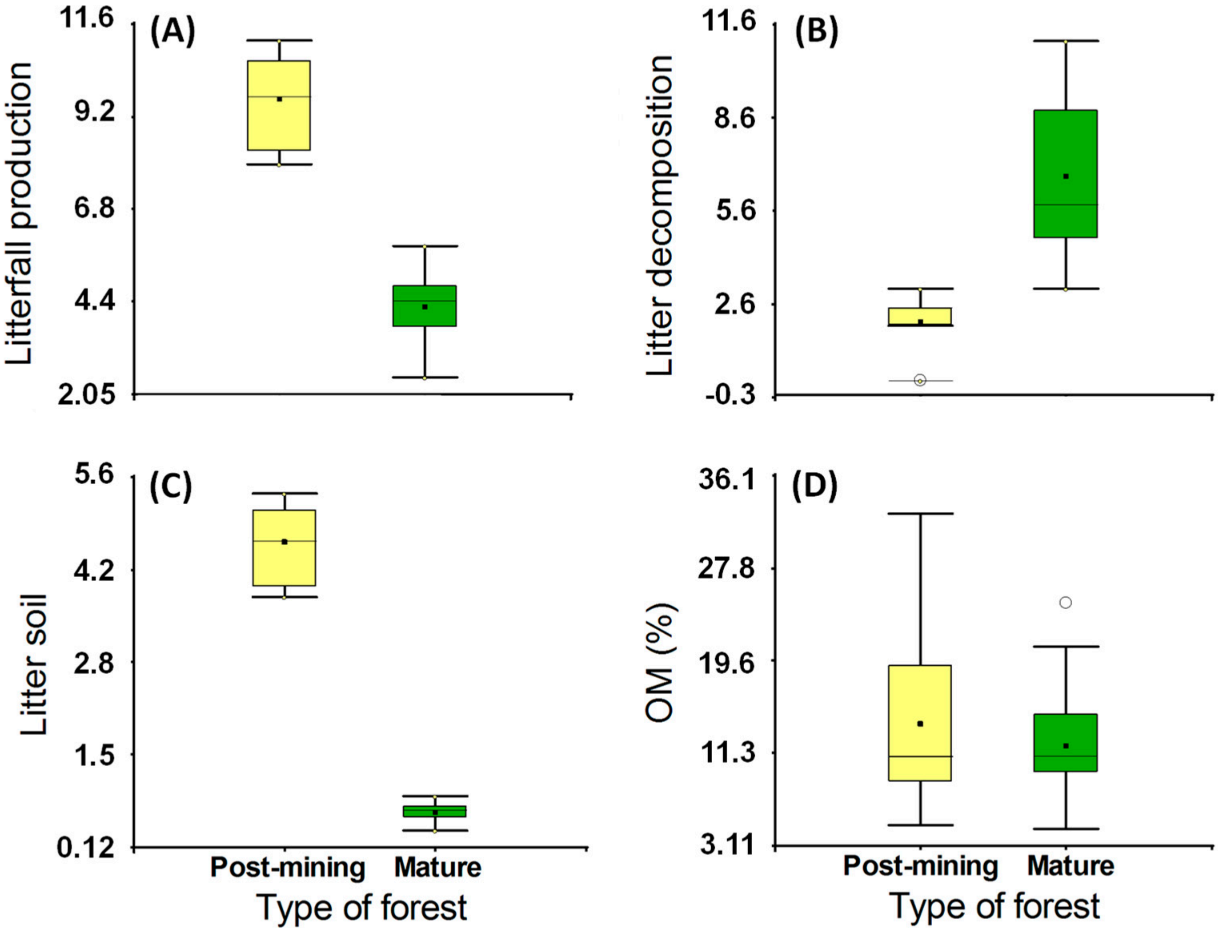

Figure 2. Effects of mining on (**A**) litterfall, (**B**) litter decomposition, (**C**) litter mass on the ground, and (**D**) organic matter in tropical rain forests of the Colombian Pacific. Post-mining: post-mining forest and Mature: mature forest without significant anthropogenic intervention.

3.3. Leaf Nutrient Content

It was determined that in mature forests there was a higher leaf content of N and Ca, respectively (Figure 3A,D), while in post-mining forests there were higher foliar contents of nutrients such as K, Mg, P, and Fe (Figure 3B,C,E,F). For its part, the foliar content of micronutrients such as B was higher in mature forests (Figure 4A); however, foliar contents of Cu, Mn, and Zn were higher in post-mining forests (Figure 4B–D).

