Improvement of plant availability of phosphates during coagulation

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Abstract

Mineral P reserves are dropping down and probably will be over within next 30-50 years. Thus, phosphates are becoming a scarce resource. At the same time, domestic wastewater contains a large amount of phosphates. These phosphates can be removed during the coagulation water treatment. Therefore, coagulated sludge contains phosphorous which can be reused as a fertilizer. The aim of this research is to increase the plants availability of phosphorus (PAP) by trying various combinations of organic and inorganic coagulants for wastewater treatment process. It will help to document the mechanisms and to suggest practical dosing combinations. For this purpose the jars test was carried out with two types of aluminum coagulants (AlS and PAX-18), as well as the plant growth experiment with wheat and achieved coagulated sludge. The influence of adding organic polymer simultaneously with AlS on the PAP was also studied.

Keywords: Wastewater treatment, coagulation, sludge, nutrients, phosphorous, plant availability of phosphates (PAP), biomass allocation.

Introduction

In the wastewater treatment, after coagulation, sludge – is produced. Due to the high phosphorous content in coagulated sludge, the most profitable way of its utilization is to use it as a fertilizer. Studies indicate that Al and Fe hydroxides are strong adsorbents of soil P. For example, experiments with sludge, obtained by coagulation water treatment using aluminum coagulants conducted in Harwood Mill, Newport, United States indicate that growth rate of lawn grass using alum sludge decreases. This took place due to binding phosphorous in soil with aluminum or toxic effects of aluminum or heavy metals (Lucas et al., 1994).

Michael Kyle and Samuel McClintock studied few different types of sludge: Al sludge, Fe sludge, BPR sludge. The test's results show that the BPR sludge had the highest level of available P among them, and ranked the sludges Al < Fe < BPR. The chemical sludge values were very similar to each other and were much lower than the results of the nonchemical sludge and fertilizer (Kyle et al., 1995).

In Norway, more than 70% of wastewater is treated using coagulation and over 85 % of wastewater sludge is used in agriculture. The problem of using coagulated sludge as a fertilizer is that not all phosphorous is available for plans. Thus, despite farmers are not paying for sludge today, this may reduce their willingness to accept even free sludge. That is why it is important to improve plant availability of phosphates and by this to increase its value.

For increasing the PAP it is important to understand the mechanism of coagulation. During coagulation particles are assumed to be removed both by the adsorption – charge neutralization and sweep floc mechanisms. However, when coagulating with low basicity (OH/Me low) coagulants, the dominant mechanism for particle removal is suggested to be the sweep floc mechanism, while when the coagulants with high basicity are used, particles are removed dominantly by the adsorption – charge neutralization mechanism. An increasing OH/Al ratio of aluminium coagulants positively influences particle removal in domestic wastewater treatment. The OH/Al ratio of the coagulants influences the mechanisms of phosphate removal as well. When the OH/ Al ratio of the coagulant is low, phosphates are removed predominantly by the initial formation of negatively charged aluminium - hydroxo - phosphate complexes. When the OH/Al ratio of the coagulant is high, less phosphate is removed, and the dominant mechanism is suggested to be the adsorption of phosphate ions on to the hydrolysis products (Ratnaweera et al., 1992).

Speaking of plants availability of phosphates, phosphorus is absorbed by plant roots from the soil solution. That is why, while using coagulated sludge as a fertilizer, plants availability of phosphates is related to the solubility of phosphates. Such factor as P-fixation affects PAP a lot. P-fixation is a term that is used to describe both P-sorption and P-precipitation. Phosphate precipitation is a process in which phosphorus reacts with another substance to form a solid mineral. In contrast, dissolution of phosphate minerals occurs when the mineral dissolves and releases phosphorus. Precipitation and dissolution reactions greatly influence the availability of phosphate in the soil. Since both P-sorption and P-precipitation reduce phosphorus availability, sludge with a great P-fixation capacity has less available phosphorus than sludge with a low P-fixation capacity.

Experimental design

Different types of wastewater were analyzed for phosphorous content during the planning stage. It was decided to choose wastewater from Drøbak WWTP.

