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PLANT AVAILABILITY OF PHOSPHORUS IN ASH, CALCIUM PHOSPHATE AND DIFFERENT TYPES OF SEWAGE SLUDGE

Fosforns växttillgänglighet i olika typer av slam, mineralgödsel samt aska

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Abstract

Different types of phosphorus fertilizer were evaluated in a three-year field experiment with oats and barley in mid-western Sweden. The treatments were, except a control, mineral fertilizer (calcium phosphate); ash; sewage sludge precipitated with iron, aluminium or lime; and biologically treated sewage sludge. To ensure that only the effect of the phosphorus source was evaluated, all differences in nitrogen, potassium and lime were compensated for. The treatment plot size was 8 x 40 m^2 and the experiment was repeated in three blocks.

During dry conditions (first experimental year) the easily soluble phosphorus in calcium phosphate (mineral-P) gave better crop growth than all other treatments. In the two following years, there were no significant differences between the treatments. The results show that successful phosphorus fertilization involves keeping the soil in a state in which it can supply the crop with phosphorus when other conditions are optimal.

Although three years of field experiments is too short a time for evaluation of fertilizers, the results indicate that in the long run, crop supply of phosphorus is more dependent on a correct comprehensive evaluation of soil type - crop – fertilizer than on the chemical form of the phosphorus in the fertilizer.

Key words – recycling, sewage sludge, precipitation chemicals, field experiment, phosphorus.

Sammanfattning

I ett fältförsök med havre och korn studerades fosforns växttillgänglighet. Försöket var treårigt och låg i Långshyttan. De fosforgödselmedel som studerades var mineralgödsel, aska samt järnfällt-, aluminiumfällt-, kalkfällt- och biologiskt slam. I försöket ingick även ett kontrolled som inte fick någon fosforgödsel. Försöket kalkades delvis. Försöksplatsen hade normal halt av fosfor i jorden. Fosfortillförseln var mängdmässigt lika i alla behandlingar utom kontroll och utgjorde 45 kg fosfor/ha, dvs. motsvarande bortförsel av fosfor med grödan under 3 år. Alla behandlingar gödslades alla tre försöksåren med kväve och kalium i mängder som var normala för området.

Första året visade alla behandlingar, utom den med mineralgödsel, fosforbrist på grödan,. Detta år (1994) var mycket torrt och mineraliseringen av det organiskt bundna fosforn gick sannolikt långsamt. År 2 och år 3 fanns det inga signifikanta skillnader mellan skörden från de olika gödslingarna. Skördenivån var låg 1994 och 1995, men 1996 var ett rekordår med extremt hög skördenivå för området. Den stora skörden sista året visade att en mark med normal fosforhalt kan klara av att försörja grödan med fosfor utan extra fosfortillförsel, om tillväxtbetingelserna är gynnsamma.

Växternas försörjning med fosfor i det långa perspektivet är mer beroende av en riktig helhetsbedömning av jordart, gröda och gödsling, än av vilken form fosforn har i gödselmedlet.

Introduction

Nutrients from human food digestion travel with waste-water to a waste water treatment plant (WWTP). During the 1970s, treatment plants in Sweden introduced chemical precipitation of phosphorus, also called tertiary treatment, to avoid heavy eutrophication of lakes and rivers. Iron and/or aluminium salts are most commonly used as precipitation chemicals, or more rarely lime. In the chemical sludge, phosphorus is precipitated or flocculated, as different types of phosphates or hydroxides (5). In Sweden, an activated sludge method is commonly used for biological treatment (secondary treatment) of wastewater. Excess sludge from this treatment step is normally mixed and treated together with the chemical sludge.

Phosphorus in soil

The topsoil (0–20 cm depth) often contains several tons of phosphorus per hectare (2). It can, however, only deliver about 10 kg of phosphorus to the crop annually. A large proportion of the phosphorus in the soil is chemically bound or adsorbed to aluminium, iron and/or calcium occurring naturally in the soil (2). About 30–70 % of the phosphorus content of the soil can be found in the organic fraction (14). The nutrients become available when the organic material is mineralised (27).

Easily soluble calcium phosphate added to the soil as fertilizer is transformed into other phosphorus fractions not easily available to the crop.