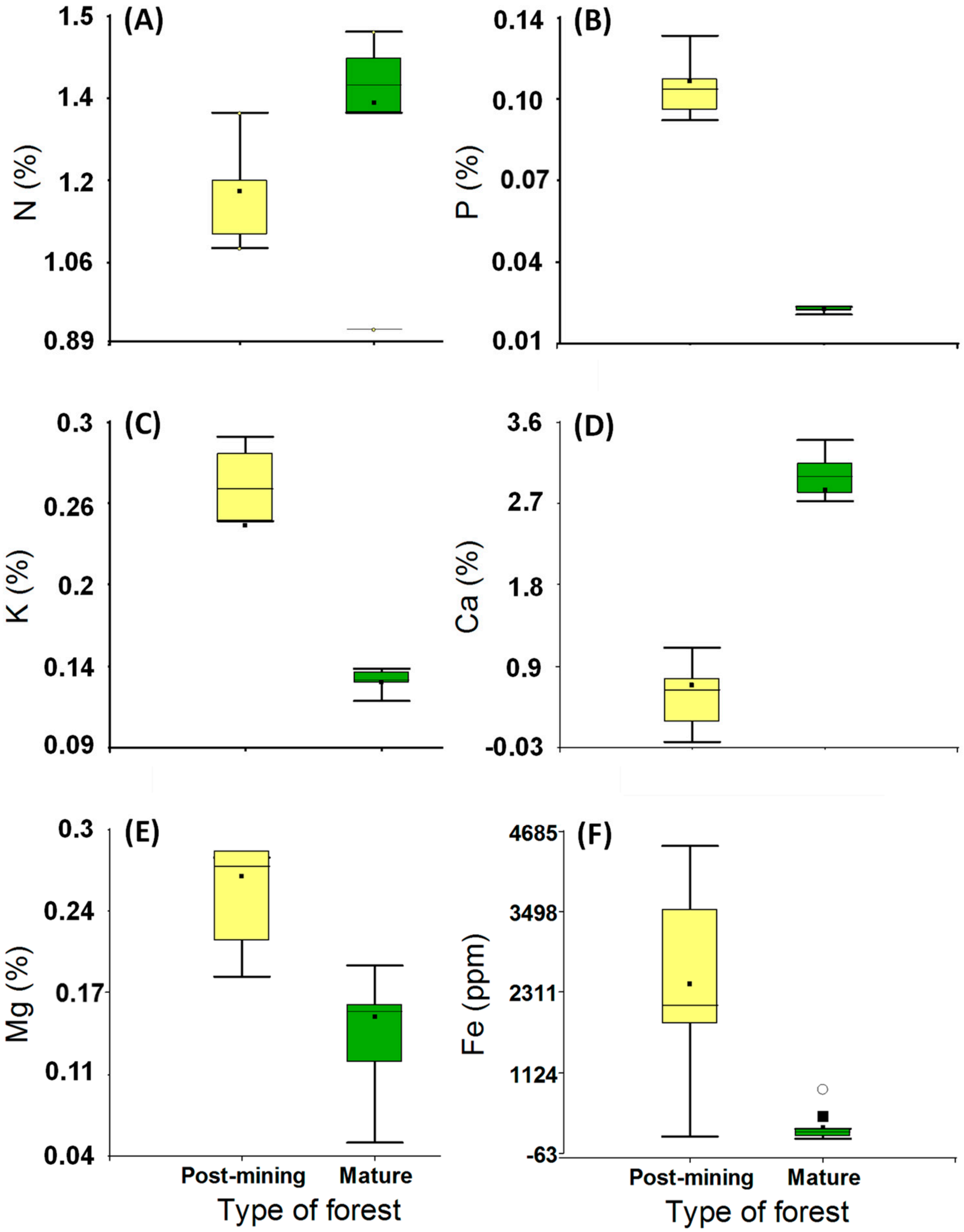

Figure 3. Effects of mining on foliar nutrients in tropical rain forests of the Colombian Pacific. (**A**) nitrogen content—N, (**B**) phosphorus content—P, (**C**) potassium content—K, (**D**) calcium content—Ca, (**E**) magnesium content—Mg, and (**F**) Iron content—Fe. Post-mining: post-mining forest and Mature: mature forest without significant anthropogenic intervention.