Two different aluminum coagulants with different OH/Al ratio (0 and 1.2 respectively – AlS and Pax-18) were tested. Two aluminum doses and two different water types were tried. Moreover it was planned to make one experiment with a combination of AlS (2 doses) and polymer SNF FO 4350 (1g/l solution) on one type of water in order to study the influence of adding organic polymer simultaneously with coagulant on the PAP. Coagulant doses were selected based on the optimal dose (d1 = 0.25 mmol Al/l) and excessive dosage of coagulant (d2 = 0.37 mmol Al/l). In the experiments with the polymer, were used the same dosages of AlS and was added 1 ml/l of polymer 4350. As control experiments, it was decided to grow plants with a balanced nutrient solution with phosphorus; nutrient solution without phosphorus and without adding any nutrients. Received experimental design is shown in Fig. 1.

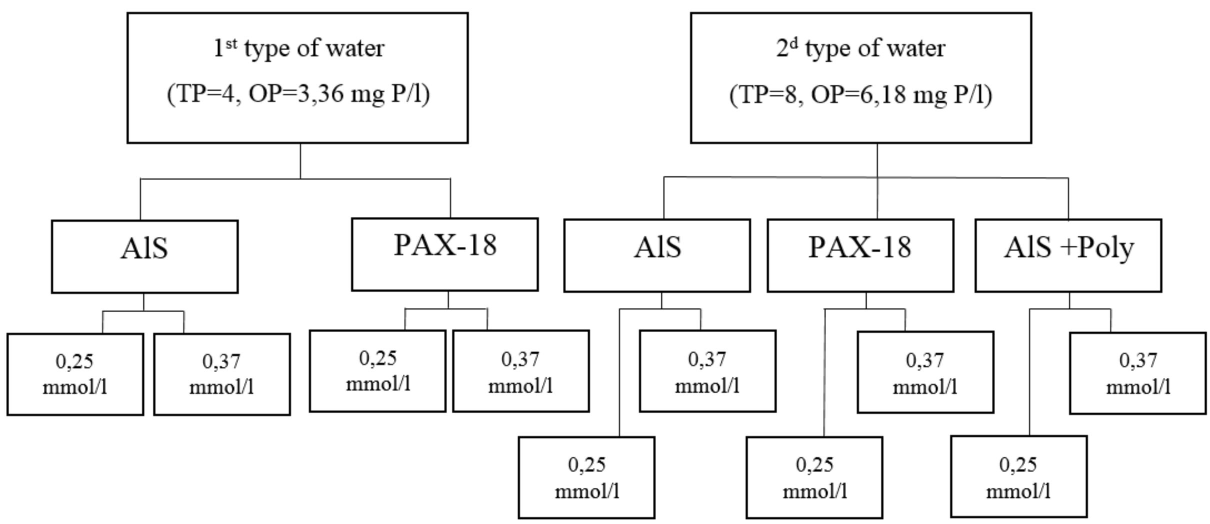


Figure 1. Plan of the experiment.

Methods, equipment and procedures

The content of total phosphorus in water from Drøbak WWTP was 1.4 mg P/l. To create two different types of water with total phosphorus content 4 mg P/l and 8 mg P/l K_2HPO_4 was used.

Sludge collection and analysis. The coagulation process was carried out with the use of jars test unit and such a conditions: fast mixing mode – 30 seconds, slow mixing mode – 10 minutes, sedimentation – 30 minutes. After coagulation, sludge was separated by decanting. Then it was analyzed for total phosphorous content using Phosphate (ortho / total) cuvette test 2.0 – 20.0 mg/l PO4-P of Hach Lange.

It is important to note that for the equal conditions for growing plants, it is necessary to put the same amount of all nutrients in every pot. The amount of phosphorus, which was put in each pot, is 3 mg. Therefore, based on the data of total phosphorus content in the sludge samples (mg/ml), the amount of sludge, which must be added to each pot was calculated.

The analysis of Al content of sludge, which was obtained with and without addition of polymer was made with the use of Aluminum, Aluminon Method 8012-Powder Pillows - Hach Lange.

Preparation of nutrients solutions. For the reference, the nutrient solution with phosphorous was prepared with a ratio of N : P : K : Mg : Ca = 1 : 2 : 4 : 0.65 : 0.8. For this were used K_2HPO_4, $(NH_4)_2SO_4$, $MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 6H_2O$. In addition, the nutrient solution without phosphorus which retains the all other nutrients at the same level was prepared using the following salts: KI, $(NH_4)_2SO_4$, $MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 6H_2O$. pH of nutrient solutions is kept at 6.5.

