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Short-Term Growth Response of Young Pine (*Pinus silvestris*) Seedlings to the Different Types of Soil Media Mixture with Phosphogypsum Formulations under Poland Forest Environmental Conditions

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Abstract: The production of phosphoric acid produces "waste heaps" that have not yet been tapped, but which have the character of weak fertilizers and can perhaps be reintroduced into the elemental cycle in the forests. Two variants of mixing with organic ash and with sewage sludge were carried out. One-year-old pine seedlings (*Pinus sylvestris* L.) from the Trzebież forest district (northern Poland) were planted in pots with soil that also came from the same field. Preparations containing phosphogypsum were applied topically to the soil in four doses (1, 2, 3 and 5 t/ha). The trial, which lasted one growing season, was conducted in four replicates. At the end of the trial, the height of the above-ground parts and root length, needle and root area, root neck diameter and photosynthetic performance were measured. The phosphogypsum-based preparations used showed no harmful (toxic) effects on the potted pine seedlings during the six-month trial period. The loosely prepared preparation made from a mixture of phosphogypsum and organic ash began to have a positive effect on the development of the seedlings' root system, and it was also easier to mix with the soil surface than phosphogypsum with sewage sludge, which also contained a sticky form. The photosynthetic performance of one-year-old pine seedlings decreased after one growing season following the application of phosphogypsum preparations and most of the growth parameters tested did not differ from the control, so observations over a longer period (at least two to three growing seasons) are required. However, dosages of 1 and 2 t/ha seem to be the most promising, and these lower dosages are more economical to manage in nurseries or plantations, especially on poor sites. Formulations should be tested for heavy metals and their effects on seedling development. Testing should also be continued to monitor changes in the microbiome.

Keywords: phosphogypsum; sewage sludge; Scots pine; seedlings; soil revitalization

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Citation: Oszako, T.; Pasławski, T.; Szulc, W.; Rutkowska, B.; Rutkiewicz, A.; Kukina, O.; Bakier, S.; Borowik, P. Short-Term Growth Response of Young Pine (*Pinus silvestris*) Seedlings to the Different Types of Soil Media Mixture with Phosphogypsum Formulations under Poland Forest Environmental Conditions. *Forests* **2023**, *14*, 518. https://doi.org/10.3390/f14030518

Academic Editors: Cate Macinnis-Ng, Chao Wang, Fan Zhang and Wei Liu

Received: 27 January 2023
Revised: 16 February 2023
Accepted: 2 March 2023
Published: 7 March 2023

1. Introduction

Phosphogypsum is considered a waste product produced in the manufacture of extractable phosphoric acid, which is used, among other things, in the production of phosphate fertilizers [1]. For one tonne of orthophosphoric acid produced, 3.5 to 4.5 tonnes of moist phosphogypsum [2] are obtained. Phosphogypsum as a by-product of fertilizer production requires an attempt to solve the problem of its storage and recycling. However, since it cannot be used in agriculture or even forestry before its category (waste code) is changed, our attempt was limited to potted plants. This research step is necessary to proceed with broader experiments in forests. However, it is worth playing a game because this “waste” contains calcium sulphate dihydrate (the basic ingredient of phosphogypsum), which has no negative impact on the environment unless it is mixed with heavy metals, lanthanides or radionuclides [3]. The literature indicates that contamination of phosphogypsum with heavy metals and radioactive elements applies primarily to waste from the processing of phosphorites and only to a lesser extent to waste from apatites [4]. Apatites have a much lower content of such pollutants compared to phosphorites [2]. Phosphogypsum produced from apatite raw material can be considered as waste, practically free from this type of compounds, which should be tried in forest plantations in the future.

The management of phosphogypsum is difficult due to the above-mentioned impurities it contains; its treatment is energy-intensive, and significant amounts of wastewater are produced, so the main method of managing phosphogypsum is storage, although this is highly controversial due to its environmental impact. Indeed, numerous expert studies have shown that phosphogypsum stored in stockpiles can pose a real threat to the balance of the soil and water environment, mainly due to insufficient protection of the stockpiles [5]. Investigations of the phosphogypsum dump in Wiślinka (northern Poland) show that leachates from the dumps have a very low pH (2–4) and elevated concentrations of phosphates, fluorides, sulphates and nitrates, heavy metals/metalloids (mainly Cd) and radionuclides. Pollutants from the phosphogypsum landfill in Wiślinka entering groundwater may contribute to changes in local physico-chemical conditions of surface waters and also pose a risk to groundwater quality. Phosphogypsum contains heavy metals/metalloids in its composition, and leachates from the landfill also pose a significant risk to the quality of the soil environment. Chemical analyses of soil samples from areas adjacent to the landfill have shown that contaminants contained in the waste migrate from the landfill to the adjacent areas [6]. Another risk is the accumulation of heavy metals/metalloids in plants, which can lead to them entering the food chain. As for the risk from radioactive elements in phosphogypsum, no real risk to the environment near the landfill has been demonstrated.

The heaps heaped up for the storage of phosphogypsum (PG) increase in volume every year and look like ‘white mountains’ because of their colour. According to estimates from 2009, the amount of phosphogypsum produced worldwide is 100 to 280 million Mg per year [6]. In 2006, phosphogypsum plants worldwide generated about 5 trillion tonnes of waste, of which 70–90% was sent to landfills [7]. In Poland, phosphogypsum waste is generated near Szczecin (Police), Gdańsk (Wiślinka) and Silesia (Wizów), among others. The disposal of phosphogypsum is energy-intensive and generates large amounts of wastewater. Therefore, it is necessary to look for alternatives for the management of this waste [2]. To date, its use in construction, road building or agriculture has been studied [8].

Currently, we would like to test whether phosphogypsum can be used to improve the habitat of pines in a fresh boreal forest. Phosphate fertilizers based on phosphogypsum are not used in Polish agriculture because phosphogypsum contains heavy metals but they should not have negative effects when used in forestry. Therefore, it was hypothesized that this could be a good way to provide pine seedlings with sulphur, calcium and phosphorus in their first years of life. To date, no similar studies have been conducted in Poland. Before conducting comprehensive field studies, the addition of phosphogypsum formulations to the soil is currently being investigated in a pot trial, as they are safer for the environment. The main objective of the present study is to investigate the effects of phosphogypsum formulations on annual pines (*P. sylvestris*), including seedling growth parameters and photosynthetic efficiency. We hypothesize that the phosphogypsum-based preparations studied in the variants—mixtures of phosphogypsum with organic ash and mixtures of phosphogypsum with sewage sludge—could be used as soil conditioners to improve seedling growth in forestry. Furthermore, we presume that the work will emphasize the phosphogypsum formulation’s effect on the young potted seedlings under outdoor conditions.

2. Materials and Methods

2.1. Plant Material and Soil

One-year-old Scots pine seedlings (*P. sylvestris*), also prepared by a local forest nursery, were planted in the soil of a forest growing area in the neighbouring Trzebiez Forest District, Division 598h, Tytania Forest District, Trzebiez Forest District, RDSF Szczecin, and preparations were added to the soil at different doses (per hectare) to observe their effects on plant growth and development, including photosynthetic efficiency. In the control (C), two formulations were used for the study: a phosphogypsum/ash mixture (A) and a phosphogypsum/sludge mixture (S) in a ratio ensuring a soil pH recommended for pine culture (4–4.5). The soil used for planting pine seedlings came from a not very nutrient-rich, fresh coniferous forest where pines are commonly planted in Tatynia forestry (Trzebież forestry district). It was assumed that, in case of positive results, further field studies should be conducted on the use of these previously unused "wastes" in forests, especially in fresh coniferous forests, which account for about 20% of the area of state forests.