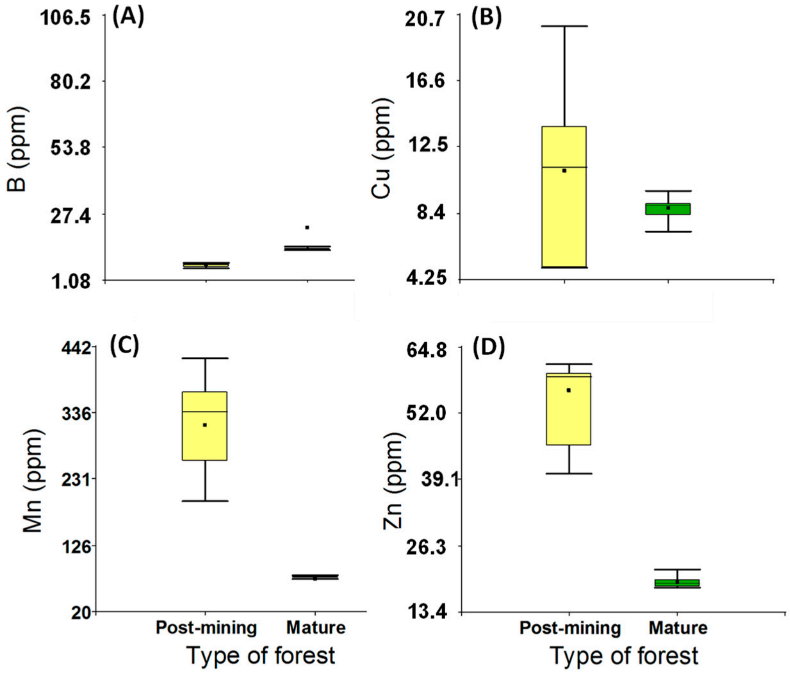

Figure 4. Effects of mining on foliar nutrients in tropical rain forests of the Colombian Pacific. (**A**) boron content—B, (**B**) copper content—Cu, (**C**) manganese content—Mn, and (**D**) zinc content—Zn. Post-mining: post-mining forest and Mature: mature forest without significant anthropogenic intervention.

3.4. Nutrient Use Efficiency (NUE)

It was determined that in post-mining forests there was a greater NUE of N, P, and K (Figure 5A–C), while in mature forests, there was a greater NUE of Ca (Figure 5D).

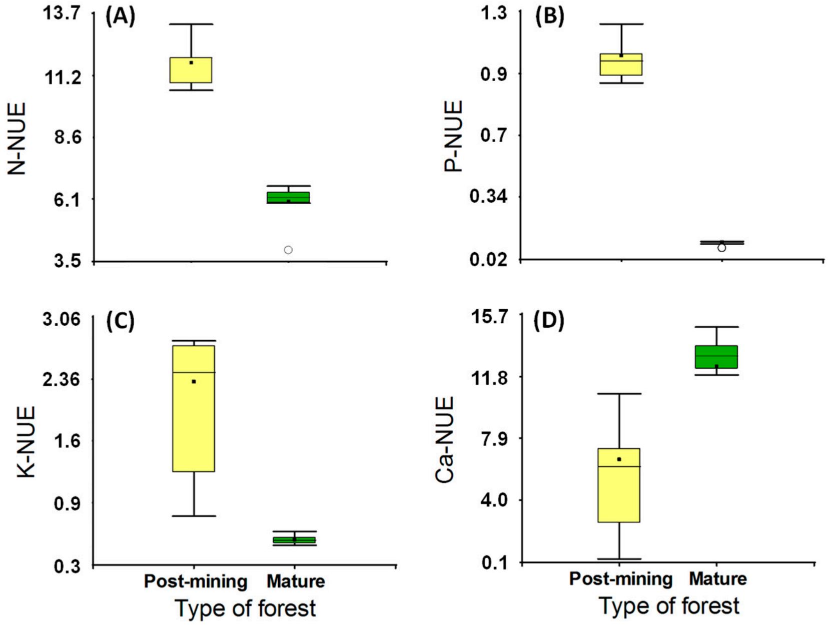

Figure 5. Effects of mining on nutrient use efficiency (NUE) in tropical rain forests of the Colombian Pacific. (**A**) nitrogen use efficiency—N, (**B**) phosphorus use efficiency—P, (**C**) potassium use efficiency—K, and (**D**) calcium use efficiency—Ca. Post-mining: post-mining forest and Mature: mature forest without significant anthropogenic intervention.

4. Discussion

4.1. Influence of Mining on Soil Nutrient Content

In the rainforests of the Colombian Pacific, open pit mining generated a significant increase in the contents of soil nutrients such as P, K, Ca, Mg, and ECEC. This increase is probably due to the fact that with the semi-mechanized mining (with backhoes) that is carried out in the region [57,73], the forests are deforested, the organic soil is destroyed, the organic and inorganic horizons of the soil are altered, and the density, texture, and aggregates of the soil are affected due to the mechanical action of the machines [22,57,58]; likewise, the ecosystem is contaminated and biodiversity is lost [59,73]. In addition, due to mining, soil rocks are affected and degraded [73], thereby releasing nutrients that remain available in the soil solution [22]. In short, mining accelerates the release of nutrients resulting from the weathering of rocks.

