

# DESCRIPTION OF SOIL AND BBFs CHARACTERISTICS AFFECTING PHOSPHORUS LEACHING

Deliverable 3.4 – D16 – WP3

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# OPTIMISING BIO-BASED FERTILISERS IN AGRICULTURE – PROVIDING A KNOWLEDGE BASIS FOR NEW POLICIES

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# Deliverable 3.4 – D16

Work-package n°3

Nature of the deliverable						
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Dec	Websites, patents, filling etc.					
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LEX4BIO aims to reduce the dependence upon mineral/fossil fertilisers, benefiting the environment and the EU's economy. The project will focus on collecting and processing regional nutrient stock, flow, surplus and deficiency data, and reviewing and assessing the required technological solutions. Furthermore, socioeconomic benefits and limitations to increase substitution of mineral fertiliser for BBFs will be analysed. A key result of LEX4BIO will be a universal, science-based toolkit for optimising the use of BBFs in agriculture and to assess their environmental impact in terms of non-renewable energy use, greenhouse gas emissions and other LCA impact categories. LEX4BIO provides for the firsttime connection between production technologies of BBFs and regional requirements for the safe use of BBFs.

The project runs from June 2019 to May 2024. It involves 20 partners and is coordinated by Luke (Luonnonvarakeskus - Natural Resources Institute Finland).

More information on the project can be found at: <u>http://www.lex4bio.eu</u>





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# D3.4: DESCRIPTION OF SOIL AND BBFs CHARACTERISTICS

# AFFECTING P LEACHING

# 1. SUMMARY

In this study we evaluated phosphorus (P) leaching in a rainfall simulation of agricultural soils originating from Finland (FIN; acidic soil), Germany (GER; slightly above neutral) and Spain (SPA; calcareous soil) after a three-week incubation period with different types of bio-based fertilisers (BBF). Following BBFs were used: Bioagenasol (BA1), Monterra 2-14-4 (MO14), meat and bone meal (MB1), struvite (CGO), AshDec (ADC), chicken manure pellets (OPU), EcoPlant-Humi (EPH), poultry litter ash (PLA), dicalciumphosphate (DCP), pyrolyzed chicken manure (MBC) and digested and composted pig slurry (CPS). Common mineral P fertiliser, triple superphosphate (TSP), was used as a reference P source.

Both soil and BBF characteristics were considered to determine factors affecting P losses. Iron- and aluminium-oxides in acidic FIN soil adsorbed P and reduced P leaching, whereas in calcareous SPA soil P was precipitated as insoluble calcium phosphates. In the GER soil having pH slightly above neutral, DRP losses were at the highest level, probably due to low content of iron- and aluminium oxides and soil pH too low for P precipitation as insoluble calcium phosphates. Soil P testing (SPT) methods that are commonly used for determining fertilisation requirement, did not predict well P losses, especially so calcium ammonium lactate with the lowest pH (pH 4.1) among the SPT methods applied. In studies involving soils with highly variable characteristics, conventional SPT methods for predicting P losses should be interpreted cautiously.

All the studied BBFs caused lower total P losses than TSP in FIN and GER soils, whereas in calcareous SPA soil P sources commonly caused lower total P concentration in the leachates than in FIN and GER soils. However, several BBFs (MO14, MBC, EPH, PLA), with high proportion of low soluble P content, caused lower total P losses than TSP in SPA soil, whereas BBFs having both easily mineralizable carbon pool and high share of water-soluble P content caused equal total P losses as TSP in SPA soil. Furthermore, most of the BBFs increased electrical conductivity (EC) of the leachates, depressing turbidity, and consequently particulate P losses. Especially EPH decreased particulate P losses in all soils, and even to a lower level than in the control treatment with no P addition. Inorganic BBFs, ADC, CGO, DCP and TSP, had no effect on EC of the leachate, and these P sources also increased DRP losses in FIN and GER soils. Also, BA1 (GER soil) and CPS (FIN and GER soils) increased DRP losses. In calcareous SPA soil, TSP, DCP and CPS increased DRP losses to the highest level, whereas application of the other BBFs led to the lower DRP losses than TSP.

This study clearly demonstrated that P losses are affected both by soil and BBF properties. Until now nutrient-rich side-streams are mainly utilized at the close vicinity of the production sites, whereas new Fertilising Products Regulation (2019/1009) permits transportation of CE-marked fertilisers across the EU. For minimising P losses to surface waters in association with their use as fertilisers, both soil and BBFs properties needs to be considered.



# 2. INTRODUCTION

Since the Second World War, increased agricultural production has strongly relied on availability of mineral fertilisers for ensuring food production. Intensive animal production has also created regions with surplus of nutrients due to manure disposal. Unbalanced use of both mineral and manure-based nutrients, mainly nitrogen (N) and phosphorus (P), has increased environmental deterioration through nutrient leaching, and clear evidence from this is eutrophication of surface waters. Urbanisation has also led to situation where sewage-sludge based nutrients are concentrating to small areas. Both manure and sewage-sludges form the main source of nutrient-rich side-streams (NRSS) but their utilization in agriculture has mainly taken place at the close vicinity of the production sites, sometimes at excessive rates for covering crop needs. This can lead to very high soil P status, often called as legacy P (Recena et al., 2022; Ylivainio et al., 2014). Also, their value as a fertiliser is often neglected and they are mostly considered wastes.

For minimizing P losses to the environment and avoiding excessive P concentration in soils, fertilisation should be based on crop demand. This would mean transporting of P originating from NRSSs to regions with actual P demand. Optimizing the use of NRSS provides also means for reducing EU's dependency on mineral P fertilisers. Until recently, only transportation of mineral P fertilisers across the EU took place. Bio-based fertilisers (BBF) originating from NRSS required mutual recognition to cross borders, limiting transportation of BBFs across the EU.

The new Fertilising Products Regulation (2019/1009) that came into force in the EU on 16<sup>th</sup> of July 2022, allows a free movement of CE-labelled fertilisers across the EU. Depending on the properties of the CE-labelled fertilisers, they can be divided into different Product Function Categories (PFC), i.e. organic, organo-mineral and inorganic fertilisers. Another classification, in component material categories (CMC), is based on the starting material and processing technologies. Due to various NRSS and technologies for producing BBFs, several CMCs are relevant, such as compost (CMC 3), digestates (CMC 4, 5, 6), animal by-products (CMC 10), precipitated phosphate salts (CMC 12), ashes (CMC 13) and pyrolyzed material (CMC 14). The various combinations of both NRSS and production technologies result in a large variation of BBF properties.

Properties of agricultural soils vary across Europe, from calcareous soils with low organic matter frequent in the Mediterranean region to acidic, high organic matter content soils in the Boreal region in Northern Europe. The great variation in both soil properties across the EU and composition of BBFs means that BBFs do not behave alike each other, or alike in different soils. Diverse effect of BBFs affects P solubility and thus P losses to surface waters. In this study we incubated typical agricultural soils from Spain, Germany and Finland with various types of BBFs, conducted a rainfall simulation and evaluated effects of both soil and fertiliser properties on P leaching.