The pine seedlings were also obtained from Tatynia Forest Nursery and planted in 18 cm × 18 cm pots, in 9 variants and 4 replicates, using the control sample as a reference. The trial was conducted in the following variants: control; calcium sulphate with wood ash and calcium sulphate with sewage sludge. For both formulations 4 dosages were used: 1 t/ha, 2 t/ha, 3 t/ha and 5 t/ha. The dolomite base doses of 1 to 2 t/ha used for liming forest soils were used as dosing criteria, which were also increased to 3 and 5 t/ha to observe whether there would be further benefits for the pine seedlings or rather phytotoxicity of the preparations. The idea was to select the most beneficial dosages of the preparations for further field trials as a result of the tests. Four seedlings of each treatment were used in the experiment.

Seedlings from the nursery and soil were taken on 24 April 2021 and planted in 36 pots, one per pot, on 29 April 2021. Each pot was placed in a sunny, open location to create favourable growing conditions. The trial was fenced with a metal grid to protect it from damage by forest animals. On 23 May 2021, both formulations were applied to the soil surface at the following amounts: 3.24 g; 6.48 g; 9.72 g; and 16.2 g, to simulate forest conditions and future application by surface spreading. A small amount of soil was sprinkled with the formulations to prevent wind dispersal. They were maintained daily and watered as needed. In particular, the plants of the control variant were observed, their good appearance indicating normal environmental conditions conducive to plant growth. In this way, any abnormalities in the treated plants, e.g., phytotoxicity of the preparations used, were easily detected.

2.2. Measurements of Growth Parameters

During the 2021 growing season, three measurements (25 April, 19 July and 31 October) of height, diameter at the root collar and length and area of roots and needles (31 October) were taken [9].

All pine seedlings were removed from their pots and freed from soil residues on 31 October 2021. Root length was measured with a tape measure graduated to 1 mm [10].

After measuring and photographing on graph paper, one seedling each was placed in a paper bag and weighed. The plants in the paper bags were dried at room temperature for 3 weeks and then dried again at 105 °C for about 1.5 h until a constant weight was reached.

The seedlings were individually spread out on graph paper to measure the needle and root area. Each cutting was photographed. From the photos, the area was determined using the CSS Video FrameGrabber software.

2.3. Measurement of Photosynthetic Performance

On 7 July 2021, ten individual needles were taken from each seedling, two of which were placed in special clamps and left in the dark for more than 20 min to silence the photosynthetic processes. Subsequently, 360 measurements were taken with a mobile PEA fluorimeter (10 measurements on each seedling), which were transferred to a computer with appropriate software for further analysis.

Soil phosphorus tests were conducted on 8 August 2022; the pots of each experimental variant were cut in half and soil from two depths (0–5 cm and 6–10 cm) was placed in plastic containers. Each container was described and sent to the laboratory of the Warsaw University of Life Sciences for analysis of the total phosphorus content (phosphorus pentoxide) and acidity (pH) of the soil [11,12]. Soil samples were characterized as follows: pH—by potentiometric method after extraction with 1 mol/dm^3 KCl (ISO 10390:2005), available P value by Egner-Riehm method (DL).

Four parameters were included in the analysis and their values were compared with those of the control seedlings.

- Fv/Fm is a normalized ratio formed by dividing the variable fluorescence by the maximum fluorescence. The parameter Fv/Fm describes the maximum yield of the PS II photoperiod. The photosystems PS I and PS II are dye–protein–lipid complexes that determine the course of all photochemical reactions of the light-dependent phase of photosynthesis.
- Another parameter "area" or AM defines the area over the chlorophyll fluorescence induction curve. The value of the parameter AM (SM or Area) is proportional to the size of the electron acceptor pool in PS II. The measurement of AM is of great practical importance, for example in monitoring the penetration of herbicide photosynthesis inhibitors such as diuron (DCMU) into leaves. The unit of AM is bitomilliseconds (bms), i.e., the product of the fluorescence signal measured in bits and the transition time from Fo to Fm expressed in milliseconds. The faster the increase from FL to FM (faster reduction of the acceptor pool in PSII), the smaller the area above the FL induction curve of chlorophyll. When electron transport from the reaction centres to the plastoquinones is blocked (during stress), the value of AM decreases. A parameter similar to AM is its standardized version SM / FM (SM = AM). This parameter also determines the number of unreduced electron acceptors in PSII, but per total content of active chlorophyll in the sample [13,14].
- The time to reach maximum chlorophyll fluorescence FM (from the beginning of the measurement) is determined by the TFM parameter, which is usually 500–800 ms [15]. The TFM measurement is an alternative method to determine the size of the pool of unreduced plastoquinones. This time may be prolonged if the test object has been exposed to stress factors that slow the transport of high-energy electrons from the reaction centres to the plastoquinones [16]. PI (Performance index)—the performance index PS II reflects the efficiency of the photosynthetic process, taking into account all automatically measured parameters.
- However, the best parameter to characterize photosynthetic performance is the total performance index (PI Total), which reflects all the previously mentioned factors and was therefore first compared between the treatments and the control.

2.4. Data Analysis

The collected data were analysed to test the statistical significance of the differences between the experimental variants studied and the trends in the data. Two types of statistical analyses were used in the presented research.

- Analysis of variance (ANOVA) was performed for pairwise multiple comparisons using Tukey's HSD test (honestly significant difference) at $p < 0.05$. For this method comparison between the three main studied treatments (Control—C, Ashes—A, Sewage sludge—S) was performed and in the presented results we indicate, in the presented figures, whether there was found a statistically significant difference and for which compared pair.
- The evolution of the measured variables as a function of the applied dose of the phosphogypsum preparations was analysed with linear regression models. The models with linear and quadratic terms of the dose were trained. The models in which

the regression coefficients were statistically significant at $p < 0.05$ were selected. For this type of analysis, we analysed whether the found trends in data were statistically significant and in the presented results we indicated that significance by plotting the regression line. For these analyses, we have not compared whether there was a significant difference between individual studied levels of the used dose.

Data processing and statistical analysis of the data were performed using SAS 9.4 software (SAS Institute, Cary, NC, USA) via the SAS Enterprise Guide user interface and the SAS/Stat procedures [17] PROC ANOVA and PROC REG.

3. Results

3.1. Measurement of Photosynthetic Performance

The photosynthetic efficiency of the needles of the treated pines (A and S) was lower than that of the control group (C) and these differences were statistically significant. However, the treatments did not differ among themselves in this respect (Figure 1).

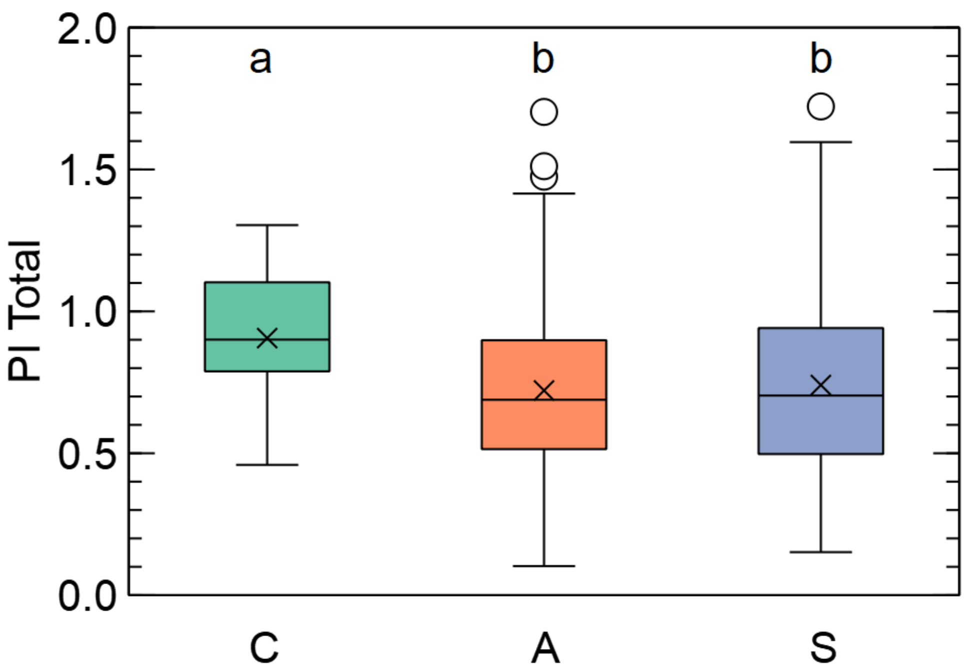

Figure 1. Photosynthetic activity (overall performance index PI total) compared to soil amendments with phosphogypsum mixed with organic ash—A, sewage sludge—S and control—C. The lowercase Latin characters above box plots, if the same, indicate that there is no statistically significant difference between the groups at $p < 0.05$. In the plot, boxes span from 1st to 3rd quantile, with the median indicated by a line, whiskers indicating 1.5 inter-quantile range, the $\times$ symbol mean value, and circles outlier observations.