Plants growth experiment. Plants growth experiment was carried out with wheat. All samples of plants were grown in three parallels.

Before germination, seeds of wheat were sterilized with 1% chlorine solution for 5 minutes, then – carefully washed with autoclaved water. Seeds were germinated for 24 hours in autoclaved water. At the same time, each portion of coagulated sludge was treated with the microwave for 4 minutes (900 W). Such sterilization measures are provided in order to prevent the fungi growth.

For the plant growth experiment the hydroponics method was chosen. For its realization were used plastic box (10 x 10 cm). In order to create drainage the holes were made in all boxes.

After germination, in each box was placed a tissue to detain water and 40 g of seeds. Then the calculated amount of sludge and nutrient solution without phosphorus was placed to the boxes. With the use of conductivity meter, the conductivity value of sludge-solution mixture was controlled. This value was maintained at the level of 1000 – 1100 μS/cm. If conductivity of the mixture was too high the autoclaved water was added.

For the references, after putting seeds into the boxes, the solution of nutrients with phosphorus (needed amount for adding 3 mg of phosphorus in each box) / nutrient solution without phosphorus / autoclaved water were added.

Thus, was achieved the same amount of nutrients in each box (except the last two references), where the only discrepancy was the source of phosphorus.

Growing of plants was carried out for 12 days in a greenhouse with the following conditions: lighting from 8:00 to 22:00 (temperature 22 °C), unlightened period from 22:00 to 8:00 (temperature 16 °C). Irrigation was made by autoclaved water three times a day every 4.5 hours during the first 5 days, and four times a day every 3.5 hours during the next 7 days. This irrigation was carried out using a spray. In each box was added the same amount of water to create an equal conditions.

Since 4 days of growth, every day at the same time were made the measurements of samples height and plant growth rate was calculated by the formula:

$$\mathbf{GR} = \mathbf{H_{plant}}/\mathbf{H_{reference}} \cdot \mathbf{100},$$

where GR - growth rate, %; $\mathbf{H_{plant}}$– the height of the sample, cm; $\mathbf{H_{reference}}$– the average height of the main reference, cm.

Definition of biomass allocation. In addition to growth rate calculation the distribution of plant’s biomass between the root and shoot was determined. For this purpose, after the end of experiment, from each box were taken 20 plants, preserving the integrity of their roots and stems. The separation of roots and shoots was carried out. Then both roots and shoots were placed in the drying cabinet at 110 °C, where they were dried to a constant weight. Distribution of biomass was calculated by the formula:

$$\mathbf{R}:\mathbf{S} = \mathbf{m_{roots}}/\mathbf{m_{shoots}},$$

where $\mathbf{R}:\mathbf{S}$ – roots/shoots ratio; $\mathbf{m_{roots}}$– dry weight of roots, g; $\mathbf{m_{shoots}}$– dry weight of shoots, g.

Analysis of the value of biomass allocation determined how does the phosphorus source affects the development of roots and stems of wheat.

Results and discussions

According to the above plan of the experiment, the plants were growth and analyzed. Fig. 2 presents the growth rate of all plants depends on the aluminum dose, coagulant type and type of water at the 12th day of the experiment.

