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Application of Phosphogypsum and Organic Amendment for Bioremediation of Degraded Soil in Tunisia Oasis: Targeting Circular Economy

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Abstract: This study was conducted at the Institute of Arid Regions of Gabes in Tunisia. Three plots were left as controls and received no input, three plots were amended with cattle manure with a dose equivalent to 37.5 t/ha, and nine plots were amended with phosphogypsum in three doses (12.5 t/ha, 25 t/ha, and 50 t/ha), with three repetitions for each dose. A pot test to determine the germination index and radioactivity analysis was carried out in the laboratory. The results showed that organic manure amendments and phosphogypsum improved the germination rate of the different crops (jute mallow, turnip, and oat) compared with the control. At the same time, the 50 t/ha dose had the highest germination rate. An increase in yield of all crops during the whole duration of the experiment was observed for the soil amended by phosphogypsum. The best yield was recorded when the highest dose of phosphogypsum was applied. The cadmium level in plants of the two applied amendments was variable but still below the toxicity threshold (7 ppm). The values recorded following the analysis of the phosphogypsum radioactivity showed that the mean value of Ra-226 equals 214.45 Bq/kg, which is below the limit announced by the EPA (Environmental Protection Agency). The radioactivity results from the control soil samples showed the presence of natural radioactivity. Samples of phosphogypsum-amended soil and plants grown in these soils have radioactivity values that are still lower than those announced by the EPA. The novelty aspect of this study is the application of phosphogypsum in different crops during two consecutive years in degraded-soil areas of Tunisia, in addition to the study of different aspects of phosphogypsum reuse in agriculture as a promising strategy for a sustainable environment.

Keywords: oasis; soil; amendment; manure; phosphogypsum; germination index; cadmium

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1. Introduction

Climate change and the COVID-19 pandemic are the most dangerous threats to the 21st century. Climate change has a negative impact on food security and has contributed to desertification and land degradation [1]. The Middle East and the Mediterranean suffer the most from water scarcity and land degradation [2,3]. Oasis agrosystems limit the negative effects of climate change in arid areas. They are at odds with desertification and land degradation and, therefore, can contribute to carbon sequestration in scarce regions [4]. Agrosystems also help to regulate the local climate and natural resources, such as water and soil, and improve biodiversity [5]. The oasis of Tunisia extends from the Mediterranean coast in the east to the Great Eastern Erg in the west and from the Gafsa mountain in the north to the Sahara in the south of the country and covers a total area of 40803 ha.

In fact, this sector, in addition to its adaptation to the desert environment, has made possible the optimization of water resources in the south, and has significantly improved the agricultural sector by creating different sources of income in the oasis. However, recently this cropping system has begun to lose its performance due to various soil degradation processes in both old and new oases. It has been reported that land degradation is also a social concern [6].

In ancient oases, the degradation processes that affect soils are compaction (structural degradation), salinization, and fertility depletion. In addition, in new oases, usually located downstream of old oases, the degradation processes that affect the soils are hydromorphicity and salinization. Oasis farmers use organic amendments such as cattle manure to cope with these different forms of soil degradation and restore crop productivity. It has been shown that oasis soils require both nutrients and organic matter (manure or compost) to improve their fertility and production capacity [7].

Organic fertilization is considered one of the best solutions to restore soils affected by high salinity and irrigated by saline waters. Some authors showed that because of their scarcity and high prices, many farmers currently use chemical fertilizers, such as NPK, instead of manure, as they are easy to use and have almost immediate effects [8]. Amendments with sandy materials in the palm groves were also applied to improve degraded soils. On the other hand, Tunisia is one of the world's largest phosphoric acid producers; the Tunisian chemical group (TCG) produces phosphoric acid, and consequently, more than 12 million tons of PG are generated as a byproduct. Over 85% of PG is stored beside phosphoric acid production units in stockpiles at industrial facilities near the city of Gabes. According to previous research, the composition of PG in terms of metals is variable. It depends on their original content in the phosphate production process [9].

PG waste is discharged directly into the sea from industrial plants nearby Gabes city, causing high pollution in the Gulf of Gabes [10]. For this reason, many attempts were carried out to use PG in different applications, such as in the gypsum industry to prepare gypsum blocks, bricks, and plasters [9,11–13], and in the cement industry as a Portland cement retarder [14,15] or as a hydraulic binder in calcium sulfoaluminate cement [11]. It has been reported that PG can substitute natural gypsum in tackling the salinization of soil [16]. However, the quantity of PG reused does not exceed 15 % of the quantity produced [17]. Therefore, researchers are focused on the transformation of PG: (i) by thermal decomposition to prepare calcium sulfoaluminate cement [17]; (ii) by thermal reduction with Sulfur [18] or coal [19] to produce calcium sulfide; or (iii) by chemical reaction with phosphoric acid to convert it into hydroxyapatite nanoparticles [20], ammonia [21], or soda under CO_2 [21,22] to obtain calcium carbonate (calcite) and ammonium sulfate or sodium sulfate. Calcium silicate compounds are in high demand, mainly in building materials as a basic material. Some studies have indicated that total N, P, and K concentrations in soils have increased significantly following the application of PG in different doses [13,23]. Moreover, the addition of PG promotes the protection of organic matter and, therefore, the stability of aggregates, which results in a change in soil texture. However, the use of PG as an agricultural fertilizer or soil stabilizer is still limited in Tunisia due to farmers' refusal [9,24,25].

In the Gabes region, PG is the main by-product generated in the production of phosphoric acid from mineral rocks. It contains mainly dehydrated calcium sulfate ($CaSO_4$-$2H_2O$), phosphate, fluoride, heavy metals, and radionuclides [26].

As a response to the current urgent call to face climate change challenges and to reach the circular economy system through the sustainable development goals (SDGs), the main objective of the present paper is the study of organic amendments (cattle manure) and phosphogypsum effects on the productivity of three crops (jute mallow (*Corchorus olitorius*), turnip (*Brassica rapa subsp. rapa*), and oat (*Avena sativa*)) during two consecutive harvesting seasons. Yield, germination rate (GR), cadmium (Cd) level in the three plants, and the radioactivity of soil samples amended by phosphogypsum were measured. The three crops used in this study represent the coastal oasis crops of Tunisia.