In particular, for the phosphogypsum–ash mixture (from burned organic material), increasing doses of the preparation (3 and 5 t/ha) resulted in a significant decrease in the photosynthetic efficiency of pine needles. For the phosphogypsum–sludge mixture, the lowest photosynthetic efficiency was observed at a dose of 2 t/ha (Figure 2).

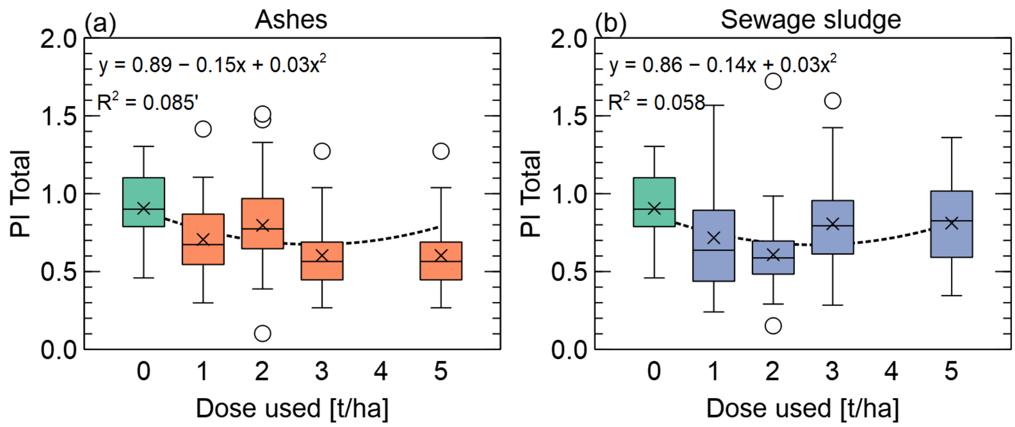

Figure 2. Photosynthetic efficiency (Performance Index total PI) versus used doses of preparations with phosphogypsum. Two studied variants of mixture with ashes (**a**) and sewage sludge (**b**) are presented. The dashed lines represent the linear regression fits of the data. The regression equations with the fitted parameters and the models' R^2 values are printed in the subfigures. The regression parameters are statistically significant at $p < 0.05$. In the plot, boxes span from 1st to 3rd quantile, with the median indicated by a line, whiskers indicating 1.5 inter-quantile range, the × symbol mean value, and circles outlier observations.

3.2. Measurements of the Growth Parameters

The addition of phosphogypsum to the soil resulted in a reduction in height growth in the pines tested and, in the case of S, the difference from the control appeared to be statistically significant (Figure 3). No statistical differences were found in the increase of the thickness of the root necks, although the tendency of the decrease was similar.

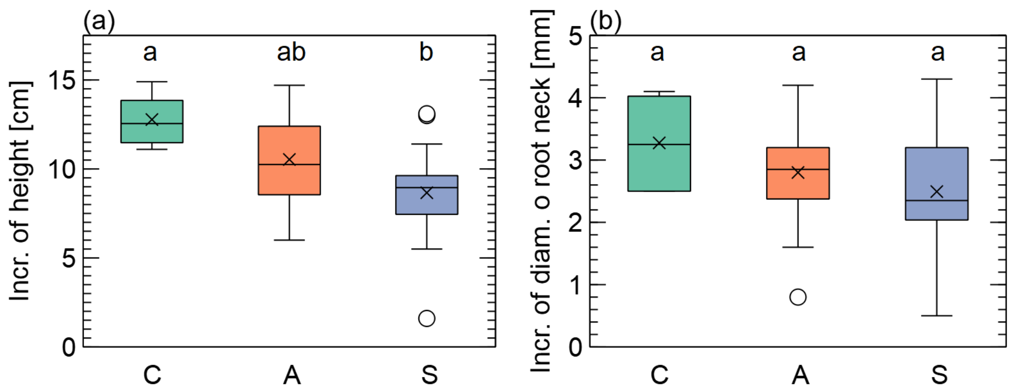

Figure 3. Increase in seedling length (**a**) and root collar diameter (**b**), calculated as the difference between measurements in October and April. Three types of treatments are presented: soil amendments with phosphogypsum mixed with organic ash—A, sewage sludge—S and control—C. The lowercase Latin characters above box plots, if the same, indicate that there is no statistically significant difference between the groups at $p < 0.05$. In the plot, boxes span from 1st to 3rd quantile, with the median indicated by a line, whiskers indicating 1.5 inter-quantile range, the × symbol mean value, and circles outlier observations.

Similarly, increasing dosages of phosphogypsum in mixed preparations in pines resulted in a deterioration of their growth in height and thickness at the root necks (Figure 4).

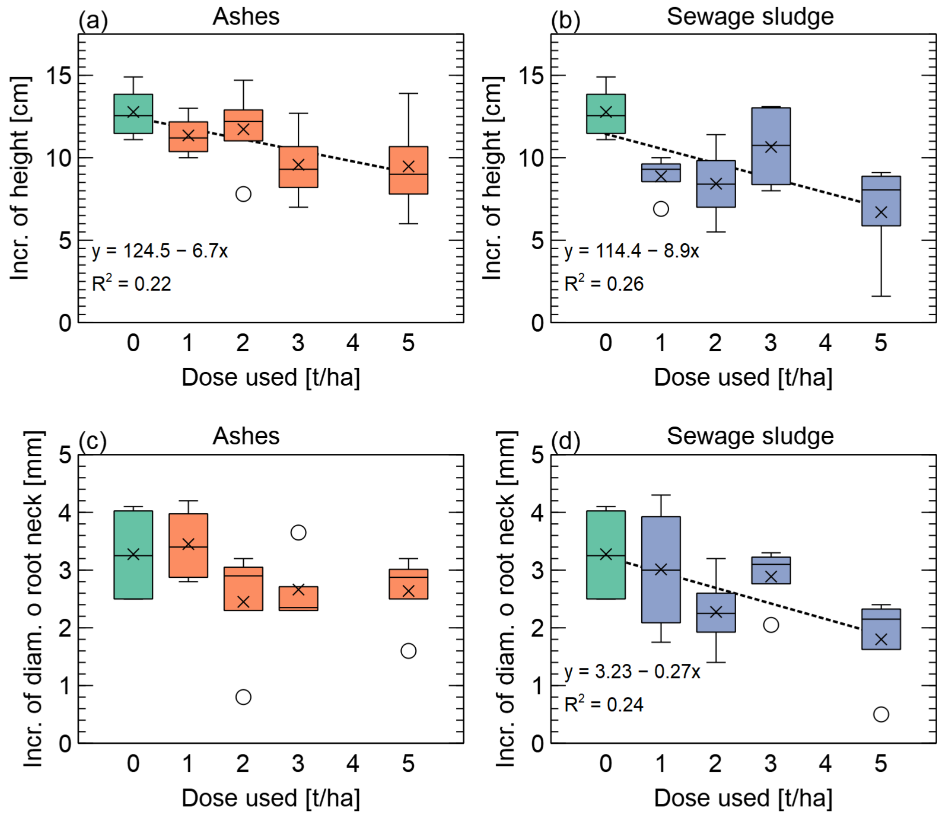

Figure 4. Increase of seedlings' lengths (**a**,**c**) and diameter of root neck (**b**,**d**) versus preparation doses. Two studied variants of mixture with ashes (**a**,**c**) and sewage sludge (**b**,**d**) are presented. The dashed lines represent the linear regression fits of the data. The regression equations with the fitted parameters and the models' R^2 values are printed in subfigures. The results of regression analysis are presented only for the cases when the regression parameters are statistically significant at $p < 0.05$. In the plot, boxes span from 1st to 3rd quantile, with the median indicated by a line, whiskers indicating 1.5 inter-quantile range, the × symbol mean value, and circles outlier observations.