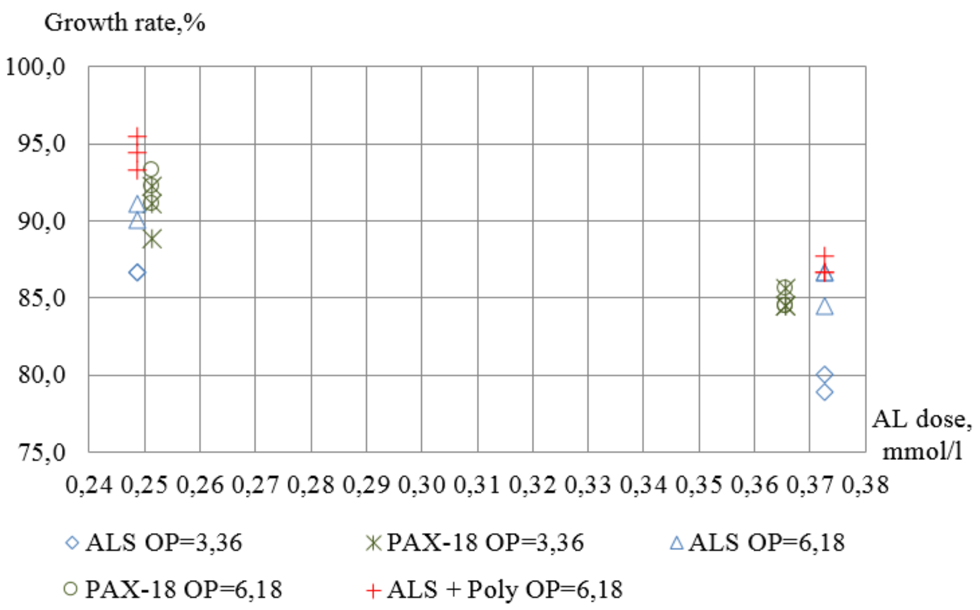
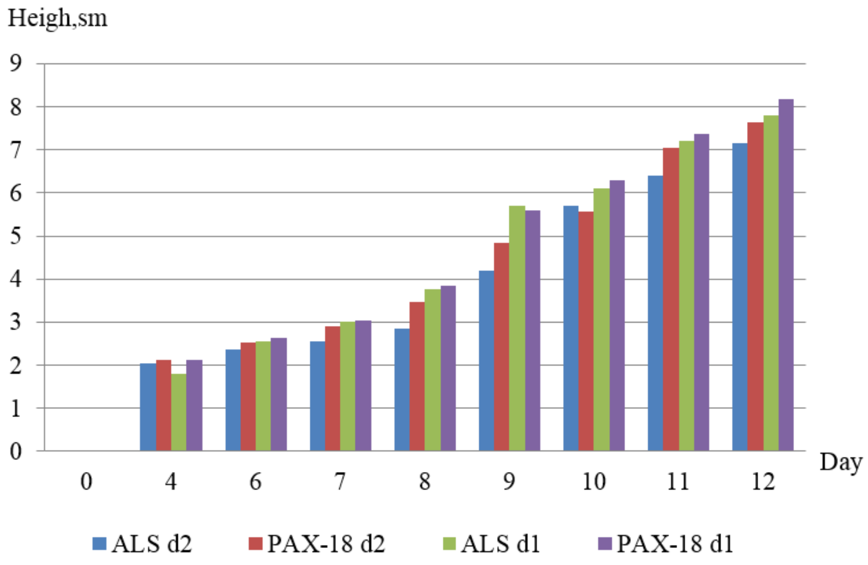
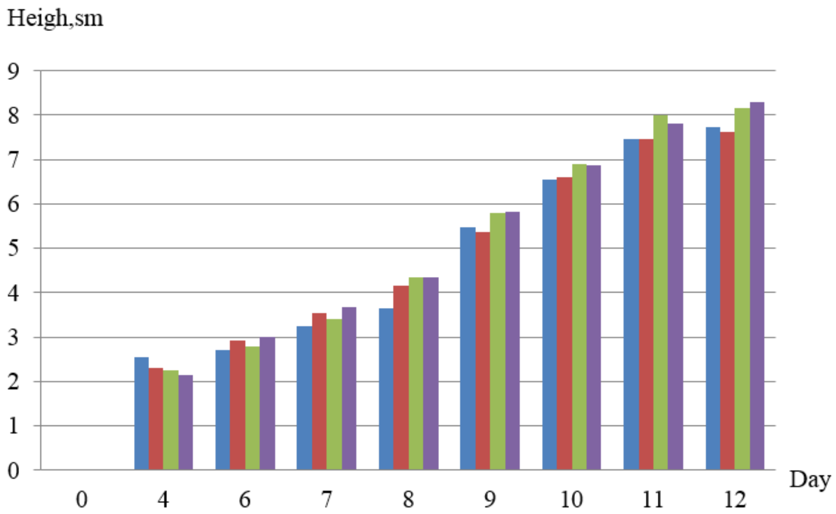


Figure 2. Dependence of the growth rate from the dose of aluminum, coagulant type and water type.