# 3. MATERIALS AND METHODS

# 3.1. Criteria for the soils used in a rainfall simulation and their properties

Experimental soils for rainfall simulation originated from Finland, Germany and Spain (Fig. 1). Soil samples were taken from the soil surface layer (0-20 cm). For the rainfall simulation the aim was to select a field that had no excessive P content and, according to current local P fertilisation recommendations, required P fertilisation for the optimal yields. The Finnish field had been under



grass during the previous two growing seasons and was fertilised with manure before establishing grass in 2018. The field was ploughed in autumn 2020 and soil samples were taken from top of the ploughing veneer in November 2020. The German field was cultivated with winter wheat (2018/2019), mustard as cover crop for maize (2019/2020) and maize (2020). The field was fertilised with mineral fertiliser only (calcium ammonium nitrate every year, magnesium sulfate in 2020) in amounts common for the respective crop, site and local farming practice. No organic materials were applied in the years preceding the sampling. Cultivation practices on Spanish field before soil sampling included fallow year before and wheat before that.



Figure 1. Red dots indicate soil sampling points (left). Finnish field sampled in November 2020 (right).

Soil samples were air-dried at room temperature and then sieved to pass 15 and 6 mm screen. For laboratory analyses soils were further passed through 2 mm sieve. Prior to analysing soil texture with a pipette method (Elonen, 1971), possible carbonates from soils originating from Germany and Spain were removed with acetic acid. Following soil testing method were used for analysing soluble P concentrations: Olsen-P (Kuo, 1996), acetic ammonium acetate, pH 4.65 (Vuorinen & Mäkitie, 1955) and calcium ammonium lactate (OENORM L 1087:2019-08-01).

Solubility of P in soils was also analysed with a sequential Hedley fractionation method (Sharpley & Moyer, 2000). Hedley fractionation consists of four sequential extractions: twice with water, then with  $0.5 \text{ NaHCO}_3$  (pH 8.5), 0.1 M NaOH and 1 M HCl, using in each step extraction ratio of 1:60 (w/v). Shaking was done in an end-over-end shaker (27 rpm) with extraction time of 16 h, except 4 h for the first water extraction. Samples were then centrifuged (3000\*g) for 15 min. Inorganic P (P<sub>i</sub>) was analyzed from supernatant passed through  $0.2 \mu m$  Nuclepore (Whatman) membrane filter. Total P was determined from unfiltered supernatant after autoclave digestion at 120°C with sulfuric acid and peroxodisulfate. Concentrations of P in filtered (P<sub>i</sub>) and digested (total P) samples were analysed using the molybdate colorimetry method (Murphy & Riley, 1962). Organic P (P<sub>o</sub>) was taken as the difference between total P and P<sub>i</sub>. In-house reference soil sample was included in each batch of analyses to ensure quality of the analyses.

Total elemental concentrations (P, Al, Fe, Ca) were analysed with ICP-OES after *aqua regia* dissolution in a microwave oven and oxalate extractable Al, Fe and P concentrations with the method of Schwertmann (1964). Soil carbon and nitrogen concentrations were analysed after dry combustion (LECO 628). Soil pH and electrical conductivity (EC) was analysed from a soil-water suspension (1:2.5, v/v) and carbonate concentration with a Bernard calcimeter method (Black, 1965).



# 3.2. BBF selection and their elemental composition

For the study, BBFs with different properties were selected to cover a wide range of PFC/CMC categories described in the EU Fertilising Products Regulation (2019/1009). Total of 11 BBFs were selected for the rainfall simulation (Table 1), including all eight BBFs used in P response field trials in Spain, France, Hungary, Austria and Finland (Deliverable 3.1). These BBFs were Bioagenasol (BA1, wheat and maize residues from fermentation and distillation), Monterra 2-14-4 (MO14, vegetable by-products, animal protein and apatite to increase P content), meat and bone meal (MB1, Biorga Vianos), struvite (CGO, Crystal Green, Ostara), AshDec (ADC, calcinated phosphate, sewage sludge), Hühnermist (OPU, chicken manure pellets), EcoPlant-Humi (EPH, sunflower husk ash) and poultry litter ash (PLA, BMC Moerdijk). In addition to these BBFs also dicalciumphosphate (DCP, originates from sewage sludge ash, EasyMining), pyrolyzed chicken manure (MBC, Hitachi Zosen, Japan) and digested and composted pig slurry (CPS, Emomylly Ltd, Huittinen, Finland) were included to have wider selection of BBFs with different chemical properties. Common mineral P fertilizer, triple superphosphate (TSP), was used as a reference P source.

Studied P sources	PFC/ CMC	DM, %*	Ρ	N	С	Са	Fe	AI
Bioagenasol (BA1)	1A/4,6	90.4	13.6	62.1	478,7	1.3	0.2	<0.1
Monterra 2-14-4 (MO14)	1A/6,10	91.7	67.4	24.9	237.6	165.5	2.0	1.5
Biorga Vianos (MB1)	1A/10	97.6	63.4	81.3	362.1	129.0	0.2	<0.1
Ostara Green (CGO)	1C/12	54.8	227.5	101.5	4.0	4.0	5.6	0.1
AshDec (ADC)	1C/13	100	80.5	0.5	1.0	98.3	91.9	59.1
Chicken manure pellets (OPU)	1A/10	84.9	19.6	31.5	371.9	80.3	1.4	0.8
EcoPlant Humi (EPH)	1C/13	97.1	19.5	1.3	57.7	104.5	1.8	1.5
Poultry litter ash (PLA)	1C/13	92.1	52.3	0.1	6.1	157.5	4.9	11.4
DCP	1C/12	96.6	222.0	0.4	0.6	292.0	1.0	1.5
Chicken manure biochar (MBC)	1A/14	98.3	30.6	29.4	363.4	180.5	1.2	0.6
Digested, separated and composted pig slurry (CPS)	1A/5	93.3#	13.2	19.3	456.5	18.0	1.2	0.3
TSP	1C	93.0	221.0	0.5	6.5	190.5	1.3	1.9

Table 1. Elemental composition of the BBFs selected for the rainfall simulation, g kg<sup>-1</sup> DW.

\*Dry matter content determined from ground samples. <sup>#</sup>Dry matter content of fresh sample was 23.7% and was air-dried at 37 °C prior to grinding



For the laboratory analyses, all BBFs were ground with a ball mill. Total P, Al, Fe, Ca, C and N concentrations of BBFs were analysed as described for soil above. Hedley fractionation for BBFs was conducted as above as well. Dry matter content of BBFs was determined by drying the samples at 105°C for two hours.