When a mixture of phosphogypsum and sewage sludge was applied to the soil, the surface area of the assimilate (compared to the control and ash) decreased significantly (Figure 5).

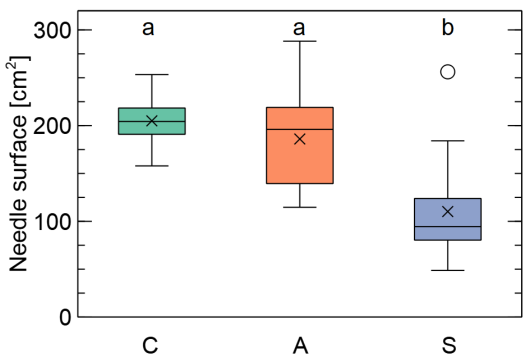

Figure 5. Changes in the needle surface of the Scots pine seedling. Three types of treatments are presented: soil amendments with phosphogypsum mixed with organic ash—A, sewage sludge—S and control—C. The lowercase Latin characters above box plots, if the same, indicate that there is no statistically significant difference between the groups at $p < 0.05$. In the plot, boxes span from 1st to 3rd quantile, with the median indicated by a line, whiskers indicating 1.5 inter-quantile range, the × symbol mean value, and circles outlier observations.

The above phenomenon reduced the needle area at concentrations of 2.3 and 5 t/ha of the sludge–phosphogypsum mixture (Figure 6).

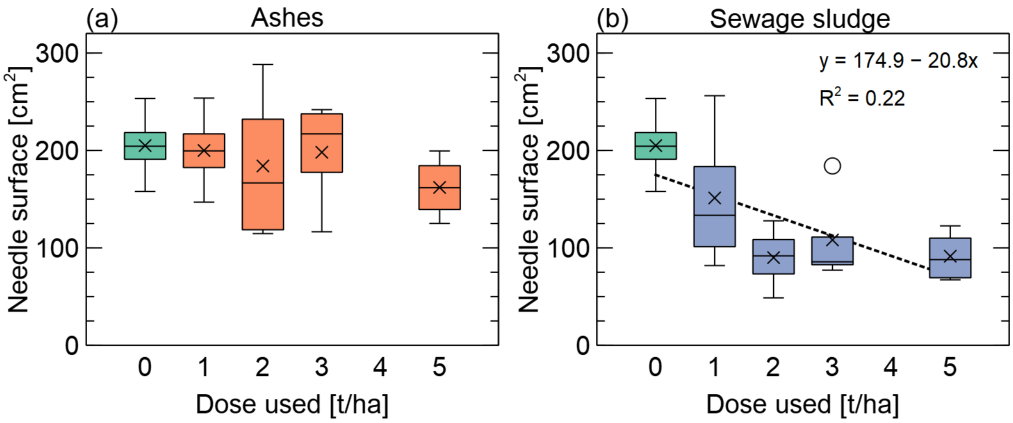

Figure 6. Changes in the needle surface of Scots pine seedlings versus preparation doses. Two studied variants of mixture with ashes (**a**) and sewage sludge (**b**) are presented. The dashed line represents the linear regression fits of the data. The regression equation with the fitted parameters and the model's R^2 value is printed in the subfigure. The results of regression analysis are presented only for the case when the regression parameters are statistically significant at $p < 0.05$. In the plot, boxes span from 1st to 3rd quantile, with the median indicated by a line, whiskers indicating 1.5 inter-quantile range, the × symbol mean value, and circles outlier observations.

A slight improvement in root length (not yet statistically significant) was observed when a mixture of phosphogypsum and ash (A) was added to the soil (Figure 7). However, no statistically significant differences were observed between the treatments and the control at the surface either, although the variant with the addition of sewage sludge (S) performed the worst (Figure 7).

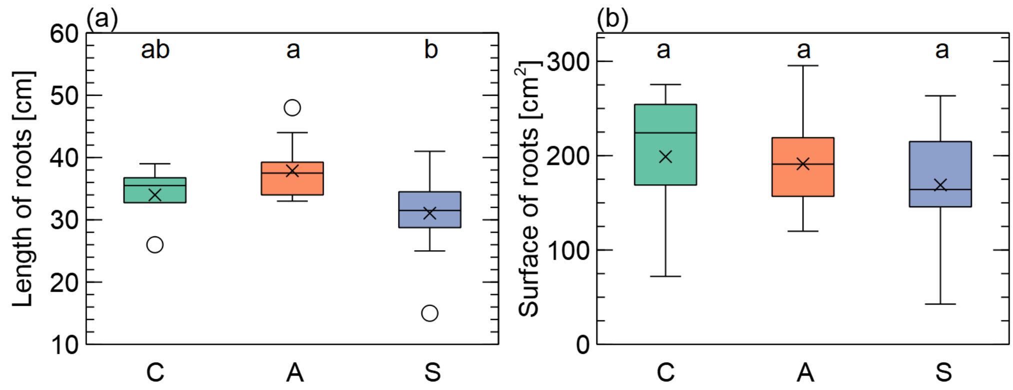

Figure 7. Length (**a**) and surface area (**b**) of roots of Scots pine seedlings. Three types of treatments were used: soil amendments with phosphogypsum mixed with organic ash—A, sewage sludge—S and control—C. The lowercase Latin characters above box plots, if the same, indicate that there is no statistically significant difference between the groups at $p < 0.05$. In the plot, boxes span from 1st to 3rd quantile, with the median indicated by a line, whiskers indicating 1.5 inter-quantile range, the × symbol mean value, and circles outlier observations.

In this case, higher application rates (5 t/ha) appear to have a positive effect on root length when A was added to the soil and a negative effect when S was added (Figure 8). Similar trends of improvement or deterioration in root area were observed for phosphogypsum mixed with A and S (Figure 8).