2. Materials and Methods

2.1. Geographic Localization and Characteristics of the Experimental Site

The study was carried out on an experimental plot in the Chenini oasis of the governorate of Gabes. The Chenini oasis extends along the coast of the Gulf of Gabes (latitude 33°53 north; longitude 10°12) in the southeast region of the country. This oasis covers an area of 165 ha and is part of the coastal oasis of southern Tunisia. The village of Chenini and its oasis is located west of Gabes city. The PG used in this study was obtained from the reaction between natural phosphate rock (Gafsa, Tunisia) and sulfuric acid to produce phosphoric acid.

The soils of the Gabes oasis are finely sandy on the surface to finely sandy–silty in depth. In addition, they are low in organic matter (<2%) and characterized by 2 fundamental constituents: gypsum (20–30%) and limestone (5–20%). The oasis soils are gypsum and limestone according to the WRB classification and they can be classified as gypsum isolates. On the surface, several meters of limestone gypsum sand form a layer of crusted gypsum [27], and the pH of oasis soil was 7.22–8.68. Generally, soils in arid and semi-arid regions in the country's south are characterized by a coarse, sand-dominated texture and a low stock of organic carbon, reflecting a strong climate influence. The experiment was undertaken at the experimental station of the Arid Regions Institute of Medenine located in Chenini-Gabes with a surface of 810 m^2 (27 m wide and 30 m long).

2.2. Preparation of the Experimental Plot and Application of the Amendments

The selected experimental plot underwent mechanical weeding, deep tillage, and grading. The plot was then subdivided into 15 elementary plots of 24 m^2 each (2 m wide and 12 m long). The amendment materials used for our test were sheep manure and phosphogypsum from the Gabes chemical group. Finally, 5 3-replicate randomized treatments were performed:

- Three elementary plots were left as untreated soil (C).
- Three elementary plots were initial soil amended with manure (SI + M) at a dose of M = 90 kg/24 m^2 (37.5 t/ha).
- Three elementary plots were initial soil amended with phosphogypsum (SI + PG1) at a dose of phosphogypsum PG1 = 60 kg/24 m^2 (12.5 t/ha).
- Three elementary plots were initial soil amended with phosphogypsum (SI + PG2) at a dose of phosphogypsum PG2 = 90 kg/24 m^2 (25 t/ha).
- Three elementary plots were initial soil amended with phosphogypsum (SI + PG3) at a dose of phosphogypsum PG3 = 120 kg/24 m^2 (50 t/ha).
- The mixing of the soil with the added materials was undertaken homogeneously.

2.3. Agronomic Test Scenario

Three crops (jute mallow, turnip, and oat) were planted sequentially (without a soil rest period) and repeated twice (1st and 2nd year) throughout the study period. The crops adopted in this trial were grown under conditions similar to those of the farms in the region. Irrigation was carried out according to the needs of the plant. The seedlings were made with 40 g of jute mallow seed in each elementary plot. The harvest of the jute mallow was undertaken in August, then manual weeding was undertaken before the turnip experiment. A new seedbed was prepared with superficial tillage of the first 20 cm in early September. A total of 13 g of turnip seeds were planted in each elementary plot. After the harvesting season of turnip, manual weeding was undertaken for all experimental units to eliminate any weeds. A new seedbed preparation with superficial tillage of the first 20 cm of the experimental units was undertaken at the beginning of January. The sowing of oats was performed at the end of January with 300 g of oat seeds in each elementary plot.

2.4. Agronomic Analysis (Yield, Germination Rate (GR), and Cd Levels in Plants)

The yield for each elementary plot was determined by simply weighing the total quantity harvested (kg/24 m^2). The germination test was completed using pots, where each pot was filled with a representative soil sample of each experimental unit (3 replicates). A total of 20 seeds from each crop were sown in each pot and the GR was calculated as follows:

$$[GR] = \left(\frac{\text{Number of germinated seeds}}{20}\right) * 100$$

To determine the amount of Cd accumulated in the plants, the samples were reduced to powder and 1 g was heated at 450 °C in the oven for 2 h. After cooling for 20 min, the samples were filtered using 0.2 µm filters supplemented by ultra-pure water. Finally, each sample preparation was repeated in triplicate and the Cd value was measured using atomic absorption spectrophotometry.

Radioactivity Analysis (Uranium (U-238), Radium (Ra-226))

Soil samples from (C) and others from PG-amended plots at dose 3 (SI + PG3) were sampled to measure their radioactivity, which consisted of 3 replicates at the following depths: 0–10 cm, 10–20 cm, 20–40 cm, 40–60 cm, and 60–80 cm. These samples were collected at the beginning of the experiment, just after the PG was applied. On the other hand, 2 samples of PG used for the amendment were taken to measure its radioactivity.

A U-238 analysis was performed using alpha spectrometry, where 0.5 mL of U-232 trace was added to 0.5 g of soil sample. Then, 0.2 mL of nitric acid (HNO_3) and 0.6 mL of chlorodric acid (HCl) were added. After 1 hour, the sample was placed in the oven at 180 °C for 90 min, then filtered and followed by 24 h of evaporation and agitation. During this step, H_2O, 1 mL of Fe^{3+} and 1 mL of hydrazoic acid (HN_3) were added to change the color and the sample's pH, which must be between 8 and 9, was measured. Next, the sample was placed to cool in the open air, centrifuged for precipitation for 10 min, and then exposed to light for 2 h. After that, to remove Ra and lead (Pb), 10 mL of HNO_3 (8 mol) and 5 mL of tributyl phosphate (TBP) were added. The sample was then shaken by an agitator for 10 min. After stirring, the upper part was removed, and this step was repeated 3 times to get rid of Rd and Pb. The next step was the elimination of thorium (Th) by adding 20 mL of xylene, 15 mL of HCl (1.5 M), agitating for 10 min, and finally, removing the bottom part (3 repetitions).

The final step before the U-238 activity measurement consisted of adding 15 mL of H_2O to the sample and stirring for 10 min. The sample was then placed in a coded spade and evaporated, and 0.5 mL of sulfuric acid (H_2SO_4) and 5 mL of H_2O were added. Next, the sample's code was noted on a disc, plugged with the electrodes, and 2 drops of TIMOL were added. The pH value should be equal to 2; if not, it should be adjusted using H_2SO_4. The voltage must be equal to 1.2 and the sample must remain for 1 h to be prepared. Finally, the disk was dried and subjected to alpha spectrometry to measure U-238 activity.