# 3.3. Rainfall simulation

Prior to the rainfall simulation, BBFs and TSP were mixed with the experimental soils (1.1 kg as soil dry weight) and incubated for three weeks at a moisture content of 70% at pF2 (field capacity) at 20 °C (Fig. 2). Application rates of BBFs and TSP were based on total P at a rate of 100 mg kg<sup>-1</sup> soil. Each treatment was replicated three times. Water content during incubation was checked twice a week by weighing, and deionized water was used for replacing evaporated water.

After the three-week incubation period, 100 g of soil as dry weight was removed and air-dried for later analyses (pH, Hedley fractionation), and rest of the soil (1 kg DW) were transferred to a PVC cylinder (diameter 15 cm and average height of the soil column 6.8 ± 0.8 cm) with a nylon mesh at the bottom and slightly compacted (Fig. 2). Soils were moistened to pF2, covered with a lid, but ensured air ventilation, and rainfall simulation was started the following morning.

Rainfall simulation (Fig. 3) was conducted with an intensity of 5 mm h<sup>-1</sup> and three 100 ml leachates were collected. Turbidity, pH and electrical conductivity (EC) of percolated water were analysed immediately after water collection, followed by filtration (0.2  $\mu$ m) of small subsample (20 ml) for the analyses of dissolved elements. Both filtered and unfiltered samples were frozen for later analyses. Filtrated water samples were analyzed for dissolved molybdate-reactive P (DRP), NO<sub>3</sub>-N and NH<sub>4</sub>-N. Total P and N were analyzed from unfiltered water samples after acid peroxodisulphate digestion in an autoclave (120 °C, 100 kPa, 30 min). Concentrations of P and N were analysed with a Lachat autoanalyzer. Dissolved organic carbon (DOC) was analysed with Shimadzu TOC analyser after passing unfiltered water samples through GF/C (1.2  $\mu$ m) glass filters. In data processing, data for each replicate consists of average from three 100 ml subsamples.



Figure 2. Incubation of soils (left) prior to rainfall simulation (right).





Figure 3. Set-up for the rainfall simulation. Picture on the right shows the capillars that produced rain for the simulation.

## 3.4. Statistical evaluation

Data on percolation water quality obtained from rainfall simulations were analyzed with ordinary twoway analysis of variance with interaction, taking 0.05 as alpha threshold. The soils and fertilisers were included as explaining variables. Dunnet post-test was used to see if, for a given soil, parameter concentrations measured in percolation water of fertilized soil differ from those obtained from untreated control or TSP fertilized soils. Analyses were conducted by using GraphPad Prism 6, version 6.07 (GraphPad Software Inc., San Diego, CA, USA).

# 4. RESULTS

# 4.1. Soil properties

### 4.1.1. Experimental soils in the rainfall simulation

Soils from Finland (FIN) and Spain (SPA) were clay soils, whereas that from Germany (GER) was a clay loam (Table 2). Soil pH varied from slightly acidic (FIN), slightly above neutral (GER) to basic (SPA) reaction. Electrical conductivity varied alike soil pH, being highest in calcareous soil and lowest in the most acidic one. Soil P test values in the experimental fields were at the level that P fertilisation is recommended (Table 1). In Finland, acidic ammonium acetate, P<sub>AAAc</sub>, (pH 4.65) is the official soil testing method, whereas in Germany and Spain respective methods are calcium ammonium lactate (CAL) and Olsen-P. According to the P fertilisation recommendations, 10, 30-35 or 20 kg P ha<sup>-1</sup> are recommended for usual field crops such as cereals in Finland, Germany and Spain, respectively, when agricultural field soil would contain similar P status as the soils in this study.

Oxalate extraction provides information of soil P adsorption capacity, e.g. potential to adsorb P in less soluble form. Oxalate extractable iron (Fe) content was at the far highest level in slightly acidic FIN soil



as compared to GER and SPA soils (Table 1). Also, aluminium (Al) concentration was at the highest level in FIN soil.

## 4.1.2. Phosphorus content in the experimental soils

Commonly used soil testing P methods (AAAc, CAL and Olsen) extracted variably P concentrations from the experimental soils (Table 2). Olsen-P values were similar for FIN and GER soils, but was far less for SPA soil (Table 2). Soil testing method used in Finland (AAAc), having a pH of 4.65, extracted highest P concentration from GER soil and lowest one from SPA soil, whereas most acidic extractant, CAL (pH 4.1), extracted lowest P concentration from FIN soil and highest one from SPA soil.

Origin of soil	Finland (FIN)	Germany (GER)	Spain (SPA)
Soil texture, %			
Clay (<0.002 mm)	59.4	31.2	71.1
Silt (0.002 – 0.02 mm)	14.3	34.6	18.8
Fine sand (0.02 – 0.2 mm)	18.9	33.4	9.6
Sand (0.2 – 2 mm)	7.5	0.8	0.6
Carbon content, % (air-dry)	4.5	1.4	3.9
Soil pH (in water)	5.7	7.4	8.1
CaCO <sub>3</sub> content, %	not detected	not detected	30.5
Electrical conductivity, µS cm <sup>-1</sup>	1.5	2.5	2.9
Soluble P concentrations			
Olsen-P, mg kg <sup>-1</sup>	61.6	61.9	10.4
Acid ammonium acetate, mg l <sup>-1</sup>	8.0	42.0	2.3
Calcium ammonium lactate, mg kg <sup>-1</sup>	15	47	60
Hedley fractionation			
water-soluble (P <sub>i</sub> ), mg kg <sup>-1</sup>			
water-soluble (P <sub>o</sub> ), mg kg <sup>-1</sup>	7.0	35.6	4.2
0.5 M NaHCO <sub>3</sub> (P <sub>i</sub> ), mg kg <sup>-1</sup>	22.1	22.6	10.9
0.5 M NaHCO <sub>3</sub> (P₀), mg kg <sup>-1</sup>	118.7	68.7	16.4
0.1 M NaOH (P <sub>i</sub> ), mg kg <sup>-1</sup>	88.4	19.5	6.4
0.1 M NaOH (P₀), mg kg <sup>-1</sup>	644.4	116.7	10.8
1 M HCl (P <sub>i</sub> ), mg kg <sup>-1</sup>	364.9	45.4	18.7
$\sum P_i + P_o$ , mg kg <sup>-1</sup>	372.5	318.6	422.6
Total P, mg kg <sup>-1</sup>	1618	627	490
	1910	1020	720
Oxalate extractable elements, mg kg <sup>-1</sup>			
P	1400	511	460
Fe	22000	3090	1290
Al	4090	1470	1900



Both FIN and GER soils had the same Olsen-P values (62 mg kg<sup>-1</sup>). However, water-soluble  $P_i$  concentration (Hedley fractionation scheme) was far higher in GER soil (37.1 mg kg<sup>-1</sup> soil) as compared to FIN soil (7.0 mg kg<sup>-1</sup> soil), whereas in SPA soil (4.2 mg  $P_i$  kg<sup>-1</sup> soil) it was comparable with FIN soil, although Olsen-P value was at a far lower level (Table 2).