In this sense, Jordan [10] determined that the cycling, dynamics, and availability of soil nutrients can be influenced by environmental factors such as temperature, humidity (precipitation), productivity, and decomposition, among others, as well as by anthropic factors such as the type, size, and intensity of disturbances that affect an ecosystem [10,18,19]. Consequently, it has been noted that after disturbances such as deforestation, burning of forests, and changes in land use (livestock and crops), among others, there was an increase in the contents of Ca, N, Mg, K, and available P in the soil during the early years [10,19], similar to what was reported in areas degraded by open pit mining [22]. Also, similar to what was reported by Guariguata and Ostertag [19] in an analysis carried out at the level of tropical forests that noted that after deforestation, changes occur in the soil such as increases in the availability of nutrients such as P, Ca, K, Al, and ECEC [19]. These increases are due to the fact that the nutrients that were stored in the plant biomass (leaves, stems, branches, and roots) become available in the soil solution after deforestation and decomposition of the material [10,11]. In summary, the availability of nutrients present in post-mining areas is due to the residues of deforested trees and the minerals released by the mechanical action of mining on the ground.

It is important to mention that not all nutrients increase their availability with mining. For example, total soil N presented similar values in mature forests and post-mining, which indicates that the availability of this nutrient was not affected in principle by deforestation and the impact of the ecosystem by mining [22]. Although a decrease in total N was expected in post-mining areas, its content in the soil was similar to that recorded in mature forests, which is probably due to the interaction and influence of different factors, among which we can mention the following: (1) the presence and abundance of plant species with the capacity to symbiotically fix atmospheric N, of which more than 70 individuals have been recorded, in trees of the Fabaceae family (legumes) in the evaluated post-mining forests (*Inga chocoensis*, *Inga lopadadenia*, *Abarema barbouriana*, *Lonchocarpus monilis*, *Calliandra laxa*, *Diplotropis* sp., *Pentaclethra macroloba*) [74]; (2) the colonization of bacteria (free and symbiotic) fixing atmospheric N, since, if conditions allow, after >30 years of succession, these biological groups can begin to colonize, and thereby increase the rates of nitrification, ammonification, and N fixation in the ecosystem [8,19,22,54,55]; and (3) the presence of total N product of plant biomass and plant residues of trees, bushes, and herbs [14,19] that remained after mining and that are in decomposition and mineralization deposited in the soil, and that would also explain the similarity in availability of N in both forest ecosystems studied.

The high precipitation that occurs in the Colombian Pacific region can favor the leaching of nutrients from the soil [15,16,42], as long as the topography and inclination of the land allow it [14], because in some places in post-mining areas, the miners left holes, gaps, channels, mounds of earth, and concave topographies of the terrain [57,58], in which a large amount of OM accumulates water and minerals; despite the high rainfall, this condition would also explain the high accumulation of nutrients in the post-mining soil.

With open pit mining in soils of the Colombian Pacific, the amount of Al increased and the strong acidity of the soil was maintained [22], which is possibly due to the influence of high precipitation and rocky and clay minerals in the soil [12,71]. Specifically, high precipitation and temperature generate greater acidity of the soil, and also the accumulation of Al in the soil, due to the increase in the weathering of aluminosilicate minerals based on the reactions of hydrolysis, dissolution, carbonation, oxidation, reduction, and hydration, which generate as products the disintegration of the structure of rocks and minerals, and the release of Al and other elements to the soil [12,71].

With precipitation and rock weathering, mineral losses through leaching increase due to its solubility [15]; however, Al can remain in the soil in different forms, such as the following: (1) soluble in the soil solution; (2) exchangeable retained on the surface of negatively charged clays; (3) complexed (fixed) in the soil OM; and (4) precipitated as a secondary mineral as oxide and hydroxide and, as such, remain on the ground [71]. These characteristics would explain the greater accumulation of Al in post-mining soils, where the mechanical action of backhoe machines degraded rocks containing Al in the soil, increasing its availability. However, this increase in the availability of Al in post-mining areas will surely generate toxicity for most of the plants that colonize these degraded areas since the Al saturation is greater than 23.4%, which indicates possible toxicity for most plants [12,71]. This edaphic condition can be a significant problem for the recovery of the ecosystem, because Al toxicity affects the absorption of nutrients, generates chlorosis and necrosis, decreases the size of the leaves, alters metabolic processes, increases nutritional stress, alters physiological processes, affects the development of roots, stems and leaves, reduces the photosynthetic rate and growth of plants, and decreases the biomass and primary productivity of the ecosystem [12,71,75,76]. In summary, despite the release of nutrients that occurs in mines due to the degradation of minerals, the presence of Al, with its respective toxicity, could be a predominant limiting factor that can affect the growth and recovery of biomass and biodiversity of these degraded ecosystems.