Ra-226 was measured using gamma spectrometry, which allows the determination of the mass activity (or volume) of gamma-emitting radio elements in the samples. The gamma spectrometry chain includes high purity, 80% efficiency, a coaxial type P (HPGe) germanium detector mounted in a vertical cryostat, a multi-channel analyzer comprising 8192 channels, a lead castle, and a digital acquisition system.

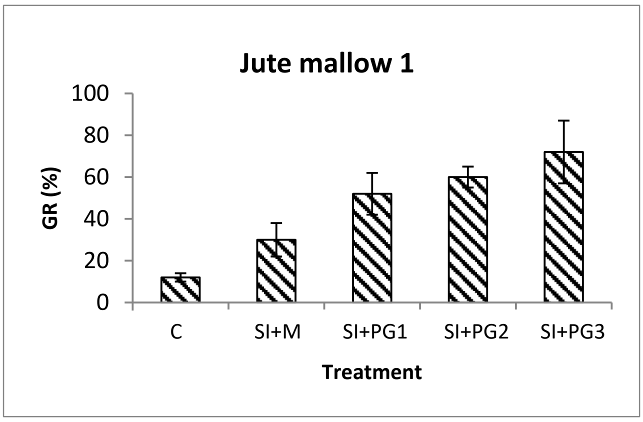
2.5. Statistical Analysis

The statistical analysis was based on the analysis of the 3-factor variance (applied treatment, soil depth, and date of collection) on the physical–chemical parameters of the soil. The statistical analyses were undertaken using SPSS statistics software 21.0 and the statistical test used was ANOVA with HSD Tukey and a significance threshold of 5%.

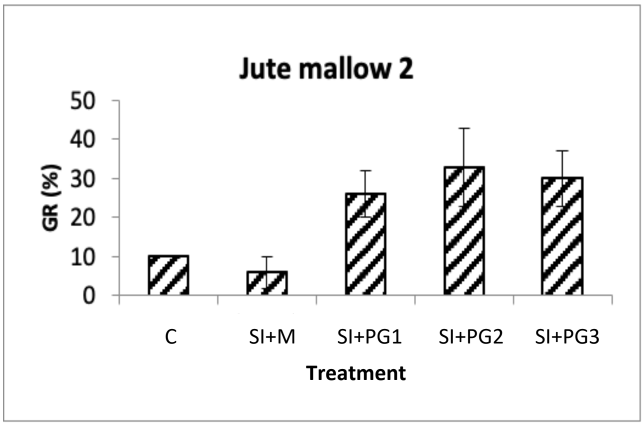
3. Results and Discussion

3.1. Effect of Organic Amendment and PG on Germination Rate (GR)

A germination test was carried out to determine the GR for jute mallow, turnip, and oat throughout the experiment, with two replicates for each crop. The results obtained are presented below in Figure 1a,b, Figure 2a,b and Figure 3a,b.

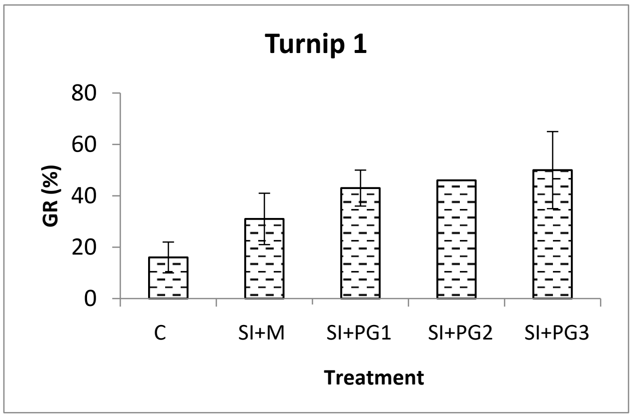


(**a**) Jute mallow plantation in the first year.

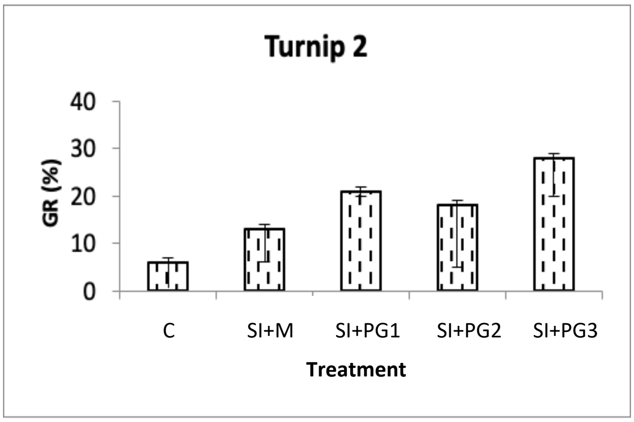


(**b**) Jute mallow plantation in the second year.

Figure 1. (**a**,**b**): Effect of organic amendments and PG on GR of jute mallow during two consecutive years.

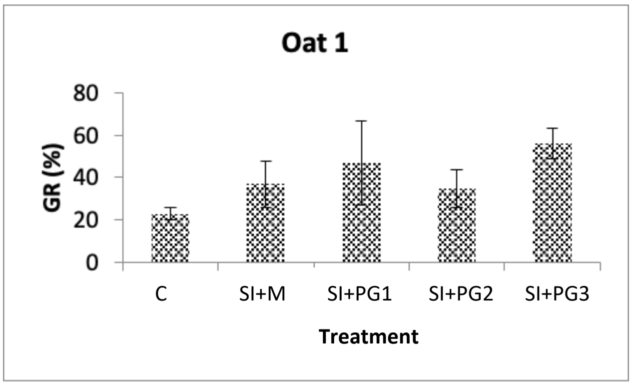


(**a**) Turnip plantation in the first year.

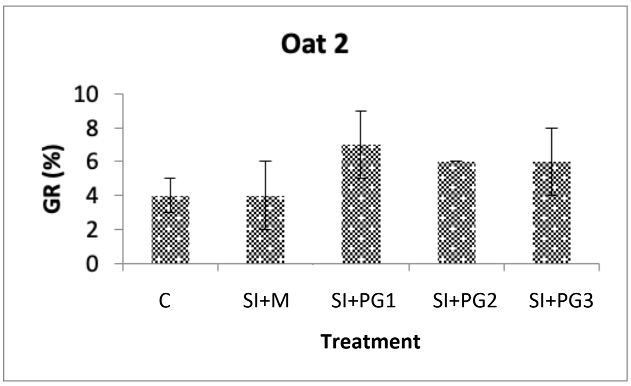


(**b**) Turnip plantation in the second year.