 $0.5 \text{ M} \text{ NaHCO}_3$  soluble  $P_i$  concentration in the Hedley fractionation was slightly higher than corresponding Olsen-P values in GER and SPA soils (Table 1), whereas in FIN soil  $P_i$  concentration was almost twice as that compared to Olsen-P method. This may be partly due to different soil-to-solution extraction ratios and extraction times in Olsen-P (extraction ratio 1:20 and extraction time 30 minutes) and Hedley fractionation scheme (extraction ratio 1:60 and extraction time 16 hours).

According to the Hedley fractionation scheme, P solubility is divided into different pools and 0.1 M NaOH extractable P<sub>i</sub> is considered to represent Fe bound P<sub>i</sub>. Iron is one of the main P binding element in soils and oxalate extractable Fe concentration was far highest level in FIN soil and lowest level was detected in SPA soil, GER soil having slightly higher oxalate extractable Fe concentration than SPA soil. Probably due to the variation in oxalate extractable Fe concentration, 0.1 M NaOH extractable P<sub>i</sub> concentration was at the highest level in slightly acidic FIN soil (644 mg kg<sup>-1</sup>), whereas in calcareous SPA soil it was only 11 mg kg<sup>-1</sup>. Acid soluble (1 M HCl) P content is the least soluble P fraction, considered to represent apatite based P (Hedley, Stewart, & Chauhan, 1982). Phosphorus content of this fraction was about at the same level in all experimental soils (Table 2).

FIN soil had the highest concentration of organic P ( $P_0$ ) among the studied soils (Table 1). Water-soluble  $P_0$  concentration was lowest, followed by 0.5 M NaHCO<sub>3</sub> and 0.1 M NaOH -fractions. Out of the total  $P_0$ , 0.1 M NaOH -extractable  $P_0$  represent 77, 52 and 52% of the total  $P_0$  in FIN, GER and SPA soils, respectively.

# 4.2. Elemental composition of BBFs

### 4.2.1. Total elemental concentrations

Total P concentrations in BBFs varied from 1.4% up to 22.8% on a dry weight basis (Table 2). Lowest P concentrations were found in manure-based BBFs (CPS, OPU) and BA1, followed by the BBFs containing animal by-products (MB1) or apatite (MO14). Ash-based BBFs (EPH, PLA and ADC) had variable P concentrations, lowest in sunflower husk ash (EPH) and highest in fertiliser originating from sewage sludge ash (ADC). Highest P concentrations were in BBFs produced by extracting P from waste streams (CGO and DCP), having the same P concentrations on a dry weight basis as in TSP.

Highest N concentration was in CGO, containing 10.2 % of N on a dry weight basis, followed by MB1 with 8.1 % of N. Lowest N concentrations were obviously found in ash-based products, having as low as 0.01% of N (Table 1). Carbon concentration varied from less than 0.1% up to 47.9%, highest one being found from plant and animal based BBFs. Lowest Ca, Fe and Al concentrations was in BA1, whereas some BBFs contained low Fe and Al, but high Ca concentrations. Only ADC had high concentrations of all these three elements (Table 1).

### 4.2.2. Hedley fractionation

On average, total sum of extractable P by the Hedley fractionation represent 93.3% of the total P concentration (*aqua regia* digestion), varying between 72 – 108%. Majority of the P was found in an inorganic form and only BA1 had 70% of P<sub>o</sub> out of the total sum of the P fractions (Fig. 4). Seven out of the studied 12 P sources had P<sub>i</sub> concentrations above 98% of the total sum of the P fractions. Rest of



the P sources had 97 (CPS), 96 (MB1), 92 (MBC) and 72% (OPU) in  $P_i$  forms. Water-soluble  $P_o$  concentration was 90% out of the total  $P_o$  concentrations in BA1 and OPU (Fig. 4).

Highest shares of water-soluble P concentrations were found in TSP (97%), followed by BA1 (92%), CPS (57%) and CPU (45%). Rest of the P sources had water-soluble P less than 10%. Water- and 0.5 M NaHCO<sub>3</sub>-soluble P fractions are considered to represent plant available, also called as labile P fraction. Share of labile fraction followed the same order as only water-soluble P share, highest one in BA1 and TSP (97%).

Most of the BBFs contained less than 4% of 0.1 M NaOH -soluble  $P_i$  (Fig. 4) and only CGO (17%) and DCP (19%) exceeded this value. Highest share of 0.1 NaOH-extractable  $P_o$  was detected in BA1 (3%) and OPU (4%), having also the highest share of total  $P_o$  concentrations.

In most of the P sources, except in BA1, CPU, CPS and TSP, most of the P was present in the least soluble fraction (1 M HCl), and its share varied from 67 up to 95%, highest shares in PLA (95%), MO14 (94%), ADC (91%) and MB1 (90%) (Fig. 4).

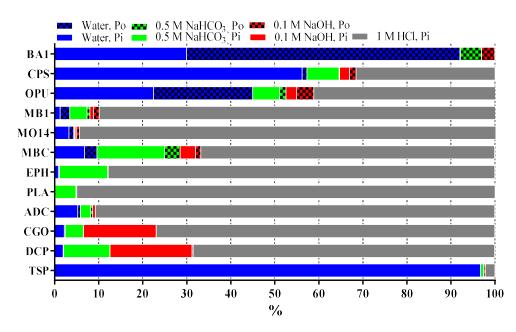


Figure 4. Distribution of phosphorus to various fractions in the studied P sources according to the Hedley fractionation scheme.

## 4.3. Rainfall simulation

### 4.3.1. Soil pH after incubation period

Soil pH of the control treatments did not change during the three-week incubation period (Fig. 5). Soil pH in all soils was increased most by EPH, and the effect was most pronounced in GER soil, up to 0.84 pH-unit. None of the BBFs lowered pH in FIN soil, whereas BA1 reduced soil pH to the lowest level in GER and SPA soils. In GER soil, pH difference was up to 1.4 pH unit between EPH and BA1 treatments (Fig. 5).



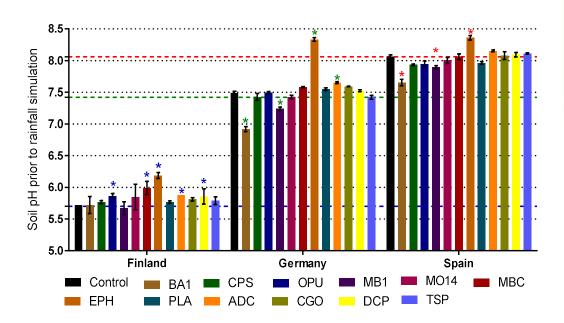


Figure 5. Soil pH of the experimental soils after a three-week incubation period with different BBFs and prior to rainfall simulation. Blue (FIN soil), green (GER soil) and red (SPA soil) dotted lines indicate initial soil pH values before incubation. Asterisks above the bars indicate statistically significant difference (p < 0.05) as compared to control treatment in a given soil. Error bars ± SD.