In the mature forests of the Colombian Pacific, infertility and the low nutrient content of the region's soils were evident, which agrees with what was stated by Jordan [10], Vitousek and Sanford [77], Whitmore [9], Metcalfe et al. [13], Alvarado [12], and Quinto and Moreno [16], who consider that the majority of tropical rainforests, including those of Chocó, have acidic, weathered, infertile, and nutrient-poor soils. In this sense, Jordan [10] concluded that in poor and infertile (oligotrophic) tropical ecosystems, plants develop nutrient conservation mechanisms, among which we can mention strategies such as the following: (1) The production of greater biomass of fine roots in soils poor in nutrients, as has been previously evidenced [77] and as has been evaluated in Chocó forests [67]. This mechanism occurs because, with a great system of fine roots, more nutrients can be acquired from the soil [55]. (2) The greater concentration of fine roots on the soil surface to acquire more nutrients [78]. (3) The formation of associations with mycorrhizal fungi to increase the absorption of nutrients in conditions of low availability [55,79]. (4) The relocation of nutrients from old leaves to other plant structures before their abscission [13,19,77], where there is greater mobility of nutrients such as P, N, and K. [12,80]. (5) The storage of nutrients in plant biomass [13,19,38]. In this sense, it has been observed that in tropical very rainy forests, there is (>2000 mm annually) greater storage of nutrients in leaves, compared to stems; likewise, it has been noted that Ca and K are stored more in the aboveground biomass than in the soil surface (20 cm deep), while N and P contents tend to be higher in the soil [10]. These nutrient conservation mechanisms are possibly those that the mature rainforests of the Colombian Pacific are using to maintain their nutritional status and cycling, and therefore their primary productivity.

4.2. Influence of Mining on Litter Dynamics

In the rain forests of the Pacific, litterfall production was greater in post-mining secondary forests. This trend is probably due to the greater availability of nutrients such as available P, K, Ca, and Mg present in the soil previously degraded by open pit mining. This corroborates what was reported a few decades ago by Jordan [10] and Vitousek and Sanford [77], who concluded that tropical forests with fertile soils and higher nutrient content have greater litterfall production [10,77]. Some years ago, Paoli and Curran [7] reported greater litterfall production in soils with higher nutrient content (K, Ca, Mg, available P, total N, and ECEC) in Lowland Forest at Gunung Palung National Park, in Borneo, Indonesia. Also, Montagnini and Jordan [11] concluded that tropical forests with more fertile soils and/or with greater availability of nutrients have greater litterfall production. Recently, in forests of the Colombian Pacific, a significant relationship between litterfall production and soil nutrient content was noted [34]. Due to the observed correlations and fertilization experiments carried out in different tropical forests, soil N, P, and K have been considered as limiting elements of forest productivity [33,35–37].

In terms of ecosystems degraded by mining, this greater litterfall production is a positive factor for their recovery [48,60], since the litter production and decomposition are the main processes of nutrient cycling [10,12,41], and, consequently, soils with higher nutrient content have greater litterfall production and, respectively, greater nutrient cycling [11]. This high litterfall production seems to be the main mechanism to maintain the proper functioning of eutrophic forests, where there is a high availability of nutrients in the soil compared to oligotrophic forests where litterfall production is usually lower, but the aboveground biomass of trees is greater [81], as reported by Jordan [10] in tropical forests of Sarawak with similar climatic conditions and differences in soil fertility, as was also corroborated in the present study, where post-mining areas with nutrient-rich soils and lower aboveground biomass presented greater litterfall production, and mature forests with infertile soils and greater aboveground biomass presented lower litterfall production. In summary, it is evident that in ecosystems in oligotrophic conditions and nutrient shortages, there is greater aboveground biomass and more nutrients are stored in the plant biomass, while in eutrophic conditions, it produces more litterfall and greater circulation of nutrients [11,12,77,81]. Likewise, after mining in the forests of the Colombian Pacific, nutrients in the soil increase, and aboveground biomass decreases, but leaf litter production increases; consequently, nutrient cycling increases.