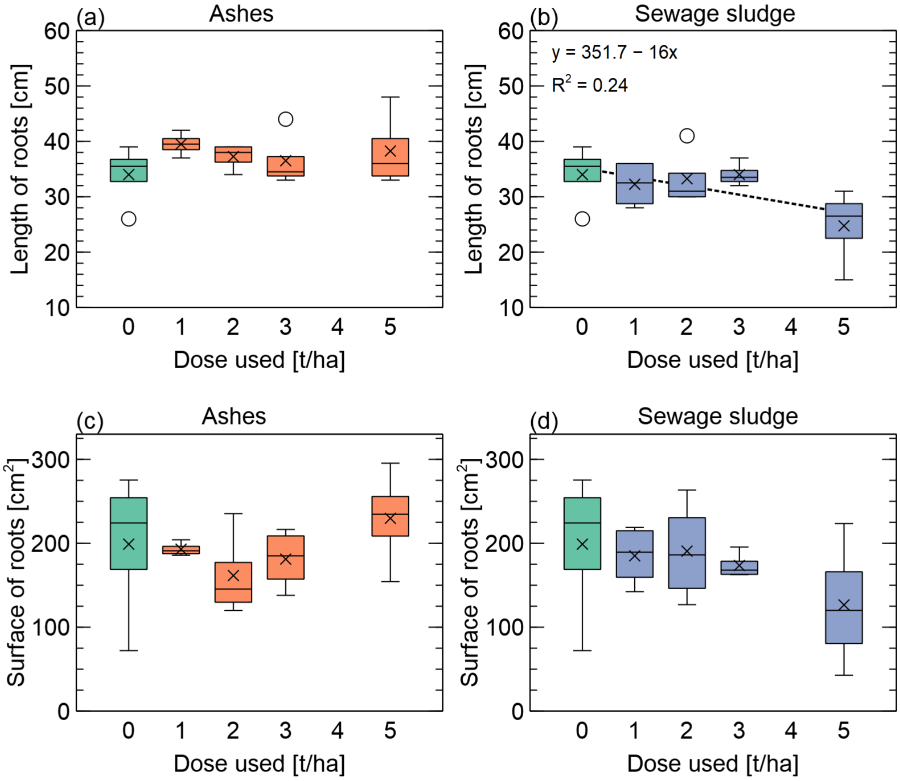

Figure 8. Roots length and surface area of Scots pine seedlings as a function of preparation dosage. Two studied variants of mixing with ash (**a**,**c**) and sewage sludge (**b**,**d**) are shown. The dashed line represents the linear regression fit of the data. The regression equation with the fitted parameters and the R^2 value of the model is shown in the sub-figure. The results of the regression analysis are presented only for the case where the regression parameters are statistically significant at $p < 0.05$. In the plot, boxes span from 1st to 3rd quantile, with the median indicated by a line, whiskers indicating 1.5 inter-quantile range, the × symbol mean value, and circles outlier observations.

Fresh and dry biomass of pine seedlings decreased uniformly with both treatment options, with the greatest decrease occurring after the addition of sewage sludge (Figure 9).

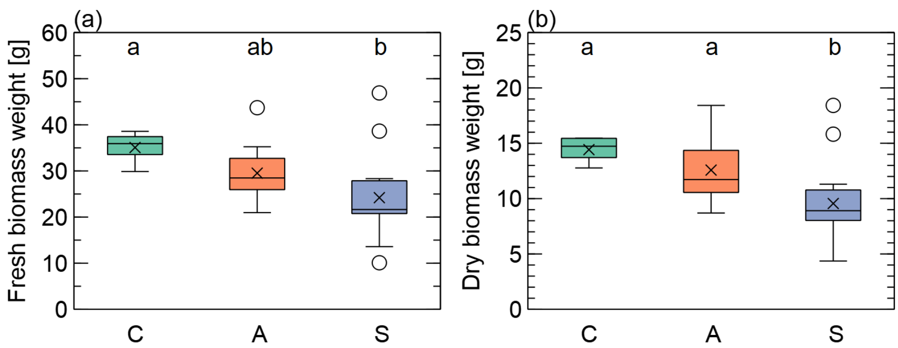

Figure 9. Fresh and dry biomass of Scots pine seedlings. Two studied variants of mixing with ash (**a**) and sewage sludge (**b**) are shown.Three types of treatments were used: Soil amendments with phosphogypsum mixed with organic ash–A, sewage sludge–S and control–C. The small Latin letters above the boxplots, when the same, indicate that there is no statistically significant difference between the groups in $p < 0.05$. In the plot, boxes span from 1st to 3rd quantile, with the median indicated by a line, whiskers indicating 1.5 inter-quantile range, the × symbol mean value, and circles outlier observations.

The higher the treatment doses, the more negative the effects on pine seedling biomass (Figure 10). Phosphogypsum mixed with sewage sludge in an amount of 5 t/ha had a particularly negative effect (Figure 10).

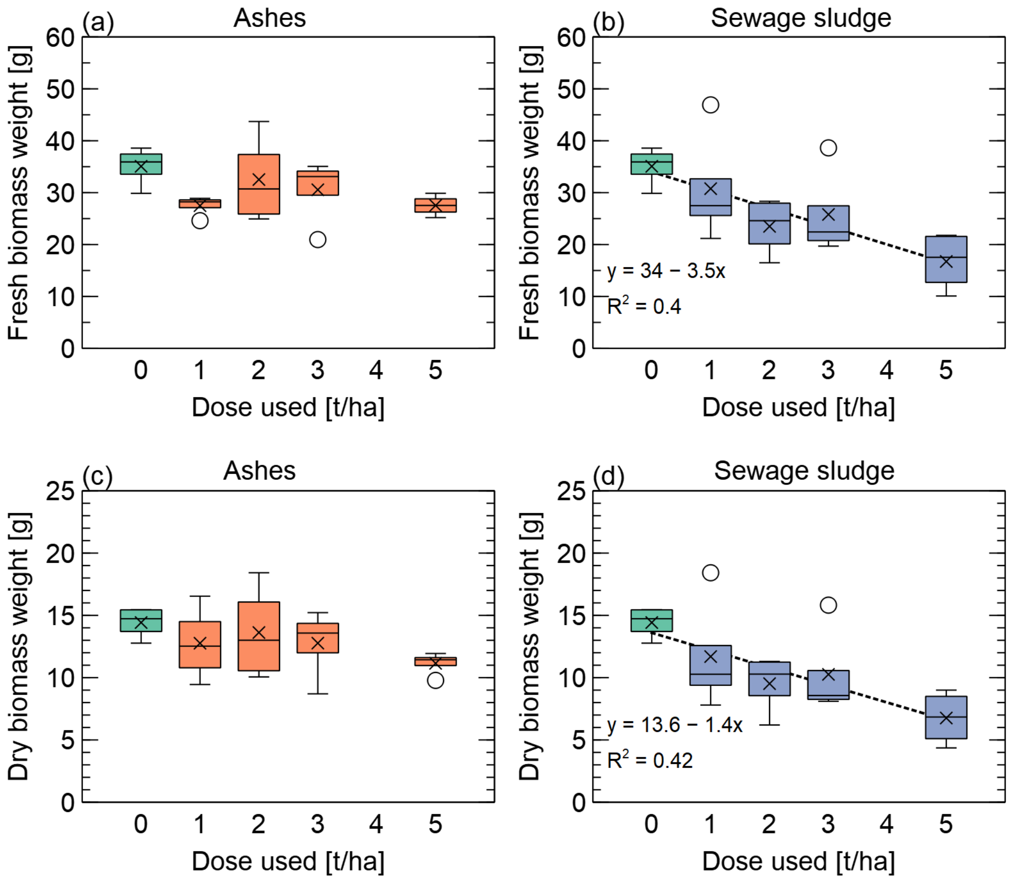

Figure 10. Fresh and dry biomass of Scots pine seedlings compared to preparation doses. Shown are two investigated variants of the mixture with ash (**a**,**c**) and sewage sludge (**b**,**d**). The dashed lines represent the linear regression fits of the data. The regression equations with the fitted parameters and the R^2 values of the models are shown in subfigures. The results of the regression analysis are presented only for the cases where the regression parameters are statistically significant at $p < 0.05$. In the plot, boxes span from 1st to 3rd quantile, with the median indicated by a line, whiskers indicating 1.5 inter-quantile range, the × symbol mean value, and circles outlier observations.

3.3. Measurements of Soil Parameters

The acidity of the soil samples studied is generally acidic, which affects the availability of phosphorus to plants (Table 1). In an acidic environment, poorly soluble compounds with aluminium and iron are formed. Although the P2O5 content in some samples was more than twice as high as in the control soils, it was not absorbed by the pines. The addition of ash (A) with a higher calcium Ca content (CaO-oxides) changed the pH of the forest soil (control—pH 3.52), which varied between 3.06 and 4.84 after treatment, the latter value being reached at an addition of 5 t/ha. However, the mean value (A) calculated from all measurements was identical to that of control C (3.52). For the preparation (S), the pH values were lower (from 3.38 to 3.57), due to the acidic nature of the phosphogypsum sludge (average 3.43). In addition, phosphorus tended to be in the upper layers (O) when treated with preparation (A), while it moved deeper into the root zone (1) to some extent after treatment with preparation (S): 0—sample from the soil layer 0–5 cm, 1—sample from the soil layer 5–10 cm.