Figure 2. (**a**,**b**): Effect of organic amendments and PG on GR of turnip during two consecutive years.



(**a**) Oat plantation in the first year.



(**b**) Oat plantation in the second year.

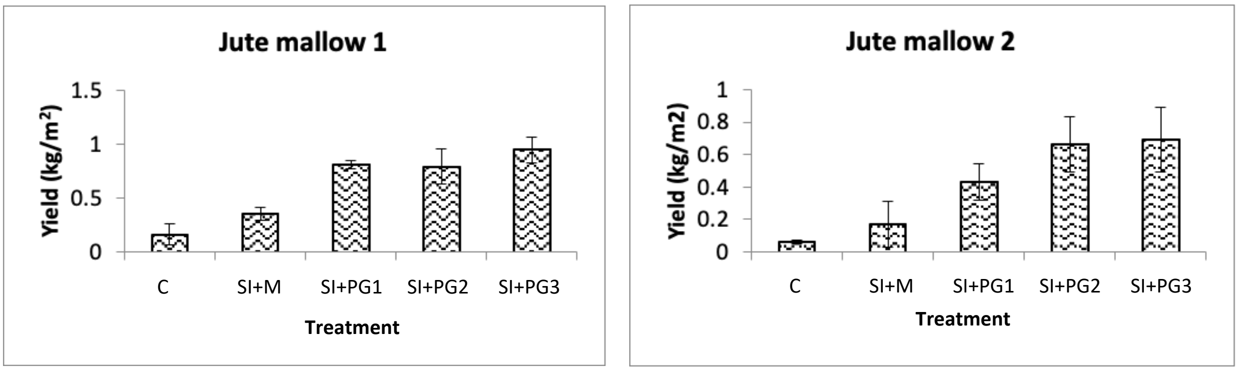
Figure 3. (**a**,**b**): Effect of organic amendments and PG on GR of oat during two consecutive years.

A highly significant difference was observed between the treatments for jute mallow 1 ($p < 0.0001$). For turnip 1, oat 1, and jute mallow 2, the difference was significant ($p < 0.05$), while turnip 2 and oat 2 showed results with a non-significant difference ($p > 0.05$).

For all crops and during both replicates, the C had the lowest GR except jute mallow 2, where (SI + M) had the lowest GR with [GR] = 6% compared to C ([GR] = 10%). Soils amended with PG at different doses had the highest GR during both replicates and for all three crops. Indeed, seed germination is a process that is closely related to the moisture of the soil, a well-determined temperature, and air circulation. The porosity of the C at the surface layer presented a seed bed equal to 52%, while the porosities of (SI + M), (SI + PG1), (SI + PG2), and (SI + PG3) are, respectively, 59%, 59%, 61%, and 63%. The humidity of the C at the same layer was lower than that of the (SI + M), (SI + PG1), (SI + PG2), and (SI + PG3), which may explain the variations in the observed GR. Other causes for the seed germination could be the humic acid in manure and the PG with an acidic pH (2–3). In a previous research study it was proven that PG improved GR [28], which explains the effect of different doses on this parameter. Figures 1a, 2a and 3a show that the highest GR was recorded for PG dose 3. Figures 1b, 2b and 3b show variations in the best GR. The calculation of the average GR for each plant shows that the GRs of the jute mallow are 11%, 18%, 39%, 46.5%, and 51%, respectively, for (C), (SI + M), (SI + PG1), (SI + PG2), and (SI + PG3); for turnip, the GRs are 11%, 22%, 32%, 32%, and 39%; and for oat GRs are 13.5%, 20.5%, 27%, 20%, and 31%. From these results, it can be concluded that dose 3 of PG (50 t/ha) still provides the best GR.

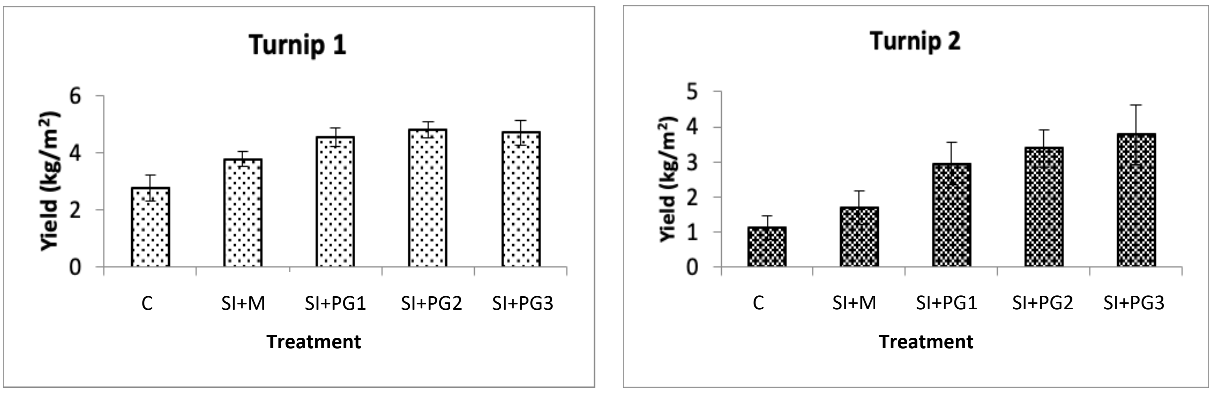
3.2. Effect of Organic Amendments and PG on Yield

The results of the yields according to the treatments applied are presented in Figure 4a,b, Figure 5a,b and Figure 6a,b below.