As it is seen from the graph, the deviations of growth rate values of wheat between each three parallel experiments are insignificant. This demonstrates the adequacy of the results. Therefore, for making next figures the average values of plants height between three parallel experiments were used. Fig. 3 (a, b) shows the results of determining the influence of aluminum coagulant's with different (OH/Al) ratios on PAP availability of coagulated sludge.



a)



b)

Figure 3. Height of wheat depending on the coagulant dose and type of water for each day of the experiment:

a) Orthophosphates content in water 3,36 mg P/l;
b) Orthophosphates content in water 6,18 mg P/l.

From the graphs, it is clear that with the use PAX-18 as a coagulant wheat is growing better comparing to AlS use. In addition, a smaller dose of coagulant during water treatment is added, there is a more intensive growth. This is fully consistent with the expected results.

Moreover, it should be noted that while using the same doses of AlS with an increase of raw water orthophosphates content – growth rate increases. At the time when the PAX-18 is used, growth rate with both types of raw water showed the same results.

To study the impact of the polymer addition simultaneously with coagulant during the coagulation Fig. 4 is shown.

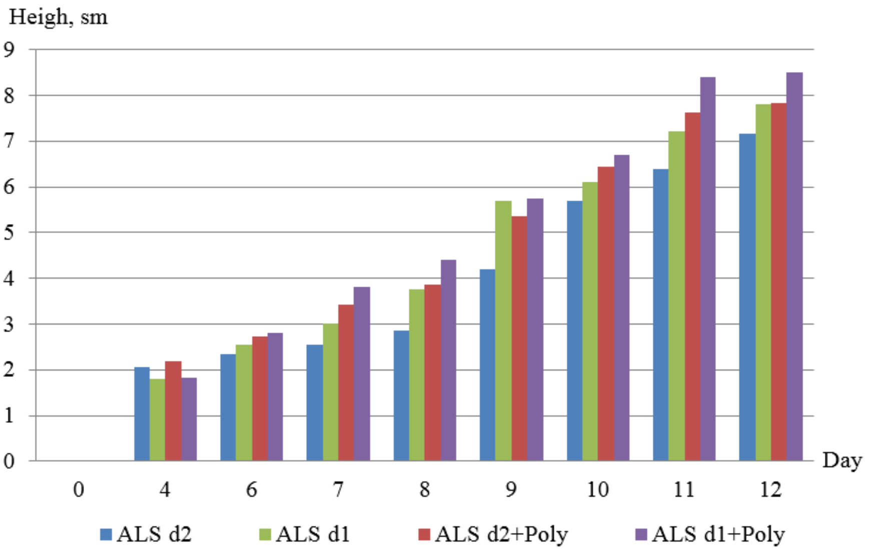


Figure 4. The dynamics of the wheat growth with the use of sludge obtained by coagulation with AlS with and without addition of polymer 4350 when the content of orthophosphates in water is 6,18 mg/l.

It can be concluded, that the addition of polymer increase the growth of wheat, compared with the only use of coagulant. Moreover, it should be noted that by the addition of polymer we can obtain even better results comparing to PAX-18 without polymer. It can be concluded comparing figure 3b and 4. This means that the addition of polymer increase PAP significantly.

The plant availability of phosphates cannot be measured only by height of the plants and growth rate. Because these plants can have weak roots, which adversely affects the development of plants, despite its rapid growth. Therefore, we analyzed the biomass allocation between the root and the shoots of each sample. Fig**.** 5 shows the results of this analysis.