### 4.3.2. Inorganic P concentration in soil prior to rainfall simulation

Out of the BBFs, CGO led to the highest increase in water-soluble P<sub>i</sub> concentration most in each of the experimental soils (Fig. 6); three-fold in FIN and GER soils and up-to 18-fold in SPA soil as compared to the control treatment. Other BBFs increased water-soluble P<sub>i</sub> concentration far less and for FIN and GER soils the increase was at the most about twice as compared to the control treatment. Water-soluble P<sub>i</sub> concentration in FIN soil was increased least by BA1 and MO14. In GER and SPA soils water-soluble P<sub>i</sub> was increased least by MB1. Overall, inorganic BBFs and CPS increased water-soluble P<sub>i</sub> concentration most among P sources.

In FIN soil all BBFs increased 0.5 M NaHCO<sub>3</sub> -extractable P<sub>i</sub> and CGO led to the highest values (Fig. 6). Other BBFs increased extractable P<sub>i</sub> concentration almost to the same level in FIN soils and was about twice compared to that of the water-soluble P<sub>i</sub>. Inorganic P sources in general increased 0.5 M NaHCO<sub>3</sub> -soluble P<sub>i</sub> concentration in GER soil to the highest level, and OPU was the most effective in increasing it. Among soils, water-soluble Pi concentration, as compared to 0.5 M NaHCO<sub>3</sub> -soluble concentration, was far lower level in FIN soil, whereas Pi concentrations where almost equal in GER soil. In FIN soil share of water-soluble P<sub>i</sub> as compared to labile P<sub>i</sub> (water- + 0.5 M NaHCO<sub>3</sub> -soluble) was 11 ± 2% among all P sources, whereas in SPA and GER soils respective shares were 34 ± 14 and 40 ± 7 %. Although highest relative increase in 0.5 M NaHCO<sub>3</sub> soluble P<sub>i</sub> fraction was observed in SPA soil after BBF application, P<sub>i</sub> concentration remained at a far lower level than in FIN and GER soils.



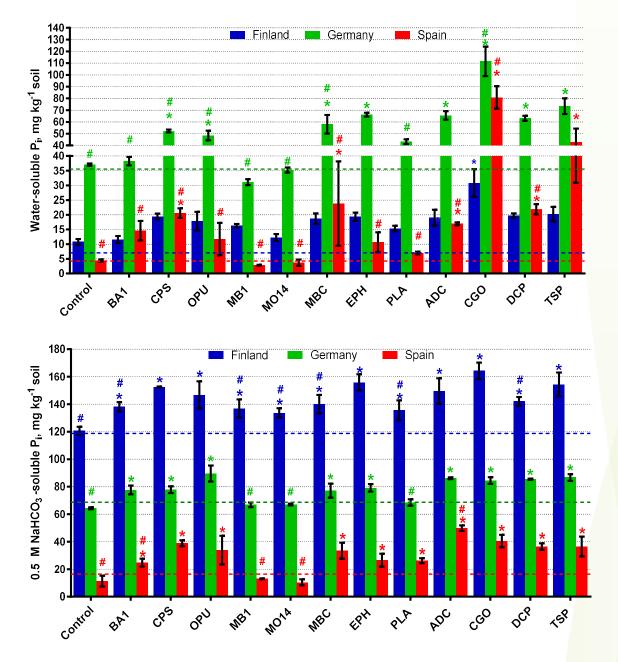
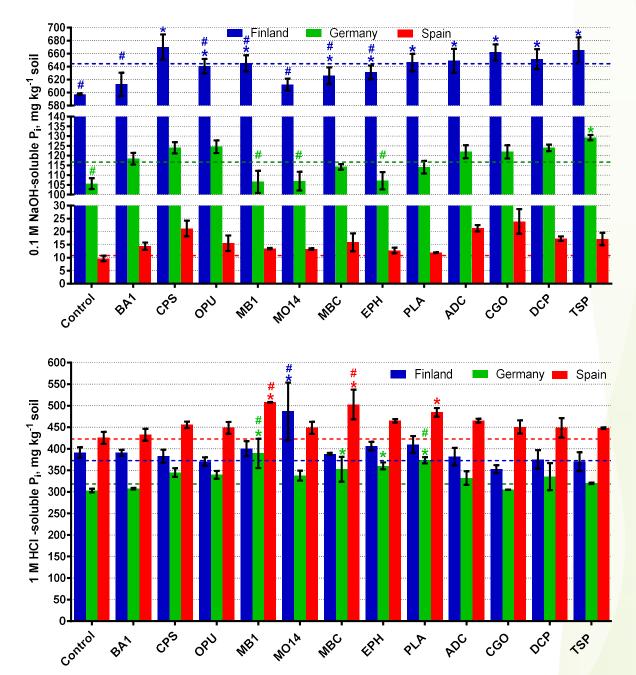


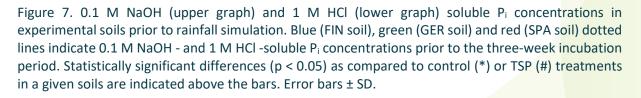
Figure 6. Water- (upper graph) and 0.5 M NaHCO<sub>3</sub> -soluble P<sub>i</sub> concentrations (lower graph) in experimental soils prior to rainfall simulation. Blue (FIN soil), green (GER soil) and red (SPA soil) dotted lines indicate water- and 0.5 M NaHCO<sub>3</sub> -soluble P<sub>i</sub> concentrations prior to the three-week incubation period. Statistically significant differences (p < 0.05) as compared to control (\*) or TSP (#) treatments in a given soils are indicated above the bars. Error bars ± SD.

Iron-bound P<sub>i</sub> concentration (0.1 M NaOH -extraction) was slightly reduced in all non-fertilised soils during the incubation period. Most of the BBFs retained this P<sub>i</sub> fraction in FIN and GER soils around the level or slightly above prior to incubation period. In SPA soil, CGO, DCP, ADC and CPS increased this fraction most (Fig. 7). Acid soluble (1 M HCl) P<sub>i</sub> concentration was not affected by the incubation period





nor BBFs in FIN soil. In GER and SPA soils acid soluble P<sub>i</sub> concentrations was increased most by PLA, EPH, MBC and MB1 (Fig. 7).





4.3.3. Organic P concentration in soil prior to rainfall simulation

Organic P concentration in the studied soils was less affected by the BBFs as compared to  $P_i$  concentrations. Most soluble  $P_o$  concentrations, water- and 0.5 M NaHCO<sub>3</sub> -soluble, were not significantly affected by the BBFs in FIN soil. Only slight increases were observed in these  $P_o$  fractions in GER and SPA soils. In GER soil only 0.5 M NaHCO<sub>3</sub> -soluble fraction was increased significantly by BA1 and MB1 and in SPA soil water-soluble fraction by BA1 (Fig. 8). Both of these fractions are labile and thus probably mineralize into  $P_i$  form in a short period of time.