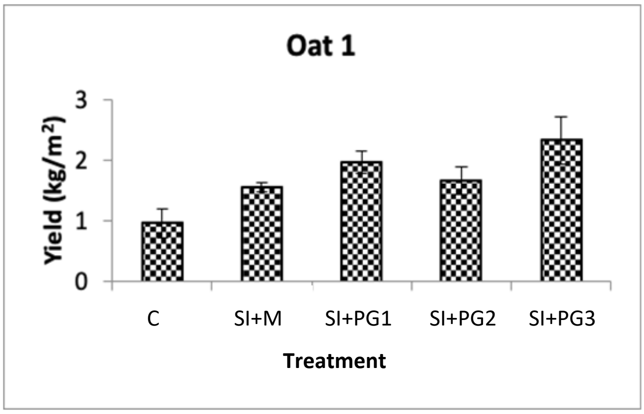
(**a**) Jute mallow yield in the first year. (**b**) Jute mallow yield in the second year.

Figure 4. (**a**,**b**): Effect of organic amendments and PG on jute mallow yield during two consecutive years.

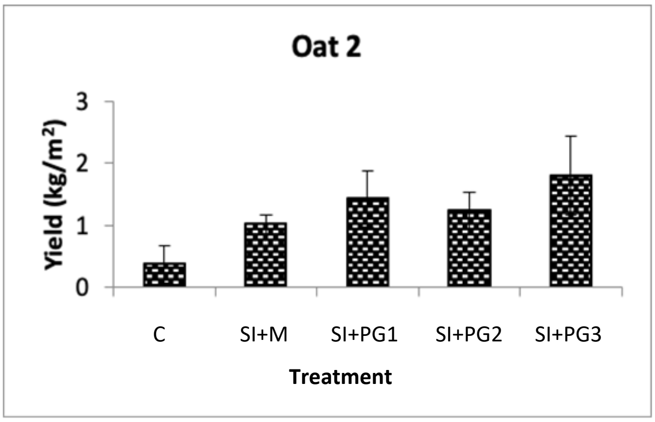


(**a**) Turnip yield in the first year. (**b**) Turnip yield in the second year.

Figure 5. (**a**,**b**): Effect of organic amendments and PG on turnip yield during two consecutive years.



(**a**) Oat yield in the first year.



(**b**) Oat yield in the second year.

Figure 6. (**a**,**b**): Effect of organic amendments and PG on oat yield during two consecutive years.

A highly significant difference is observed between the treatments for coret1 ($p < 0.0001$). For turnip 1, oat 1, jute mallow 2, and turnip 2, the difference is highly significant ($p < 0.001$). Oat 2 showed a significant difference ($p < 0.05$).

For all crops and during both replicates, the C showed the lowest yields of 0.16 ± 0.01 kg/m^2, 2.75 ± 0.46 kg/m^2, 0.96 ± 0.24 kg/m^2, 0.06 ± 0.01 kg/m^2, 1.12 ± 0.33 kg/m^2, and 0.37 ± 0.3 kg/m^2, respectively, for jute mallow 1, turnip 1, oat 1, jute mallow 2, turnip 2, and oat 2.

By comparing the C yield for the first and second repetitions, the results show that the yield of each crop decreases with time, from 0.16 ± 0.01 to 0.06 ± 0.01 kg/m^2 for jute mallow, from 2.75 ± 0.46 to 1.12 ± 0.33 kg/m^2 for turnip, and from 0.96 ± 0.24 to 0.37 ± 0.3 kg/m^2 for oat. This can be explained as C, as it has not received any amendments, weakens over time and, consequently, its productivity decreases while knowing that a phosphorus deficiency results in stunted growth, reduced cell and leaf growth, and limited respiration and photosynthesis.

It is well known that vegetative plant growth positively correlates with nutrient uptake, particularly nitrogen [29]. Inputs of organic amendments are necessary to maintain soil carbon content and agricultural production at an acceptable level. Adding organic waste, such as manure, increases crop yield and quality. Soil amended with manure and PG at different doses had a higher GR than the control during replicates for the three crops. The yield of plants depends not only on the plant performance, but also on the soil parameters and properties. The results obtained during the study showed that the latter decreased the density of the soil and increased its total porosity, hydraulic conductivity, and water availability. It also promoted better organic matter content and nutrients (N, P, and K) than the control. This effect of this amendment is a good explanation for the increase in the obtained yield for the three crops compared with the control. Indeed, phosphorus is classified with nitrogen and potassium as a fundamental nutrient for plants and animals. Phosphorus promotes root development and plays an essential role in fertilization, flowering, and fruit quality [30]. Phosphorus is important, especially if all parameters and nutrients are present [31]. For example, a study in sub-Saharan Africa on phosphate fertilization, including natural rock phosphates and soluble phosphates, showed an improvement of 28 to 72% in groundnut production [32]. The presence and availability of nutrients, mainly N, P and K is crucial for plants [33].

PG, due to its clay content (22.75%), changed the size of the initial soil particles while increasing the clay fraction. PG also decreased its density, resulting in an improvement of the total porosity. The latter reaches 63% at the dose 50 t/ha compared with 52% for the initial soil. In addition, PG also has increased hydraulic conductivity values, resulting in good salt leaching. The different doses of PG improved the moisture of the amended soils compared with the control soil and contributed to a decrease in soil pH. PG amendment has improved the soil's phosphorus and potassium contents. These changes explain the highest yield obtained for the different doses applied for the three crops experiments. In this context, a study was carried out on soil cultivated in barley and amended by three doses of PG (0, 20, and 40 t/ha) for three years. The study's results show that the yield of barley increased by 47% compared with the control [34].

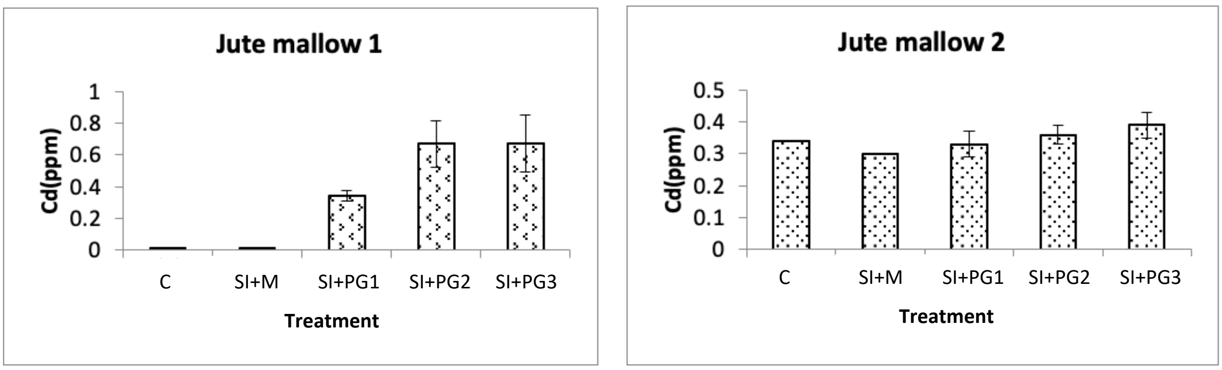
Moreover, 55.17% of the increase in potato yield was recorded using PG mixed with compost [35]. Regardless of the crop type, PG has a positive effect on yield, as reported in the literature; for example, the dry weight of canola plants increased by 66.8% compared to its weight in the control [36]. For alfalfa (*Medicago sativa*), the increase in PG rate promotes an increase in the dry shoot weight, with an increase in calcium and sulfate contents in soil (0–40 cm) [37].