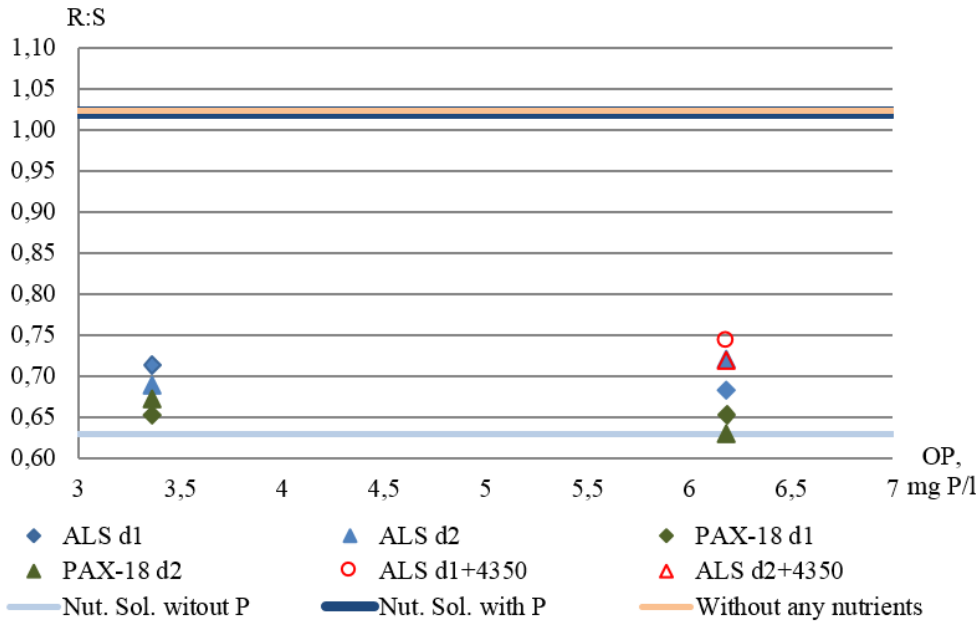


Figure 5. Biomass allocation of plants between the root and stem depending on the conditions of coagulation.

Thus, the samples of wheat, which were grown without adding any nutrients and those to which was added the nutrient solution with phosphorus, have the highest roots-shoots ratio. First of all, it indicates a good balance of nutrients in the solution. Secondly, these samples have normally developed strong roots. Those samples which were grown with the nutrient solution without phosphorus have the lowest roots-shoots ratio. It is explained by a lack of phosphorus, which is not only reflected in the growth rate of shoots, but also adversely affected the development of the root.

As for those samples that were grown with the addition of sludge as a source of phosphorus, the roots-shoots ratio is much lower than the normal value. This indicates that the part of phosphorous is unavailable for plants. Moreover, the use of a polymer with coagulant increases the roots-shoots ratio.

Additional analysis of aluminum content in sludge, which was obtained during coagulation with and without polymer addition, shows that:

- when polymer addition, Al/P ratio of coagulated sludge is 0,1367;
- without polymer addition, Al/P ratio of coagulated sludge is 0,1067.

This data is hard to explain because the mechanism of polymer reaction is not well studied yet. It can be suggested that polymer bonds more aluminum during coagulation and flocs that are produced are bigger and stronger. Due to that more phosphorous can be removed by adsorption of phosphate ions on flocs surface. And this phosphorous is more available because it is adsorbed but it's not bonded with aluminum. That's why PAP is higher comparing to the sludge without polymer.

Conclusions

It was planned and conducted an experiment for improving the plant availability of phosphorus from coagulated sludge, by trying different doses of AlS and PAX-18. The influence of OH/Al ratio of coagulant on PAP was studied. When PAX-18 is used as a coagulant the PAP is higher comparing to ALS due to higher OH/Al ratio.

At the same time it was made a research of influence of adding polymer simultaneously with AlS during the process of wastewater treatment may increase the PAP. The results show that the sludge by the level of available phosphorous is ranked AlS < PAX-18 < AlS+Poly.

There is also a relationship between the dose of coagulant and availability of phosphorus for plants: the smaller the dose – the greater availability of phosphorus. This can be explained that when adding less Al to wastewater – less phosphorus is binding by P-Al bond, which is very hard to break.

Recommendation for further research

It is proposed in the future to make more accurate and detailed experimental design based on the problems that occurred during this work, and perform research with larger number of coagulants and their combinations with different polymers. The experiment with aluminum coagulants with different OH/Al ratio will allow to understand the influence of OH/Al ratio of coagulant on PAP availability of coagulated sludge. Moreover, it is important to try ferric coagulants as well.

In order to determine the plants availability of phosphorus in sludge, obtained by coagulation treatment of domestic wastewater, it is necessary to conduct additional analysis of main nutrients (N, P, K) content of wheat samples. This will allow to determine how much phosphorous was available for plants.

It is also important to make a longer experiment to see the prolonged influence of sludge as a source of phosphorous on plants. Furthermore, it is necessary to study the influence of different types of sludge's treatment (dewatering, heating etc.) on sludge's properties as a fertilizer.

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