Phosphorus in sewage sludge

Sewage sludge contains biologically bound phosphorus, flocculated phosphate ions and chemically bound phosphorus depending on the origin of the wastewater, treatment of the wastewater and sludge and precipitation chemical used.

Lime is rarely used for precipitation, but can be used for hygiene reasons in a step after the precipitation. More recently, biological removal of phosphorus has been introduced in some plants.

Aluminium

When a non-alkaline aluminium salt is added to wastewater, the phosphate is chemically bound or flocculated to aluminium. The reaction can be described by:

$$Al^{3+} + (3-x)H_20 + {}_xH2PO_4^- > Al(OH)_{3-x}(H_2PO_4)_x + (3-x)H^+$$

or

$$Al(OH)_3 + xH_2P0_4^- > Al(OH)_{3-x}(H_2PO_4)_x + xOH^-$$

Iron

Iron(III) salts can be used as a precipitation chemical in the pH range 4–8 (5, 11).

The phosphorus and hydroxide precipitation can be described by:

$$3Fe^{3+} + 2P0_4^{3-} + 3H_2O > (FeOH)_3(PO_4)_2 + 3H^+$$

$$Fe^{3+} + 3H_2O > Fe(OH)_3 + 3H^+$$

Iron(II) salts cannot be used to flocculate organic matter, only to bind phosphorus:

$$3Fe^{2+} + 2PO_4^{3-} > Fe_3(PO_4)_2 + 2H^+$$

This means that these salts can only be used for simultaneous precipitation in combination with, for example, biological flocculation:

$$4Fe^{2+} + O_2 + 2H_2O > 4Fe^{3+} + 4OH^-$$

$$Fe^{3+} + 3H_2O > Fe(OH)_3 + 3H^+ \ (11).$$

Lime

Some sewage treatment plants use slaked lime as a precipitation chemical:

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- > Ca_{10}(PO_4)_6(OH)_2$$

The amount needed in the process is dependent on the alkalinity of the wastewater and the content of carbonate, but not the phosphorus content in the water.

The carbonate is precipitated as calcium carbonate above pH 9 (11):

$$Ca^{2+} + CO_3^{2-} > CaCO_3$$

Lime can also be used in the final treatment of the sludge. If slaked lime is added before dewatering the sludge, the result is sludge almost free from odour and easier to dewater. Sometimes lime is used for sanitary reasons. If quicklime is added after dewatering, an intense increase in temperature in the sludge occurs and this has a sterilising effect together with the increase in pH.

Objectives

The plant availability of phosphorus, which is bound to aluminium and/or iron in the soil, has been discussed in many studies (2, 6, 13, 17, 18, 19, 28, 30). The plant availability of phosphorus in chemical sludge has also been investigated, with varying results (3, 4, 7, 8, 9, 10, 12, 13). Some authors conclude from experiments that plant availability of phosphorus in sewage sludge is low (6, 30), others the opposite (4) and in some studies no differences have been observed (13). One of the reasons for the diverging conclusions could be that very high doses of phosphorus have been used. For example, Vigerust (29) added the equivalent of 970 kg/ha of phosphorus in the sludge together with 80 kg/ha of mineral-P in a pot experiment. Other reasons could be that no or little compensation has been made for effects of other available nutrients in the fertilizer investigated (3) or too short an experimental period (12).

A problem when working with sewage sludge experiments is that every sludge is unique and contains several elements that can affect the yield. Kuile et al. (12) studied oilseed rape grown for 25 days and showed that chemical sludge precipitated with lime had a fertilizing effect of 111–136 % compared to mineral-P. Gestriing and Jarrel (4) used chemical sludges to which different kinds of precipitation chemicals had been added to grow mangolds in pots in a greenhouse. Phosphorus was not a limiting factor in the soils used. The yield of mangold was lowest in the treatment with mineral-P. These results indicate factors in addition to the phosphorus content in the fertilizer are responsible for the observed differences in yield. Probable factors could be nitrogen, potassium or lime in added sludge or increased mineralisation of organic matter in the sludge treatments, which increases the available phosphorus and nitrogen in the soil.

During the 1990s, an increasing amount of sludge was incinerated in Europe. The possibility of using such ash as a phosphorus fertilizer had not been properly investigated. Erich and Ohno (15, 16) carried out experiments with wood ash and came to the conclusion that the availability of phosphorus in ash from burnt wood was dependent on the properties of the soil. The same conclusion was drawn from field experiments in Finland with different ashes (20, 21). The positive effect of wood ash on fertile clay soil is probably an effect of increased pH.