In acidic soils, applying PG may be useful to manage the adverse effects of the subsurface soil. This application causes deep root growth and plants effectively absorb water and nutrients [38]. Improving the yield of a plant is relative to improving the performances of its organs, so PG promotes higher production while increasing vigor, number of leaves, etc., and in this context, it has been noted that PG application improves seed growth and yield of several species and shoot dry weight for alfalfa (*Medicago sativa*) [39].

In the sodium saline soils of northeastern China, some researchers [40] added three different quantities of PG (15, 30, and 45 t/ha) to rice fields and obtained a large production at 30 t/ha. The increase concerns the individual weight of the kernels, their number of spikelets (m^2), number of panicles (m^2), percentage of spikelets filled, and weight of 1000 kernels. A 37.7 % increase in post-treatment seed yield with PG (2100 kg/ha) was reported [12]. In Brazil, it has been reported that the application of 12 t/ha of PG improved corn (*Zea mays*) and wheat (*Triticum aestivum*) yields [41]. Figure 4a,b, Figure 5a,b and Figure 6a,b show that the highest yields were recorded for PG dose 3 (50 t/ha) except turnip 1, where the yield corresponding to dose 2 (4.8 ± 0.3 kg/m^2) was slightly higher than that corresponding to dose 3 (4.7 ± 0.42 kg/m^2). The (SI + PG3) yields are 0.95 ± 0.12 kg/m^2, 4.7 ± 0.42 kg/m^2, 2.33 ± 0.39 kg/m^2, 0.69 ± 0.2 kg/m^2, 3.77 ± 0.85 kg/m^2, and 1.8 ± 0.63 kg/m^2, respectively, for jute mallow 1, turnip 1, oat 1, jute mallow 2, turnip 2, and oat 2. These results are consistent with previous research [42]. The study of the effect of PG amendment on plant growth showed that the addition of PG at a rate of 5 and 10 % led to a significant increase in plants, and that the addition of 5, 10, and 20 % of PG led to a significant improvement in plant length at an order of 31, 68, 31.6, and 37.9%, respectively. In addition, a significant improvement in root dry weight was recorded when PG was added at 10 and 20%.

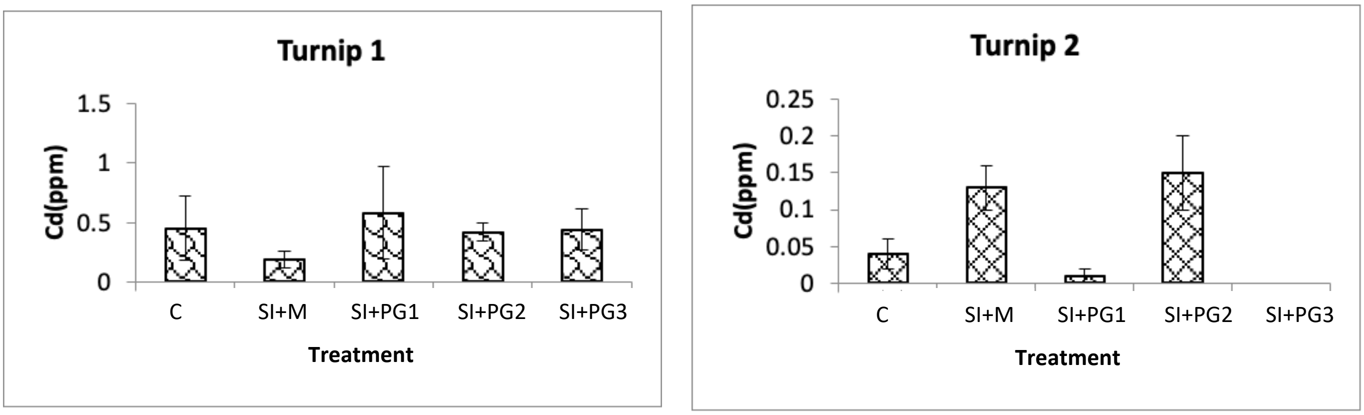
3.3. Effect of Organic Amendment and PG on Cd Content in Plants

The Cd content in plants after each treatment was applied are presented in Figure 7a,b, Figure 8a,b and Figure 9a,b below.



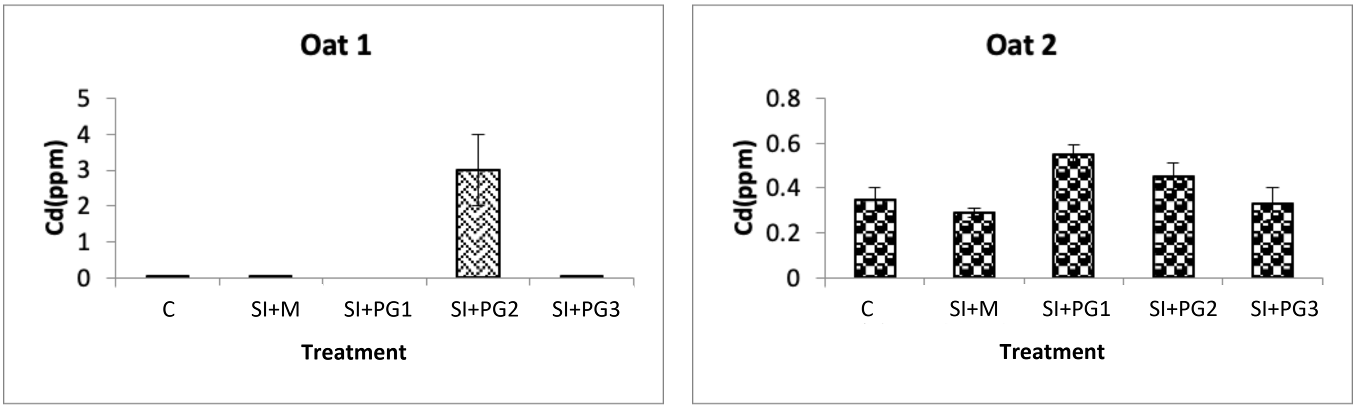
(**a**) Jute mallow Cd content in the first year. (**b**) Jute mallow Cd content in the second year.