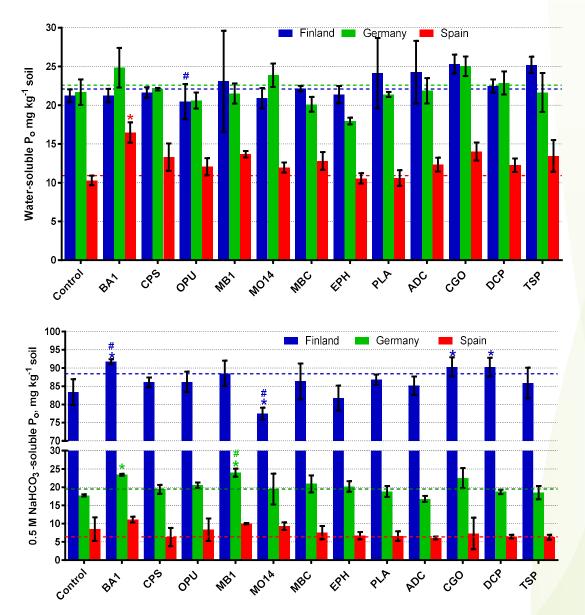


Figure 8. Water- (upper graph) and 0.5 M NaHCO<sub>3</sub> -soluble organic P (P<sub>o</sub>) concentration (lower graph) in experimental soils prior to rainfall simulation. Blue (FIN soil), green (GER soil) and red (SPA soil) dotted lines indicate water- and 0.5 M NaHCO<sub>3</sub> -soluble P<sub>o</sub> concentrations prior to the three-week incubation period. Statistically significant differences (p < 0.05) as compared to control (\*) or TSP (#) treatments in a given soils are indicated above the bars. Error bars ± SD.



Concentration of 0.1 M NaOH -extractable  $P_o$  concentration was clearly at a higher level in FIN soil as compared to GER or SPA soils (Fig. 9). After the incubation, 0.1 M NaOH -soluble  $P_o$  concentration in FIN soil was at a lower level in several BBF treatments than in the control treatment, whereas several BBFs (BA1, CPS, OPU, MB1, PLA, ADC and CGO) increased it to a higher level than TSP (Fig. 9). In GER and SPA soils, all BBFs, except CPS in GER soil, retained 0.1 M NaOH -extractable  $P_o$  concentration at the same level as in the control treatments (Fig. 9). In all three soils, BA1 increased  $P_o$  concentration of this fraction to the highest level among the BBFs (Fig. 9).

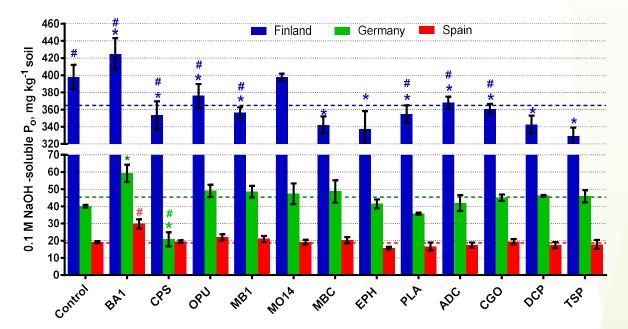


Figure 9. 0.1 M NaOH -extractable  $P_o$  concentrations in experimental soils prior to rainfall simulation. Blue (FIN soil), green (GER soil) and red (SPA soil) dotted lines indicate 0.1 M NaOH -soluble  $P_o$  concentration prior to the three-week incubation period. Statistically significant differences (p < 0.05) as compared to control (\*) or TSP (#) treatments in a given soils are indicated above the bars. Error bars ± SD.

### 4.3.4. Turbidity, electrical conductivity and pH of percolating water

An average time from the start of the rainfall simulation until water started to drain was  $1:44 \pm 0:10$ ,  $1:56 \pm 0:12$  and  $3:01 \pm 0:20$  hours for FIN, GER and SPA soils, respectively. Respective time duration for collecting 3\*100 ml of percolated water was  $3:34 \pm 0:29$ ,  $3:25 \pm 0:23$  and  $4:02 \pm 0:55$  hours. Figure 10 presents the three consecutive water samples, showing variation in percolating waters between soils and BBFs as rainfall simulation proceeded.







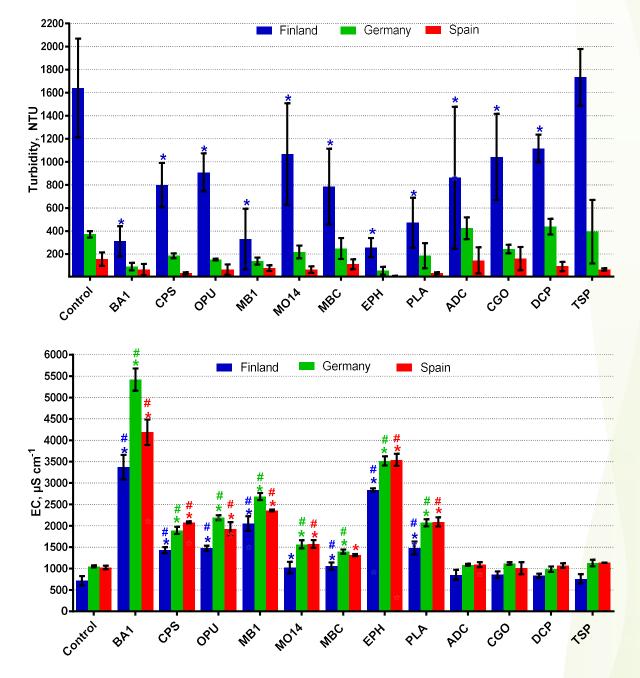
Figure 10. Water leachate from a rainfall simulation with different soil and BBF combinations. Soils originated from Finland (numbers 28 (MB1), 73 (PLA) and 101 (TSP)), Germany (numbers 13 (BA1), 50 (CGO) and 112 (TSP)) and Spain (numbers 25 (MO14), 98 (MBC) and 108 (DCP)) and incubated with different BBFs.

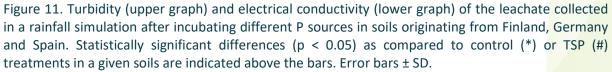
Turbidity, representing the erosion material in the percolating water, increased in the following order: SPA < GER < FIN (Fig. 11). This indicates that FIN soil was the most erodable among the studied soils. In FIN soils all BBFs decreased turbidity of the percolating water, most by the ash-based products (EPH, PLA), BA1 and MB1, whereas turbidity in the TSP treatment was at the same level as in the control treatment (Fig. 11). In GER and SPA soils none of the P sources had significant effect on turbidity.

Electrical conductivity (EC) of the leachate was increased by all P sources, except ADC, CGO, DCP and TSP, and BA1 increased it to a significantly higher level than other P sources (Fig. 11). Each of the P sources caused the smaller effect on EC in FIN soil as compared to GER or SPA soils.