Very few studies concerning phosphorus availability have been carried out as field experiments. The aim of the present study was to clarify, in a three-year field experiment, the value of ash and different types of sludge as phosphorus sources for a cereal crop. To ensure that only the effect of the phosphorus source was evaluated, all differences in nitrogen, potassium and lime were compensated for.

Materials and methods

Field, soil and place

A three-year field experiment was set up in Långshyttan in mid-western Sweden (60 27 04N, 16 02 21E). The site was chosen for its relatively low content of phosphorus in the soil, the phosphorus status of which was 5.1 mg P soluble with ammonium lactate and 44 mg P/100 mg air-dried soil soluble with HCl, which means P-AL = 3 and P-HCl = III in the Swedish soil classification system (23) The soil was a silty clay loam with a humus content of 5 % and pH (H_2O) 5.7.

The treatment plot size was 8 x 40 m² and the treatments were carried out in three blocks.

Fertilizers used

The following phosphorus fertilizers were used as treatments in addition to a control.

1. Iron precipitated sludge (Borlänge WWTP). The precipitation chemical used was iron chloride.
2. Aluminium precipitated sludge (Sågmyra WWTP). The precipitation chemical used was AVR (aluminium 8.2 % by weight and iron 1 %).
3. Lime precipitated sludge (Idre WWTP). The chemical used was slaked lime.
4. Biological sludge from the pulp and paper industry (Stora Kvarnsveden AB, Borlänge).
5. Easily soluble calcium phosphate, called mineral-P (Hydro Agri).
6. Ash from incineration of biological sludge co-incinerated mainly with wood, but also some coal (Stora Kvarnsveden AB, Borlänge).

The content of nutrients in the fertilizers used is shown in Table 1.

Lime

The lime used was ground limestone ($CaCO_3$) containing 50 % of CaO. In total, 2500 kg per hectare of limestone was applied, which means 1250 kg CaO/ha.

Potassium and nitrogen

Potassium and nitrogen were applied as ammonium nitrate potash (NK 20–15). Extra nitrogen was applied as calcium ammonium nitrate (CAN 27.5).

Table 1. *P-fertilizers used in field experiment 1994.*

	DM %	Tot N % DM	NH_4-N % DM	P % DM	K % DM	CaO % DM
Fe-ppt. sludge	45.4	2.1	0.53	1.7	0.2	
Al-ppt. sludge	22.5	2.4	0.04	1.2	0.9	
Lime-ppt. sludge	22.2	1.4	0.09	0.7	0.5	
Biological sludge	17.6	5.1	0.11	0.5	0.4	
Ash	39	0.2	<0,1	0.5	1.5	14
Method	SS028113	Kjeldahl	KLK 1950 nr 7 mod	ICP AES	ICP AES	KLK 1950 nr 7 4:59
Mineral-P		0	0	9	0	
Method	Information from the producer Hydro Agri					

Nutrient content in the phosphorous fertilizer used in the field experiment.

Table 2. *Fertilizing of a three year field experiment in Långshyttan.* All values in kg/ha.

Phosphorous source	1994 N added min-N	1994 N assumed release from sludge	1994 P	1994 K	1995 N added min-N	1995 N assumed release from sludge	1995 P	1995 K	1996 N added min-N	1996 N assumed release from sludge	1996 P	1996 K
Control	70	0	0	40	70	0	0	40	60	0	0	40
Iron precipitated sludge	65	5	45	40	65	5	0	40	60	0	0	40
Aluminium precipitated sludge	65	5	45	40	65	5	0	40	60	0	0	40
Lime precipitated sludge	65	5	45	40	65	5	0	40	60	0	0	40
Biological sludge	55	15	45	40	55	15	0	40	60	0	0	40
Mineral phosphorous	70	0	45	40	70	0	0	40	60	0	0	40
Ash	70	0	45	40	70	0	0	40	60	0	0	40

The P source was only applied in the first year. All treatments except the control received 45 kg P/ha. N fertilization was 70 kg/ha in the first year and 60 kg/ha in the second. Most of the N was applied a mineral-N and the rest assumed to be released from the P-fertilizer. In the third year any differences in nitrogen release from the sludge wew assumed to be levelled out. All treatments got 40 kg of potassium every year.