Table 1. Acidity of the investigated soil samples and their phosphorus content: 0—sample from the soil layer 0–5 cm, 1—sample from the soil layer 5–10 cm.

Sample Type	No of Sample	pH	P [mg/kg]	P_2O_5 [mg/kg]
Ashes	A1/0	3.69	24.53	56.20
	A1/1	3.46	23.03	52.76
	A2/0	3.31	50.56	115.83
	A2/1	3.06	33.21	76.08
	A3/0	3.26	26.20	60.02
	A3/1	3.29	57.73	132.26
	A5/0	4.84	61.74	141.45
	A5/1	3.28	23.53	53.91
Sewage Sludge	S1/0	3.45	29.03	66.51
	S1/1	3.38	36.54	83.71
	S2/0	3.57	59.57	136.47
	S2/1	3.44	77.59	177.76
	S3/0	3.40	43.55	99.77
	S3/1	3.44	62.41	142.98
	S5/0	3.42	45.22	103.60
	S5/1	3.34	16.02	36.70
Control	C	3.52	34.04	77.99

4. Discussion

4.1. Phosphogypsum—Possibilities for Recycling

Post-phosphate wastes, including dolomitic wastes and phosphogypsum, have been used as reclamation products in North Carolina [18], which is encouraging for such activities in Poland. In particular, soil acidification is a major obstacle to agricultural and forestry development in Poland, as in many other countries [19]. There are few effective methods to improve soil acidity, e.g., in China and elsewhere, where PG has been shown to increase soil exchangeable calcium (Ca) content. Surface liming of moderately acid subtropical soils, when properly applied, is an effective method of reducing subsoil acidity to −0.60 cm in the first year after application [20]. In a similar trial that has been running since 2002, surface application of limestone and phosphogypsum has been shown to have positive effects on root growth, nutrient supply and crop yields [21]. In tropical soils with low natural fertility, acidity can be rapidly improved by surface application of phosphogypsum in a no-till system (NT). Such improvement can be observed as early as 12 months after application. Phosphogypsum mixtures increase the concentration of K, Ca, Mg, N-NO_3^- and S-SO_4^{2-} in the subsurface layers of the soils [22]. Application of calcium dolomite and phosphogypsum (2100 kg/ha) to rice and bean crops in the highlands (in Brazil), superficially and without mixing into the soil, increases the Ca, Mg and Mn content in the leaves and increases the yields of these crops [23]. As a soil additive and soil conditioner, PG is therefore compared to the liming of soils commonly used in Poland, but PG can be used as a supplement to liming and has a comprehensive effect on improving nutrient uptake and soil acidity [24]. In addition, PG has a solubility almost 150 times higher than lime and can reduce the activity of ions toxic to plants, especially active aluminium ions (Al^{3+}), which are particularly harmful to the fine roots [25]. PG positive effects on the environmental properties of soils include the improvement of their physical properties, especially by improving aggregation and hydraulic conductivity [26]. Gypsum is used to improve soil properties in regions where acidic soils prevail; its good solubility leads to stronger growth and better distribution of the root system of plants, which increases their yields. Numerous studies have confirmed that PG increases the accumulation of carbon (C) in the soil and this effect also has a positive aspect, as carbon sequestration in the soil reduces CO_2 emissions into the atmosphere [27]. In this way, PG also improves the quality of soil organic matter (SOM) in acidic soils, which is important for the sustainability of agricultural ecosystems [28].

4.2. The Growing Problem of Phosphogypsum Deposition in the Environment

The world economy consumes very large quantities of phosphoric acid. The annual share of world production of phosphate rock is approximately: USA—25%; China—18%; Morocco—15%; Russia—9%; Tunisia—8%; Ukraine—6%; Jordan—4%; other countries—15% [29,30]. The only raw materials important to Poland for the production of phosphoric acid are phosphate minerals, which occur naturally as phosphorite and apatite deposits. The largest deposits of phosphate rock are in the USA (Florida, Tennessee, North Carolina, Louisiana); China; Africa (Morocco, Senegal, Togo, Tunisia, Jordan, South Africa, Egypt, Israel, Syria); and Russia (Kola Peninsula). In Poland and elsewhere, the amount of phosphogypsum produced in the manufacture of phosphoric acid is about 5 tonnes per tonne of phosphoric acid extracted [6]. Global production of PG is about 100–280 million tonnes per year. Phosphogypsum is stored in landfills: in so-called ponds in liquid form, in stockpiles in semi-dry form, or submerged in seas and oceans. Phosphogypsum is the most produced of all inorganic chemical wastes and unfortunately still one of the most landfilled.

The storage of PG in large landfills near factories, as in Poland, causes significant environmental damage. PG contains gypsum and a variety of impurities such as phosphates, fluorides and sulphates, and could still be used as fertilizer for forests, although it contains heavy metals and other trace elements. A deficiency of phosphorus (P) has been found in oak stands growing on the Krotoszyn plateau (western Poland) [25]. This deficiency favours damage to the root systems by pathogenic oomycetes of the genus Phytophthora. This can be prevented by an appropriate dosage of phosphogypsum, e.g., mixed with ash. They can improve degraded forest soils that have been used for agriculture for many years and other soils with stands on disaster sites (e.g., after industrial emissions or fires). In clear-cuts, they can be used to compensate for the loss of tree biomass after harvesting [9], while they can affect agricultural products, they have less impact on forest ecosystems and can probably even increase timber production. To date, up to 15% of the world's production of PG is used in the manufacture of building materials, as a soil additive and as a regulating agent in cement production. The increasing scale of mining and the growing demands for environmental protection are leading to the search for new solutions for the management of phosphogypsum [29]. This research is part of this trend and is an attempt to address a global problem at a local level. Many wastes, including PG, have a high fertilizing potential and their release into the environment complies with EU requirements. Legal regulations for the natural use of waste for fertilization purposes vary across the EU. Therefore, in June 2019, the European Parliament adopted a regulation opening the European market for mineral and organic fertilizers and new fertilizer products from waste with soil improver status (Regulation 2019/1009).

4.3. Phosphogypsum—Restrictions on Use

The current hazards posed by the storage of phosphogypsum in open landfills require a constant search for innovative methods of managing phosphogypsum dumps. The main proposed applications are: agriculture, cubic construction, civil engineering, road construction, levelling of pits and reclamation of degraded land [2]. Phosphogypsum can be used in many sectors of the economy, including the production of building materials, road construction and the production of elemental sulphur and sulphuric acid [31]. In some countries, waste phosphate compounds from industry are used in agriculture [20] and their impact on the environment has been positively evaluated [32]. Phosphogypsum contains certain amounts of beneficial plant nutrients (mainly phosphorus) that can have a positive effect on plant growth. The use of phosphogypsum in crops is permitted in Brazil [33]. Phosphogypsum can also be used to rehabilitate damaged soils [34] or as a component of mineral–organic fertilizers [35].

4.4. Phosphogypsum with Sewage Sludge

Phosphogypsum can be mixed with sewage sludge, for example, to increase the effectiveness of phosphites. Microbiological processes with organic acids dissolve the phosphites into plant-available phosphates. Usually, a ratio of organic feedstock to phosphate of about 4:1 is recommended for the production of this type of compost. This direction to increase the efficiency of phosphate meals is also attractive because the phosphates formed by the dissolution of phosphate meals have a protective function against nitrogen by binding the ammonia formed during the decomposition processes of the organic matter of the compost mass to ammonium phosphate [36]. Composting sewage sludge with phosphate meals offers a complex combination of increasing phosphorus solubility and protecting against nitrogen loss [37].

Returning the nutrients accumulated in sewage sludge to the soil is not only necessary from an economic point of view, but also important for maintaining and restoring the ecological balance. The mineral and organic composition of sewage sludge from municipal wastewater treatment plants resembles the organic matter of the soil—humus [37]. This enables their natural use, including forestry and pasture [38]. However, sludge intended for non-industrial use should meet requirements regarding its chemical composition and hygienic condition. Limitations include the content of heavy metals due to their toxic effect on living organisms and their ability to bioaccumulate [39].