Litter decomposition rates in post-mining and mature rain forests were 2.08 and 6.71 year^{-1}, respectively; these decomposition rates can be considered to be very high, according to the analyses carried out for tropical rainforests [70]. In addition, they are higher than most rates reported for areas of mining in rehabilitation (0.36–0.70 year^{-1}) [60], and in tropical forests between 0.52 and 3.42 year^{-1} [9,10]. Different studies have quantified high rates of OM decomposition in tropical ecosystems with high levels of precipitation [15,43,60] and greater fertility [10,82]. In particular, the nutrient content of the soil is an important factor that controls decomposition because it influences the activity of decomposers (microorganisms, fungi, and arthropods, among others), and thus decomposition is favored [43,52–54]. However, the results of the present study are contrary to this hypothesis, since the decomposition rates recorded in nutrient-poor mature forests (oligotrophic) were higher than those recorded in post-mining secondary forests rich in nutrients (eutrophic), with both ecosystems with high levels of average annual precipitation (>8000 mm) (Figure 1). That is, there was greater decomposition in nutrient-poor soils.

The lower litter decomposition recorded in post-mining secondary rainforests is surely due to the differences in the characteristics of the litter of each type of forest since in each type of forest there was a different composition of tree species [58,65,74], which generates differences in the chemical characteristics of the litter because each species has a different foliar nutrient content [10,12,41,55,77]. Specifically, it was observed that in mature forests there was a higher foliar content of N and Ca (Figure 4), which possibly explains the higher decomposition rate of this forest. This assertion is corroborated by what was stated by Hobbie [82], who noted that high foliar contents of N and Ca were associated with rapid rates of leaf litter decomposition. Also, this assertion is supported by the approaches of Montagnini and Jordan [11], who consider that a greater foliar content of nutrients, especially N, favors the decomposition of leaf litter and MO due to the high demand by decomposer organisms [82]. This situation possibly explains the difference in decomposition rates among ecosystems. Furthermore, it is shown that under high precipitation conditions, species composition and foliar nutrient content (Ca and N) can be the best predictors of litter decomposition.

The lower rate of litter decomposition in post-mining forests surely occurs due to nutrient relocation processes prior to leaf abscission in post-mining trees, as a nutrient conservation mechanism [10]; given that, high nutrient contents were recorded in the post-mining soil, but with a decrease in its foliar contents, especially N and Ca. This relocation of nutrients is a common strategy in tropical ecosystems, since it has been recorded in different proportions in tropical forests with moderately fertile and infertile soils [77]. Therefore, low decomposition generates an accumulation of "low-quality" litter (with low N and Ca content) in post-mining soils. The slow decomposition could also be explained by the high precipitation in the region, which generates low-quality litter, similar to what has been previously reported in tropical rainforests [15,45], and also, in forests of biogeographical Chocó [46].

Consequently, the fact of presenting low litter decomposition is a positive characteristic for the natural recovery of soil degraded by mining activity since, due to the slowness of the decomposition process, leaf litter and OM accumulate in the soil, and with this the OM content, percentage of humidity, microbial biomass, nutrient content, macroaggregates, microaggregates, and texture, among others [19,48,71]. In fact, one of the mechanisms used to restore degraded ecosystems includes the application of organic fertilizers [12,58], which in this case occur naturally in post-mining secondary forests after >30 years of succession in the Colombian Pacific.

Given the little litter decomposition in post-mining forests, a litter mass accumulation on the ground forest was noted; said accumulation was 4.62 t ha^{-1}, which is within the range of 1.9 and 11.3 t ha^{-1} recorded for tropical forests [9,10] (Table S1). In this sense, the present values of litter mass on the ground, as well as what is recorded in various studies carried out in tropical forests, show that a high litterfall production accompanied by low rates of litter decomposition generates an accumulation of litter mass in the soil [9]. In conclusion, this accumulation of litter mass as a result of reduced decomposition shows retention of nutrients in the litter, which restricts its availability for microorganisms and plants, and with this, a slow release of nutrients and a considerable obstruction to nutrient recycling is generated, which could affect the functioning of the post-mining ecosystem. However, if this special condition were not present, the fine leaf litter would decompose and mineralize rapidly, as occurs in mature forests and other regions of the Chocó biogeographic region [46], due to high precipitation that facilitates leaching of foliar and soil nutrients [15,16,42]. Consequently, if it were not for this slow litter decomposition, there would possibly be ecosystems with leached, oligotrophic, and nutrient-poor soils, like most tropical forests [77].