Figure 7. (**a**,**b**): Effect of organic amendment and PG on Cd content in jute mallow during two consecutive years.



(**a**) Turnip Cd content in the first year. (**b**) Turnip Cd content in the second year.

Figure 8. (**a**,**b**): Effect of organic amendment and PG on Cd content in turnip during two consecutive years.



(**a**) Oat Cd content in the first year. (**b**) Oat Cd content in the second year.

Figure 9. (**a**,**b**): Effect of organic amendment and PG on Cd content in oat during two consecutive years.

A significant difference was observed between the treatments for jute mallow 1 and turnip 1 ($p < 0.005$). For turnip 1, the difference was highly significant ($p < 0.001$). On the other hand, treatments given to jute mallow 2, turnip 2, and oat 2 showed a non-significant difference ($p < 0.05$).

Cd levels vary depending on the treatments applied. However, all values are below the plant toxicity threshold (7 ppm). These results agree with the literature [43], where authors reported that Cd levels in the amended soil and plant remained below EU standards for inputs of 20 to 25 t of PG/ha every two to three years since 1978. Previous work [44] has shown that metals are poorly soluble in calcareous soils with a pH close to eight, so it can be assumed that metal transfer from the soil to the plant is low. Previous researchers [45] studied the effects of PG on the concentration of trace elements in soil and vegetation. There is virtually no accumulation of trace elements except strontium for an applied PG dose of 60 t/ha, whereas for plants, these elements accumulate more. In agriculture, potentially toxic elements (PTEs) appear to be the most dangerous elements present in PG for human health. It has been reported that there are a relative lack of health risks related to consuming vegetables/fruit grown in PG-modified soils [46].

In addition, some researchers [36] used PG alone or mixed with compost (1:1 mix) at 10 or 20 g/kg of dry soil to mobilize heavy metals in contaminated soil, and showed that this practice improved canola growth and primarily immobilized PTEs for GP alone. In Wiślinka (northern Poland), PTEs were analyzed for some cultures in PG on the surface of waste piles. High concentrations were recorded compared with the control zone [47]. Although contrary to our results, in previous research [43] it has been noted that levels of

Cd, zinc (Zn), and chromium (Cr) in different parts of plants increased in proportion to the concentration of PG in soils. Apart from Cd, all analyzed elements in the tomato fruit were considered to be below the maximum permitted concentration.

3.4. Effect of PG Amendment on Radioactive Parameters

The values in Table 1 show that the average R-226 value is 214.45 and the average U-238 value is 73.05. These results are consistent with previous research [39], where the authors reported that PG contained heavy metals and radioactive nuclides. In our case, both PGs contained more R-226 than U-238, although this confirms that much of R-226 remains in PG while much of U-238 remains in phosphoric acid. The two R-226 values recorded in the table are less than 370 Bq/Kg (the advertised value by the EPA), so according to the EPA, this PG can be used as an amendment.

Table 1. Comparison between PG activity (uncertainty activity) (Bq/kg) from this study (PG Tunisia) and other PG sources [47].

Samples	Ra-226	U-238
PG (Tunisia)	211.8 ± 5.5	70.5 ± 17.3
PG (Tunisia)	217.1 ± 7.9	75.6 ± 30.5
PG (Morocco)	620	140
PG (Brazil)	744	49
PG (USA)	1140	130

Natural phosphates that are used to produce phosphoric acid are naturally radioactive. Therefore, radioactive elements can be found in PG. The radioactivity of PG is mainly due to the radium (Ra) content, so most Ra is found in PG while most U-238 remains in phosphoric acid [37]. Depending on the quality of the rock source, PG may contain up to 60 times the levels normally found before treatment [48]. A large variation in PG of Ra-226 activity concentrations (52–3219 $Bq.kg^{-1}$) was reported in the literature, which can be attributed to the nature of the phosphate rock and the sampling depth [46–48]. Ra-226 produces radon gas (Rn-222), which has a short half-life of 3.8 days, an intense radiation capacity, and causes damage to internal organs. Since 1992, the EPA has prohibited using any PG with an Ra-226 content exceeding 370 $Bq.kg^{-1}$. According to previous research [33,46], the Tunisian PG has low natural radionuclides compared to other countries (Spain, Brazil, India, etc.), and the results are presented in Table 1. This suggests that the use of PG at adequate concentrations can improve crop growth and yield of soils affected by salinization.

In this context, a study was conducted in Spain to assess the cumulative effect of PG soil amendment over three decades [43]. They observed a significant increase ($p < 0.05$) in Ra-226 in soils receiving 20–30 t/ha PG every two to three years compared with C, but the U-238 and Ra-226 concentrations were below the detection limit.

In samples from C (not amended by PG), Table 2 shows that the radioactivity exists but is still lower than the limit fixed by the EPA. The presence of deep phosphate ores in the region can explain the origin of this natural radioactivity. All U-238 values were higher than Ra-226. Similarly, the Table 3 shows acceptable levels of radioactivity, and all U-238 values were higher than Ra-226 for the different soil layers.

The highest value of Ra-226 was recorded for depths 0–10 cm, which was explained by the spreading of the amendment in the surface layer. For Ra-226, an increase was observed in the surface layers compared with the samples left as a control, while it remains comparable in the deep layers. For U-238, the increase was noticed for all depths.

Table 2. Untreated soil activity (uncertainty activity) (Bq/kg).