4.5. The Fresh Coniferous Forest as a Potential Site for Phosphate Application

Fresh coniferous forests are one of the most widespread forest habitats in Poland. At the end of 2011, these habitats occupied an area of 1,433,387 hectares (20.2% of the area under state forest management). The largest areas are located in the mesoregions, including the Masurian Forest (II.4), the Tuchola Forest (III.1), the Notec Forest (III.17) and the Lower Silesian Forest (V.2) [40].

Fresh coniferous forest colonizes moderately poor sites that are still not very moist but on soils that are already somewhat better than dry coniferous forest. Good podsolic soils with varying degrees of podsolation predominate, but fresh coniferous forest with poorly developed podsolic, podsolic–rustic or rusty soils can also be found. Characteristic of these soils is the swampy overburden humus, which is strongly acidic and has a pH value between 3.5 and 4.

4.6. Special Conditions of the Prepared Experiment

The present study was conducted over a period of six months (April to October 2021), which, based on the analysis of the results, seems to be far too short a period to obtain statistically significant differences between the experimental variants. To obtain more accurate results over a wider range, the study would have to be continued over a longer period, e.g., two or three years. Organic phosphogypsum (PG organic) as a soil conditioner improves crop yields in sandy soils in the long term. Other studies have shown that the use of PG to improve the properties of sandy soils enhances plant growth and development, but this effect is only visible after 2 years [41]. This is due to the creation of a suitable environment that promotes the uptake and assimilation of nutrients by the roots. We would also like to achieve such an effect in the long term with woody plants such as pines.

The main purpose of the experimental design was to determine the dosage to be tested over a longer period of time in plots in pine plantations, provided PG is no longer treated as a waste material. For the same reason, forest soil was taken from the Trzebież forest area near the chemical plant where the phosphogypsum is stored. The pine seedlings were also taken from the same forest area in order to be able to use regeneration material with the same gene pool in the study (currently in pots and later in the forest area).

Although the pine seedlings originated from the First Baltic forest region and were raised in the Fourth Mazovian-Podlasian forest region, the growth period after planting and the ecological conditions are similar in both regions: 200–210 days in the Baltic region and

210 days in the Mazovian-Podlasian region [42]. Annual precipitation is also 550–600 mm per year in country IV and 600–700 mm per year in country I [43,44].

As the trial started at the beginning of the growing season, the tested phosphogypsum mixtures were applied in spring to the soil of the pots in which the annual pines had been planted. Phosphorus is a nutrient with low mobility, as it moves poorly in the soil profile. Therefore, fertilization with this nutrient was done in spring when there is enough time for it to seep into the roots and for the plants to respond. Otherwise, the nutrient may not be available to the roots of the plants. However, it is known that the best time to apply this type of fertilizer, especially in the form of superphosphates, is as early as possible in the autumn, as the heavy metals from the fertilizers can then form poorly soluble compounds in the soil that are inaccessible to the plants [45]. If, on the other hand, spring fertilization is necessary, the use of a multi-component compound fertilizer [46] is recommended. In the future, the tested preparations could be enriched with other nutrients, such as nitrogen (N), and preferably applied in granular form in spring. For the time being, however, the loose form was used, as it was assumed that fertilization would take place before planting the seedlings in the soil preparation phase. Further field trials would need to test the effect of harrowing or disc fertilization to allow the preparation to penetrate deeper into the soil and facilitate phosphorus uptake by the root systems of the seedlings.

The two forms of preparation tested are not yet suitable for use in forestry practise, as the free-flowing preparation is too fine and light, so that it can be blown away by the wind and is very likely to damage the needles and leaves of the seedlings. The other, plastic form, on the other hand, is too dense and compacted and cannot be worked into the soil mechanically (without the addition of dilution liquids). It would be necessary to develop other forms of phosphate fertilizers, e.g., granules, which are also enriched with the nutrients mentioned above.

In the future, preparations from sewage sludge (from phosphogypsum landfills) and organic ash (from boiler plants) should be standardized so that there is no doubt as to whether the content of individual elements in each sample is always the same or different.

4.7. Growth of Pines after Soil Improvement with Phosphogypsum

Thus, there was no direct toxic effect of the preparations on pine seedlings, even at high doses (5 t/ha). However, a tendency was observed for both mixture A and mixture S to reduce the development of the seedlings compared to control pine C. After the treatments, the height of the above-ground parts of the seedlings was lower than in the control experiment, although the differences were not statistically significant. For mixture A (irrespective of the dose), there was a tendency to increase root length, in contrast to mixture S. The addition of phosphorus usually has a positive effect on root development [45], which was also confirmed in the present study.

Although the total phosphorus content in the soil increased after the addition of the preparations, it was observed that it remained at the soil surface in the case of mixture A, whereas the phosphorus penetrated into the deeper soil layers in the case of mixture S. It is possible that the phosphorus was better absorbed by the plants in this form. Future analyses of the phosphorus content of plant tissues (needles and roots) could provide an answer to this question. The most favourable effect of the formulations was observed at lower doses of 1 to 2 t/ha, which is encouraging for economic reasons. In view of the results of the present study, further studies should therefore be conducted for the low doses.

In the visual assessment of plant health and growth performance, the phosphogypsum A mixture performed significantly better than the phosphogypsum S mixture in the soil. The unfavourable effect of the preparation S used was evident in the wilting of the needles in the lower part of the seedlings. This phenomenon was probably caused by water droplets falling directly on the phosphogypsum mixture during the rain and spraying the needles in the immediate vicinity.

However, the reduction in needle area in this case could also have been influenced by heavy metals that inhibit plant growth. Therefore, the preparations would have to be examined for cadmium (Cd), since under the influence of cadmium ions the intensity of photosynthesis in wheat cereals is significantly reduced [47]. Presumably, the presence of these ions can have a similar effect on pine seedlings.

Although the heavy metals accumulated in the soil are slowly removed from the soil by the plants, this affects their development [48]. It should also be checked whether heavy metals contained in phosphogypsum are taken up by pine seedlings and, if so, by which plant organs. Are heavy metals transported from the roots to the needles, which then fall off, and what effects could this have on the forest litter? Plants take up heavy metals together with other elements in ionic form. Their toxic effects on plant life processes are mainly due to interactions with functional groups of molecules that make up cells, especially proteins and polynucleotides. The result of these phenomena can be poorer growth and development of the plant or even its death. The harmful effects of heavy metals become apparent at certain concentrations in the plant environment [49,50].

Therefore, it would be equally important to investigate whether fungi that live in symbiosis with trees do not take up heavy metals that could ultimately harm the organisms that consume them. Are heavy metals stored in wood and what impact does this have on the quality of the wood grown?

4.8. Phosphogypsum as an Important Source of Phosphorus for Seedlings and Microorganisms

The presence of phosphorus in the soil is an important limiting factor for the uptake of heavy metals by plants, as higher amounts of easily soluble forms of phosphorus can precipitate poorly soluble phosphates of zinc, cadmium, lead and copper [8]. However, this hypothesis would need to be confirmed by analysing the metal content of soil samples containing the formulations, which will be done later.

The pool of permanently bound phosphorus includes inorganic, poorly soluble compounds and organic compounds that are resistant to mineralization by soil microorganisms. Such compounds can be present in the soil for many years, but are not available to plants and have little impact on soil fertility [45]. About half of the total soil phosphorus reserve is accumulated in soil organic matter. The other half of this reserve is inorganic phosphorus with low mobility, mostly bound to mineral soil particles [45]. A change to a more acidic pH, e.g., strong local soil acidification with high doses of preparations (especially with sewage sludge), could also be the cause of poorer development of pine seedlings, for which the optimal soil pH should be between 4.5 and 5 [51].

Future research should also include the biological properties of the soil (microbiome), whose influence on plant health is difficult to assess, such as fungi (mycorrhizal, saprotrophic, pathogenic) and bacteria. The stockpiles themselves should also be examined for bacteria that could be inadvertently transferred to forest areas.