Turbidity and electrical conductivity correlated well in all studied soils (Fig. 12). The higher the electrical conductivity the lower was the observed turbidity in the leachate. Minimum turbidity was reached at about the same EC values of about 2000  $\mu$ S cm<sup>-1</sup> in FIN and GER soils. Although erodibility between soils varied, turbidity was about at the same level when EC was > 2000  $\mu$ S cm<sup>-1</sup>.



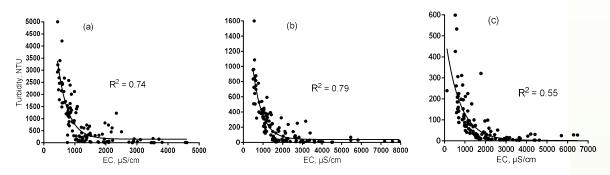


Figure 12. Relationship between turbidity and electrical conductivity (EC) of the percolated water in a rainfall simulation in FIN (a), GER (B) and SPA (c) soils mixed with different BBFs. Note the different scales on X- and Y-axes.

Some of the BBFs had a liming effect as shown by the increased soil pH after the incubation period (Fig. 5). This effect was also seen as an increased leachate pH in FIN soil, most by EPH (Fig. 13). In GER soil only EPH increased the pH of percolating water, meanwhile BA1 and MB1 decreased it. Also, in SPA soil BA1 decreased pH of the percolating water (Fig. 13).

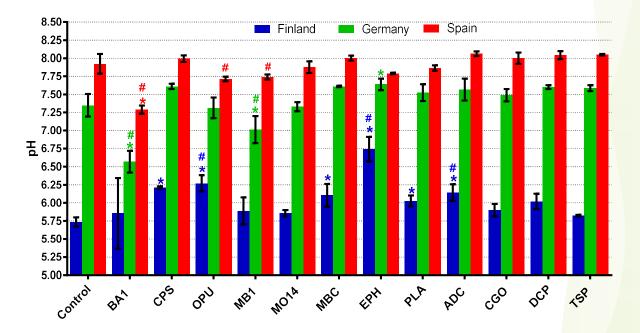


Figure 13. pH of the percolated water in a rainfall simulation. Statistically significant differences (p < 0.05) as compared to control (\*) or TSP (#) treatments in a given soils are indicated above the bars. Error bars ± SD.

#### 4.3.5. Dissolved reactive P losses in percolating water

Concentration of DRP in percolating water varied among BBFs and the highest DRP concentration was always detected in GER soil (Fig. 14). Without P application, DRP concentrations in percolating water in FIN, GER and SPA soils were 0.05, 0.21 and 0.02 mg l<sup>-1</sup>, respectively (Fig. 14). In all soils highest



increases in DRP concentrations were caused by TSP, DCP and CPS applications, followed by ADC and CGO treatments. Especially in GER soil, TSP increased DRP losses significantly more than BBFs. Contrary to other inorganic P sources, EPH and PLA, both thermally treated BBFs, as well as MO14, caused the lowest DRP losses among P sources and in most cases even lower DRP losses than in the control treatment (Fig. 14). Also, MB1 caused equal or even lower (GER soil) DRP concentration in percolating water than the control treatment.

Relative increases in DRP concentrations were highest in SPA soil and this was most evident in DCP, TSP and CPS treatments with up to 19-fold increase in DRP concentration in DCP treatment as compared to the control treatment.

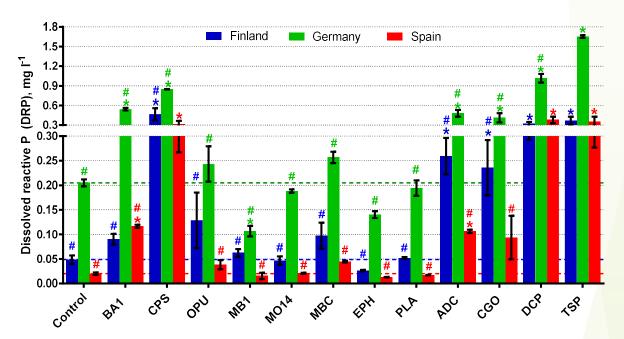


Figure 14. Dissolved reactive P (DRP) losses in percolating water after rainfall simulation. Blue (FIN soil), green (GER soil) and red (SPA soil) dotted lines indicate DRP concentration in the control treatment. Statistically significant differences (p < 0.05) as compared to control (\*) or TSP (#) treatments in a given soils are indicated above the bars. Error bars ± SD.

### 4.3.6. Particulate P losses in percolating water

Particulate P concentrations in the percolating water were generally at a higher level in FIN soil than in GER and SPA soils (Fig. 15). Particulate P concentration was decreased most by EPH, significantly so in FIN and GER soils. Highest particulate P losses in GER and SPA soils were caused by BA1 and OPU, significantly in SPA soil. In GER soil, CPS caused equal particulate P losses to BA1 and OPU (Fig. 15).



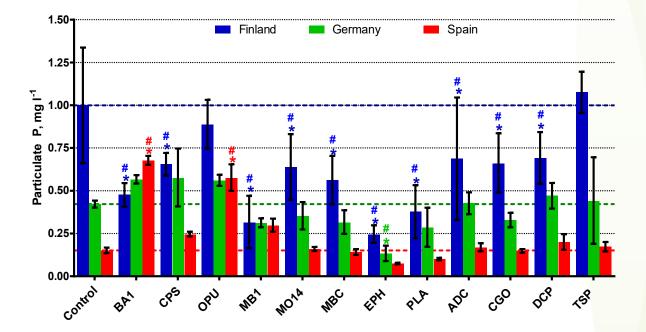


Figure 15. Particulate P concentration in the percolating water in a rainfall simulation. Blue (FIN soil), green (GER soil) and red (SPA soil) dotted lines indicate particulate P concentration in the control treatment. Statistically significant differences (p < 0.05) as compared to control (\*) or TSP (#) treatments in a given soils are indicated above the bars. Error bars ± SD.

Particulate P concentration in the leachate correlated well with turbidity in FIN soil, but the correlation was weaker in GER soil and no correlation was observed in SPA soil (Fig. 16).

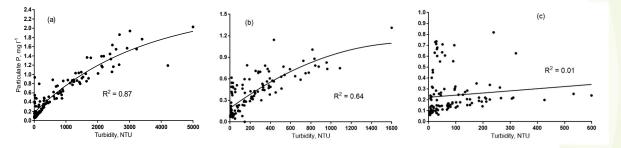


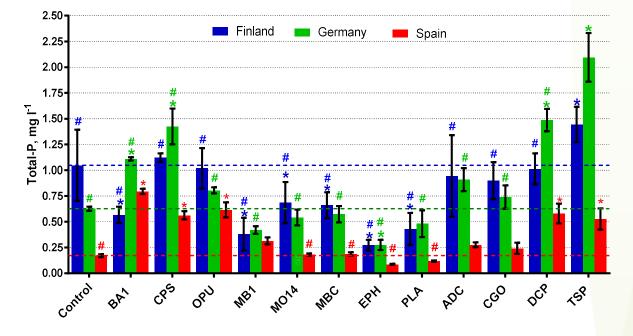
Figure 16. Relationship between particulate P concentration and turbidity of the leachate from FIN (a), GER (b) and SPA (c) soils mixed with different BBFs. Note the different scales on X- and Y-axes.