Experimental plan

All treatments except the control were fertilized in the spring of the first experimental year with 45 kg of phosphorus per hectare from the different fertilizers used. The amount was chosen to cover the three-year study period, as a normal crop in the area removes about 15 kg of phosphorus per year and hectare in the grain. No phosphorus was added to any treatment in the second and third year.

All treatments received 55 kg nitrogen per hectare as a basic amount in years one and two. In addition to this, extra nitrogen was given to compensate for the different nitrogen levels in the different phosphorus fertilizers used. The organic bound nitrogen in the biological sludge was assumed to be released over at least two years. This means in total that all the treatments, including the control, received about 70 kg of N/ha in the first and second year. In the third year, any differences in nitrogen levels were assumed to be levelled out and all treatments received 60 kg of nitrogen per hectare. In addition, 40 kg of potassium was given to all treatments every year (Table 2).

Two of the fertilizers investigated, lime precipitated sludge and ash, probably had liming effects. To investigate this, half the treatment plots were given ground limestone, 2 500 kg/ha.

Sowing, fertilizing, harvest

The sludges and the ash were spread with conventional farming equipment tested for the purpose. The potassium and nitrogen were drilled. The crops grown were oats (1994) and barley (1995, 1996).

Precipitation

Precipitation (Table 3) was recorded daily at the site.

Statistics

The grain yield in kg DM/ha was statistically analysed as a row-column design in three blocks. In each block the columns consisted of the different treatments (fertilizers) and the two rows of liming and no liming (22).

Results

Grain yields in the first year

The mean yield of oats (Table 4) was 1873 kg DM of grain/ha in the unlimed plots and 2175 kg DM of grain/ha in the limed plots. Normal yield in the area was 3235 kg DM/ha (24).

Table 3. *Sowing and harvesting dates and monthly precipitation (mm) during the three growing seasons.*

	1994	1995	1996
May	14	64 (before sowing)	55
June	46	90 (after sowing)	31
July	31	32	63
August	47	48	106
September	126	31	21
Sowing	16 May	7 June	3 June
Harvest	2 Sep.	26 Sep.	28 Sep.

Table 4. *Harvest Långshyttan 1994–1996.* Grain yield kg DM/ha.

Treatment	1994 Oat unlimed	1994 Oat limed	1994 Oat total mean	1995 Barley unlimed	1995 Barley limed	1995 Barley total mean	1996 Barley unlimed	1996 Barley limed	1996 Barley total mean
Control, no P	1638	1767	1702 d	2896	3268	3082	4758	5163	4960
Fe-ppt. sludge	1721	1872	1796 cd	3068	3396	3232	4844	5270	5057
Al-ppt. sludge	1797	1946	1872 bcd	3078	3271	3174	4917	5150	5034
Lime-ppt. sludge	1798	2209	2004 bc	3142	3524	3333	4989	5138	5064
Biological sludge	1833	2280	2056 b	2860	3170	3015	4877	5122	5000
Min-P	2200	2591	2396 a	2977	3249	3113	4934	5149	5042
Ash	2124	2559	2342 a	3108	3354	3231	4965	5253	5109
Mean	1873	2175	2024 *	3018	3319	3169	4898	5178	5038
Standard error			77, 1	Non-sig.	Non-sig.		Non-sig.	Non-sig.	

* Treatment means with the same letter are not significantly different at p= 0,05 level.
n=3.

The total mean yield of oats was significantly higher in the treatments with mineral-P and ash than in the control or in the sludge treatments (Table 4). This was also the case for total nitrogen and phosphorus (kg/ha) in the harvested grain.

There was a tendency for the lime to increase the yield in all treatments (Table 4). The biological sludge gave a significantly higher yield of nitrogen in the straw compared with unlimed treatment.

In the first experimental year, when the phosphorus was added, there were visible effects on the yield of biomass. In the middle of July it was apparent that the treatment with mineral-P gave a higher and more vigorous crop than the other treatments (Figure 1). The treatments with sludge and the control showed symptoms of lack of phosphorus (1).