We have refrained from giving the physical properties of the soil and macronutrients such as N, K, Ca and Mg because we feel that such chemical analysis adds little to the discussion, except for phosphorus (which we have done), and the physical analysis of the soil is useful in field studies (in future tests) and not in this case in a pot experiment. Providing detailed soil properties in our article would not have added anything relevant to the research conducted, as we did not investigate the relationship or impact of soil properties on seedling response to phosphogypsum fertilization. As mentioned earlier, we were mainly interested in two aspects: the absence of phytotoxicity of the doses administered and the directional (positive) response of the seedlings to additional doses of phosphogypsum. In our experiment, we determined the content and translocation of P from the upper layers, where it was applied in the form of phosphogypsum, to the lower layers as a function of the application dose. We believe that, at this stage of the research, we should confirm the validity of the direction of recycling and the use of waste produced in the manufacture of fertilizers, in this case in forestry, to bring about a change in their status from waste to poor fertilizer. It will then be possible to carry out more extensive field studies in forests.

4.9. Photosynthetic Performance of Pine Seedlings

Long-term surface application of phosphogypsum (PG) can enhance plant growth and physiological and biochemical processes [52]. Addition of PG increased root development at greater depths and improved the plant nutrition of maize. These combined effects increased the concentrations of photosynthetic pigments and gas exchange even in low water availability. In addition, the activities of Rubisco, sucrose synthase and antioxidant enzymes were improved, reducing oxidative stress. These improvements in the physiological performance of maize plants resulted in higher grain yield. Overall, the results argue for soil amendments as an important strategy to increase soil fertility and secure crop yields in regions where dry spells occur during the cropping cycle [52].

There are two types of photosystems: PS I (=PS700) and PS II (=PS680). Thus, the chlorophyll in the centre of the reaction PS I has an absorption maximum at a wavelength of 700 nm, while PS II has a maximum at 680 nm. In the chloroplasts, PS II predominates and the stoichiometric ratio of PS II to PS I is about 1.5, but can vary depending on environmental conditions [53]. PS II also contains an oxygen releasing complex (OEC). It is located on the inner surface of the thylakoid membrane. The complex contains the amino acid tyrosine on the D1 protein, four manganese atoms and the outer proteins PsbO (stabilizes the manganese cluster), PsbP and PsbQ. During the light phase of photosynthesis, the water molecules in this complex are split into protons, electrons and oxygen.

In phosphogypsum with sewage sludge these two PI (PIabs and PIinst) had a positive effect at a dose of 5 t/ha; in phosphogypsum with ash the same PI parameters (PIabs and Piinst) had an effect, but the positive effect was at a dose of 2 t/ha. Both preparations also reduce the loss of heat energy in the photosynthetic apparatus of the plants (lower DI/CS).

After analysing all the parameters, we decided to present only the overall parameter PI, as the other parameters show only weak tendencies and contribute nothing to the discussion. The other parameters mentioned and analysed in the methodology were not statistically significantly different from each other.

The weaker photosynthetic efficiency of the treated pines could be due to the presence of heavy metals, especially cadmium, in the phosphogypsum (Figure 1). This aspect should be further investigated in the future.

4.10. Restrictions on the Use of New Preparations Based on Phosphogypsum

However, to date there is little information in the literature on the applicability of PG in forestry [18,54,55] or the assessment of the use of phosphogypsum in a nursery for plant propagation [56]. Much more information is available on the impact of PG on the soil ecosystem [31,32] and on the assessment of alternative and traditional cover systems for phosphogypsum remediation [57,58]. The main problem is the content of heavy metals (HM) which, even if they comply with current standards (of the Member States or the European Community), still pose some environmental risk [8]. When HM enter aquatic ecosystems, there is an exceptionally high bioaccumulation, the concentration of which exceeds the initial uptake of toxins by the last link in the trophic chain (e.g., fish) by tens and hundreds of thousands of times [2]. The peculiarity of the behaviour of HM in the air lies in their wide distribution, which can be tens of kilometres. In soil, due to its different biogeochemical composition under different environmental conditions, different effects must be taken into account: antagonistic, synergistic and sensitizing effects, which have a strong impact on the quality of the environment and consequently on human health.

In forests, litter is formed from accumulated and decaying organic matter. The upper humus accumulation horizon (horizon A1 with a thickness of up to 10 cm) concentrates most absorbent roots, releases phytoncides, absorbs radionuclides, etc.). Heavy metals can be transferred from the roots to the leaves through soil contamination and the leaves can also absorb them directly (through leaf contamination). Raking the leaves is one way to remove heavy metals from the soil. However, removing the foliage reduces the supply of organic material to the soil, which is a strong buffer that binds heavy metals. A more environmentally friendly method is therefore to rake the leaves and place them in grooves

25–30 cm deep, i.e., in the upper soil layer where all biological processes are active. In this case, there is active mineralization of the organic matter, binding of HM and, above all, reduction of their mobile forms, which reduces the risk of exposure to HM. Mixing the preparations into the topsoil is therefore a better solution than simply spreading them and leaving them on the surface.

Signs of plant inhibition and a decrease in the activity of the assimilation apparatus could be the negative effects of increased HM concentrations in woody plants but that was not the aim of this study. However, it is known, for example, that the effect of cadmium nitrate on wheat plants manifests itself in a significant reduction in seed germination and a decrease in biometric indicators. Under the influence of cadmium ions, the intensity of photosynthesis is significantly reduced [59].

The preparations can also be mixed with organic material such as wood waste, pine bark compost or sawdust. The addition of organic material will undoubtedly improve the physico-chemical and biological properties of the soil: improvement of the soil structure; creation of a more airy condition of the upper soil horizons (humus accumulation horizon); activation of biological, including microbiological processes; promotion of a more active growth of the root system and especially the growth of suckering roots. The normal state of the root system under the conditions of a natural increase in the volumetric mass value protects against the penetration of pollutants (HM) into the terrestrial organs of phytochromes (due to the normal, optimal functioning of plant resistance mechanisms).

The present forestry study is a pioneering work, which is why it is hardly mentioned in the literature. It is not known whether there is a possibility of wider management and use of phosphogypsum hills in Poland. The basic research problem was to find an answer to the question whether preparations based on calcium sulphate in two variants—a mixture with organic ash A and with sewage sludge S—can serve as fertilizer and in what quantity per hectare?

5. Conclusions

1. The phosphogypsum-based preparations used showed no harmful (toxic) effects on the pine seedlings grown in pots during the six-month trial period.
2. The preparation made in bulk from a mixture of phosphogypsum and wood ash had a favourable effect on the development of the seedlings' root system and was also easier to mix with the soil than phosphogypsum with sewage sludge, which was in a sticky form.
3. The photosynthetic efficiency of one-year-old pine seedlings decreased after one growing season following the application of phosphogypsum preparations, so that observations over a longer period are necessary.
4. The most favourable dosages of phosphogypsum preparations for the development of pine seedlings (especially in combination with ash) are between 1 and 2 t/ha, although most of the growth parameters tested did not differ from the control. From an economic point of view, lower dosages will be more favourable for use in forestry, but further studies over a longer period of time are needed for this.
5. Formulations should be tested for heavy metals and their effects on seedling development.
6. Testing should continue for at least two to three growing seasons, including monitoring for changes in the microbiome.

Author Contributions: Conceptualization, T.O., P.B. and S.B.; methodology, T.O., P.B. and O.K.; software, T.P., P.B. and O.K.; writing, T.O., P.B. and A.R.; visualization, P.B.; supervision, T.O. and S.B.; resources, T.O. and S.B.; investigation, T.P., W.S. and B.R.; project administration, S.B. and T.O.; funding acquisition, S.B. and T.O. All authors have read and agreed to the published version of the manuscript.

Funding: The study was partly carried out within the framework: WZ/WB-INL/3/2021 and financed from the science funds from Ministry of Science and Higher Education in Poland.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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