Samples	Ra-226	U-238
01 (0–10 cm)	10.5 ± 1.4	28 ± 6
02 (10–20 cm)	10.2 ± 1.4	37.6 ± 7.2
03 (20–40 cm)	9.7 ± 1.4	40.3 ± 9
04 (40–60 cm)	8.6 ± 1.3	26.7 ± 5.4
05 (60–80 cm)	7.9 ± 1.4	50.2 ± 16.4

Table 3. Phosphogypsum-amended soil activity (uncertainty activity) (Bq/kg).

Samples	Ra-226	U-238
06 (0–10 cm)	13.4 ± 1.5	53 ± 15.6
07 (10–20 cm)	9.8 ± 1.5	39.2 ± 11.0
08 (20–40 cm)	8 ± 1.3	67.8 ± 17.1
09 (40–60 cm)	7.4 ± 1.3	62.9 ± 18.9
10 (60–80 cm)	8.6 ± 1.4	68.1 ± 18.5

The activity concentration values of Ra-226 and U-235 for phosphate amendments with high concentrations were calculated and illustrated in Figure 10, which shows a summary of the measurements for the activity concentrations (Bq/kg) and natural radioactivity due to U-238 and Ra-226 in PG amendment. It can be concluded that the mean concentrations of U-238 activity at a depth of 0–20 cm are 32.8 Bq/kg and 46.1 Bq/kg for C and PG3 samples, respectively.

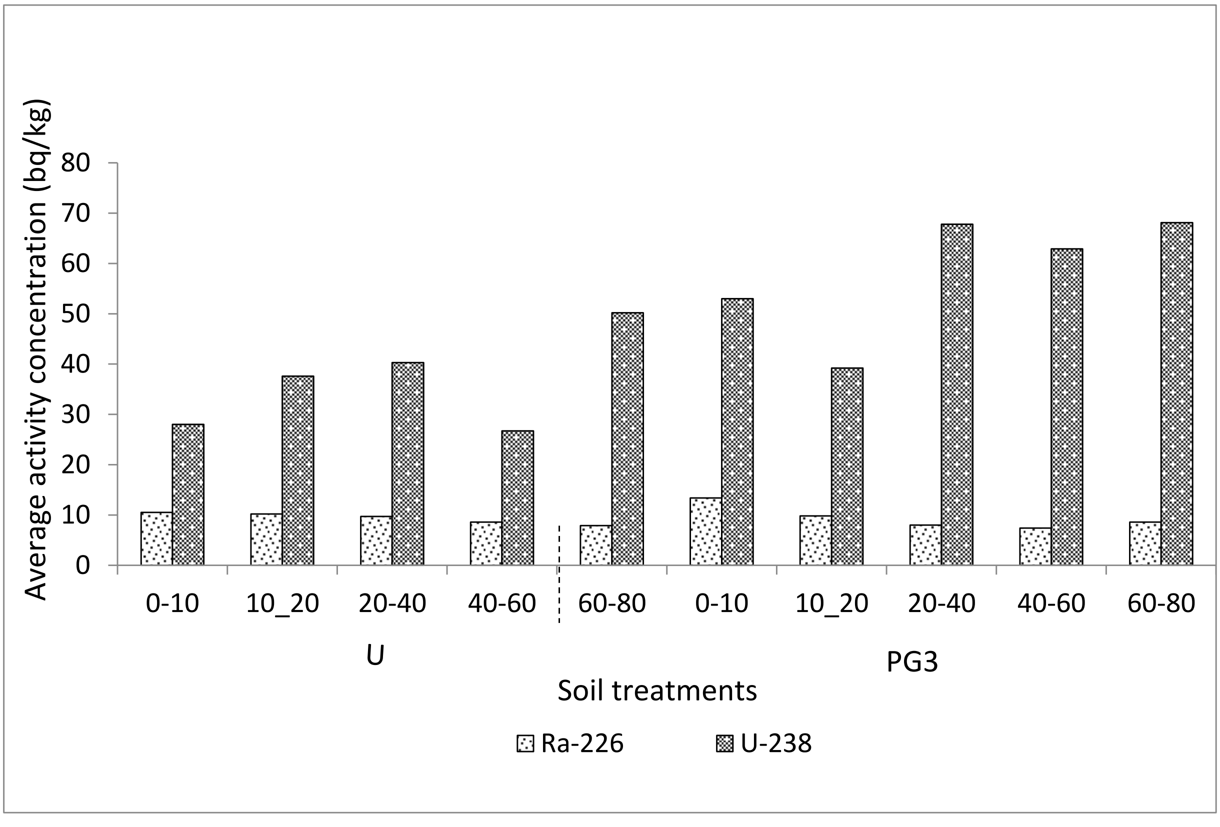


Figure 10. The activity concentration values of Ra-226 and U-235 in soil treatments.

The average activity of Ra-226 was 10.35 Bq/kg and 11.6 Bq/kg, respectively, in C and PG sample 03. It is clear from the results that the activity concentrations of Ra-226 < U-238 in all samples are due to the accumulation of dissolved U-238 and its products as a urinal complex in water during the phosphate company's production process. The activity concentration is not very high because these samples (by-products) are produced by adding sulfur phosphate ore in different wet proportions. The study was conducted on sulfur samples and it was found that it is characterized by a high presence of potassium [49,50]. Indeed, it has been noted that PG and phosphate rock did not present any impact on the radioactivity profile of the soils [51,52]. Another study noted that in northern Kazakhstan, PG is used for spring wheat fertilization and has no negative impact on the environment [39].

4. Conclusions

Organic amendments are of fundamental importance in sustainability for soil fertility and sustainable agricultural production due to their physical, chemical, and biological effects. Their influence on soil properties depends on the quantity and type of material added. PG is a mineral product used worldwide as an amendment in agriculture. This study was carried out in degraded oasis soil to determine the effect of the two amendments on agronomic and radioactive parameters and on the improvement of soil fertility. From an agronomic point of view, the use of PG and manure as an amendment did improve soil properties, and as a result, the germination rate and production were increased. The application of the two amendments did not present any toxicity in terms of Cd. Furthermore, the application of PG did not present any radioactivity above the limit. This experiment lasted for two years; therefore, authors recommend further long-term experiments to study the effect of PG accumulation over at least five years in the environment in terms of radioactivity, Cd content, and effects on soil, plants, and water. In addition, the agronomic impact of PG on different aspects (physiology, plant safety, fruit quality, phenology, etc.), life cycle assessment (LCA), as well as the safety of humans and animals should be evaluated.

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