One year after phosphorus fertilization

The second year of the experiment also had relatively low precipitation in July and August (Table 3) and the mean yield was 3169 kg DM of barley per ha. This was slightly more than the average yield in the area (2970 kg DM/ha, 25). There were no significant differences in grain yield between the different treatments. However, there was a significant difference between limed and unlimed treatments regarding phosphorus content in the grain (0.40 and 0.36 % of DM respectively, $p = 0.003$) and yield of straw (1241 and 986 respectively, $p = 0.026$).

Two years after phosphorus fertilization

The mean yield of grain (5038 kg DM/ha) was high for the experimental area in the third experimental year, where the average normal yield for the region was 2990 kg/ha (26). There were no significant differences in

Figure 1. *The first experimental year the treatment with mineral-P gave a higher and more vigorous crop than other treatments.* Photo: Kersti Linderholm.

grain yield between the different treatments or the control. Variables showing significant differences in the third year are shown below (Table 5).

Discussion

The first year of the field experiment was very dry and mineral-P had a significantly better effect on the crop (oats) than all other treatments, except ash. The exceptionally dry conditions after application of the fertilizers probably made it difficult for the microorganisms in the soil to transform the phosphorus added in sludge to plant available forms. Under dry weather conditions, it is apparently important for the plants to have access to easily soluble phosphorus in the soil, since the soil has problems in supplying sufficient phosphorus from mineralisation of the organic and inorganic pool in these conditions. There were no differences between the yields in the different treatments in the second and third years. Lime added to the soil, in sludge or separately, tended to increase the yield and the availability of phosphorus but the results were not statistically significant.

Despite dry growing seasons in all three years, it was possible to clearly see positive effects of the added lime. This could be a result of microorganisms being stimulated to make extra biologically bound nitrogen available for the plants. Ample access to nitrogen late in the season gave a relatively high content of nitrogen in the harvested straw. The reason why all the treatments except mineral-P gave a significantly lower grain yield than ash in the first year could be an liming effect of the ash.

It was noticed in July of the first experimental year that the treatment with mineral-P showed a much more vigorous crop than the other treatments. It appeared unlikely that this effect was solely due to easily available phosphorus because visible phosphorus deficiencies are nowadays rare. The possibility of sulphur deficiency was ruled out because although the mineral-P used supplied the oat crop with 4.5 kg of sulphur per hectare, oats in neighbouring areas fertilized with a 20: 3: 5 NPK product containing 0 % sulphur had equally vigourous growth.

The most astonishing result of this field experiment was that the chosen "average" field, lying in a typical grassland area with poor conditions for cereal production, gave an extremely high yield overall (an average of over 5000 kg DM grain/ha) in the third year of the experiment. There were no significant differences between the different treatments. This result indicates that successful phosphorus fertilization is a question of keeping the soil phosphorus status high so it can supply the crop requirements when conditions are optimal. On the other hand, the low yields in the first and second years show that access to NPK nutrients cannot give a sufficiently high yield if the plants are stressed by water or temperature deficiencies.

Table 5. *Variables showing significant differences in the third year of the experiment.*

Parameter	Units,	Unlimed	Limed	p-value
P in grain	% of DM	0.42	0.43	0.027
K in grain	kg/ha	26.5	29.3	0.035
Straw	kg DM/ha	2791	3245	0.031
N in straw	kg/ha	18.6	21	0.031
P in straw	kg/ha	2,5	3,6	0.027
K in straw	kg/ha	75	90	0.048

Mycorrhizal fungi and their symbiosis with agricultural crops also play a part in the delivery of phosphorus to plants. A study was made of mycorrhizal activity in soil samples from this field experiment and is reported in a separate paper.

General conclusions

Easily soluble phosphorus is of the utmost importance for the plant in a short-term perspective under dry conditions. Plants can show a lack of phosphorus in dry years when phosphorus is added to the soil in an organic form.

On the other hand, a soil with average phosphorus content can deliver enough phosphorus to give a very high yield of grain in a year with optimal moisture and temperature, without any additional phosphorus being added.

In a long-term perspective, the form of phosphorus fertilizer used, seems to be less important than a soil in balance between moisture, air, temperature and fertilizer. It is important to maintain the phosphorus content in the soil to guarantee phosphorus delivery to the crop in the future. Mycorrhizal fungi and their symbiosis with agricultural crops also play a part in the delivery of phosphorus to plants. A study of mycorrhizal activity in soil samples from this field experiment is made and presented in a coming paper.

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