The research of Valente et al. [60] concludes that litterfall production is important in degraded areas to ensure the nutrient return to the soil and suggests that the cultivation of a mixture of native trees contributes to producing higher annual litterfall, and can be a promising option for reactivation of nutrient cycling and organic matter formation in mined areas [60]. Likewise, León et al. [83] consider that a passive restoration strategy for degraded ecosystems can be via the litter mass accumulation on the ground since this allows the reactivation of the biogeochemical cycle of the ecosystem. In addition, León and Osorio [48] conclude that one of the main mechanisms of passive restoration of ecosystems degraded by open pit mining is through the recovery of nutrient recycling (litter production and decomposition), which is favored by the litter mass accumulation on the ground of the recovering ecosystem, as evidenced in ecosystems degraded by mining in the Pacific. In conclusion, after mining in the Pacific, the rate of leaf litter decomposition was reduced; however, the litterfall production and litter mass accumulation on the soil increased, thereby favoring the conditions for the slow recovery of the degraded ecosystem.

4.3. Influence of Mining on Foliar Nutrient Content

In mature forests of the Colombian Pacific, foliar nutrient content was mostly low; only N and Ca presented high foliar percentages (Table S2). Particularly, the high foliar N content possibly occurs due to the high levels of precipitation and humidity that favor the rates of atmospheric N fixation carried out by bacteria (nitrifying and ammonifying) free or in symbiosis with plants of the Fabaceae family [8,19,41,54]. This symbiosis is carried out with legumes such as *Inga* sp., *Enterolobium cyclocarpum*, *Inga coruscans*, *Hymenaea oblongifolia*, *Ormosia colombiana*, and *Andira inermis* [65]. Also, another factor that could explain the high percentage of foliar N is the high content of total N in the soil [77] since this nutrient has shown high content in the soil [16]. In this sense, Wood et al. [38] determined that in tropical forests, a higher nutrient content in the soil tends to generate a higher percentage of nutrient content in the leaves. In summary, the high contents of total N in the soil explain the highest percentage of its foliar content in Pacific forests.

The levels of foliar N recorded in forests of the Colombian Pacific (N = 1.39%) are within the range reported for low-altitude tropical humid forests between 0.58 and 2.52% [38,77]. Likewise, the values reported for foliar Ca in this study (Ca = 2.89%) are within the range of between 0.15 and 3.1% reported for tropical forests [38]. Surely, these high foliar Ca contents are explained by the high Ca content in the soil, as has been recorded in other studies [38], and due to the characteristics of low mobility of this mineral inside the plants [71], which has been evidenced mainly in nutrient retranslocation processes, in which the percentages of foliar Ca have been high prior to senescence [77]. In conclusion, it was noted that foliar N and Ca contents are high, and are possibly due to the influence of factors such as species composition (legumes), activity of atmospheric N-fixing bacteria, and soil fertility (availability of N and Ca). However, foliar N and Ca contents decreased significantly in post-mining forests; this reduction is surely due to nutrient relocation processes prior to leaf senescence [55], and as a conservation strategy of nutrients in disturbed environments [77].

In post-mining forests, foliar contents of P, K, Mg, Fe, Cu, Mn, and Zn increased (Figure 4), contrary to what was observed in the percentages of foliar N and Ca. These higher foliar nutrient contents are surely explained by the fact that with open pit mining, the availability of these nutrients in the soil increased [22], due to the degradation (weathering) of rocks by the action of the machines [57], and with this, the absorption of minerals by the plants surely increased [55], and, consequently, the foliar nutrient content, similar to what was recorded in previous studies, in which a higher nutrient content has been determined in plants that grow on soils rich in these nutrients [38,71]. In particular, foliar P presented an average value of 0.11% in post-mining forests, which is within the range of between 0.01 and 0.32% reported for tropical forests [38]. However, foliar P values were so high in post-mining forests that only average foliar P values of 0.24% and 0.32% were recorded in high rainfall (>5000 mm annually) tropical forests in India [84], and reports of moderately fertile tropical forests (leaf P = 0.12%–0.15%) [77] were higher than those presented in this study. This shows that mining activity generates atypical conditions of P content (foliar and edaphic) in the ecosystem.

Although foliar P values of post-mining litter are considered high for tropical rainforests [38,77], this nutrient affects the litter decomposition rate, probably because, stoichiometrically, its proportion with respect to the percentage of foliar N was very low (N/P ratio = 11.0), while in mature forests, the N/P ratio was higher (N/P ratio = 46.0), which could possibly facilitate the decomposition of leaf litter [12,41,55]. These values of the leaf N/P ratio are within the range reported for tropical rainforests of between 4.16 and 100.0 [19,38,77]. However, the results of the present study corroborate what was found in Amazonian forests, where the N/P ratio increased with succession age [19], similar to this study. This increase in the N/P ratio with age denotes that the trees translocate more foliar P before leaf fall as a nutrient conservation mechanism [19].

The content of foliar K (0.24%) was within the range of between 0.15 and 0.85% reported for tropical forests [38]. In addition, the percentage of foliar Mg (0.26%) was between 0.11 and 0.90%, reported for tropical forests [38,77]. However, in both cases (K and Mg), the values were lower than most foliar nutrient values reported in tropical rainforests [38,77]. These low values of foliar K and Mg are surely due to the influence of the high precipitation of the region (>8000 mm annually); therefore, according to the studies by Santiago et al. [42], increases in precipitation generate significant reductions in the foliar contents of P, Ca, K, and Mg in low-altitude tropical forests.

For its part, the foliar percentage of Ca (0.68%) post-mining was within the range reported for tropical forests, between 0.15 and 3.1% [38]. However, these post-mining foliar Ca values were higher than those reported for tropical humid forests with infertile oxisols/ultisols soils with ranges between 0.19 and 0.50% [77]. This high foliar availability of Ca, despite the possible translocation prior to leaf senescence [55], is possibly due to the high availability of the mineral in the soil after mining, which is similar to what was recorded by Proctor (1984) in tropical rainforests with calcareous soils where foliar Ca levels were extremely high (0.31%), due to the influence of its content in the soil [38], similar to what was reported for post-mining areas.

4.4. Influence of Mining on Nutrient Use Efficiency (NUE)

Mining increased the NUE of N, P, and K in Pacific rainforests. This NUE shows the nutrients that are being best used in the ecosystem. Said NUE shows the capacity of forest ecosystems to absorb and use nutrients to obtain greater productivity. Therefore, NUE involves three main processes in plants: nutrient uptake, assimilation, and utilization [12]. Consequently, the need for plants to use nutrients in altered environments, such as post-mining forests, is evident, since it is necessary to recover the functionality of ecosystems and maximize nutrient cycling and productivity [12]. In summary, the NUE evidenced the multiple nutrient limitations that have post-mining forests, while it denoted the Ca limitation in mature forests. In this sense, Vitousek [33] denoted that the amount of fine litterfall was also significantly correlated with phosphorus concentrations in moist and wet lowland tropical forests; these analyses suggested that phosphorus but not nitrogen availability limits litterfall in a substantial subset of intact tropical forests [33].

Consequently, sites on old oxisols and ultisols, especially those in Amazonia, appear to be particularly low in available phosphorus [33]. For this reason, it was hypothesized that available P was the main limiting factor in the productivity of lowland tropical rainforests [33,39]. However, this hypothesis of limitation by available P has been little tested experimentally in tropical rainforests [37]. Likewise, the limitation that soil N has on litter production in mature tropical rainforests of the Chocó biogeographic region was recently noted [66], which shows a limitation by different nutrients, not only by P in tropical rainforests. Therefore, in this study, the NUE-Ca shows the Ca that is best used in mature forests, evidencing a possible limitation due to this nutrient. Finally, N, P, and K in post-mining rainforests in the Pacific show a limitation by multiple nutrients in post-mining areas, as has been recently evidenced in fertilization experiments [66]. In summary, through the NUE, it was possible to demonstrate changes in nutrient limitations through the succession of tropical rainforests.

5. Conclusions

An increase in post-mining nutrient cycling was noted (Figure S1) as a strategy for nutrient conservation, recovery of functioning, and productivity in degraded Pacific ecosystems. This recovery of nutrient recycling is essential to increase net primary productivity, carbon capture, and biomass, and with this, contribute significantly to the recovery of forest biodiversity and the mitigation of global climate change. Consequently, it is expected that in the future, if mining continues in the region, productivity and nutrient recycling will be altered.

In general, it is noted that in the Colombian Pacific region, and in the Latin American basins in which open pit mining is carried out, the recycling of nutrients and the productivity of the ecosystem will continue to be altered. This affects the dynamics of the forest and the function of these ecosystems in mitigating global climate change.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/f15071222/s1, Table S1: litter production, decomposition and mass on the ground in tropical rainforests; Table S2: litter nutrient content in tropical rainforests; Figure S1: synthesis of nutrients cycling in mature and post-mining tropical rain forests (mature and post-mining) of the Colombian Pacific.

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