### 4.3.7. Total P losses in percolating water

Particulate P contributed 93, 60 and 88% of the total P losses in the control treatments in FIN, GER and SPA soils, respectively. Total P losses in FIN and GER soils were about the same level but the shares of DRP and particulate P losses were different in these soils. Especially DRP losses were clearly at a higher level in GER soil whereas particulate P losses were at a somewhat higher level in FIN soil.

Lowest total P concentration in percolating water was detected in ash-based products (EPH, PLA) and MB1. Highest total P concentration in the percolating water from FIN and GER soils was detected from





the TSP treatments, whereas BA1 caused highest concentration in percolating water in SPA soil. Total P losses from SPA soil were general far lower level than in FIN and GER soils (Fig. 17).

Figure 17. Total P concentration in percolation water after the rainfall simulation. Blue (FIN soil), green (GER soil) and red (SPA soil) dotted lines indicate total P concentration in the control treatment. Statistically significant differences (p < 0.05) as compared to control (\*) or TSP (#) treatments in a given soils are indicated above the bars. Error bars ± SD.

Share of DRP from total P losses varied among soils and P sources (Fig. 18). Average share among all treatments were 24, 51 and 28% in FIN, GER and SPA soils, respectively. In FIN soil, highest share was detected in CPS (45%) and lowest in the control treatment (7%). For both GER and SPA soils highest shares were obtained from TSP treatments, 82 and 66%, and lowest one from MB1 treatments, 27 and 5%, respectively.



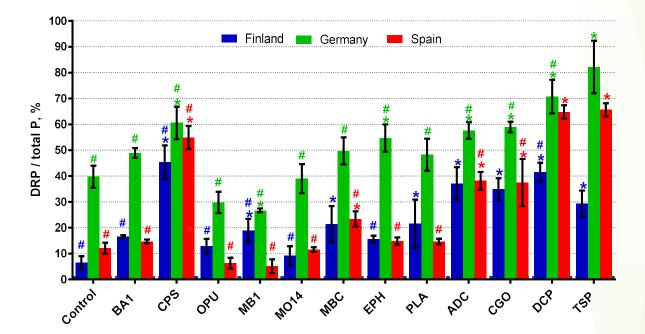


Figure 18. Share of DRP from total P in percolating water in the rainfall simulation. Statistically significant differences (p < 0.05) as compared to control (\*) or TSP (#) treatments in a given soils are indicated above the bars. Error bars ± SD.

### 4.3.8. Carbon losses in percolating water

The highest amount of carbon was added in soils treated with CPS (14900 mg kg<sup>-1</sup> soil), followed by BA1 (3900) and OPU (2300). Although MBC contained high carbon concentration, total carbon application rate was only 1200 mg kg<sup>-1</sup> due to the fixed BBF-P application rates. Lowest amount of carbon was added as DCP (0.28 mg kg<sup>-1</sup>), ADC (1.2), CGO (3.2), TSP (3.2) and PLA (12.7). Highest total dissolved carbon concentration in the leachate was observed in the SPA soil, whereas in FIN and GER soils dissolved carbon concentrations were at the same level (Fig. 19). Of the total dissolved carbon in the leachate, dissolved organic carbon (DOC) was the main fraction (Fig. 19).

Highest DOC concentration in the leachate was promoted by BA1 and OPU treatments in all three soils and in SPA soil BA1 increased it significantly more than other BBFs. Although CPS provided highest amount of carbon, it increased DOC concentrations only in GER and SPA soils. Despite of relative high amount of carbon in MBC, DOC concentration was at the same level as in the control treatments (Fig. 19).



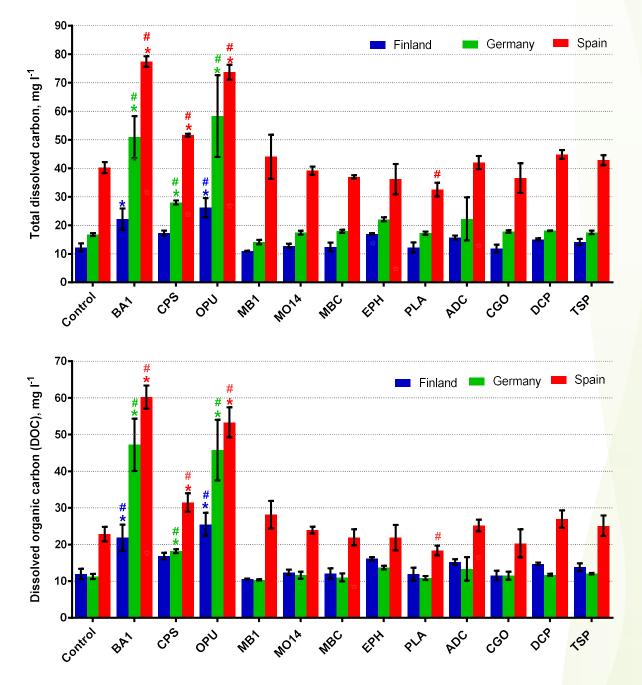


Figure 19. Concentration of total dissolved (upper graph) and dissolved organic carbon (lower graph) in the percolating water in the rainfall simulation. Statistically significant differences (p < 0.05) as compared to control (\*) or TSP (#) treatments in a given soils are indicated above the bars. Error bars  $\pm$  SD.

Dissolved inorganic carbon concentration in the leachate increased in the order of FIN < GER < SPA, being at the most 0.9 mg  $l^{-1}$  in FIN soil and varying between 4-13 and 14-20 mg  $l^{-1}$  in GER and SPA soils, respectively (Fig. 20).

29



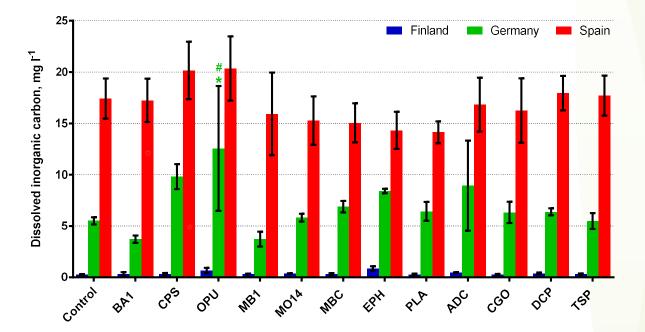


Figure 20. Concentration of dissolved inorganic carbon in the percolating water in the rainfall simulation. Statistically significant differences (p < 0.05) as compared to control (\*) or TSP (#) treatments in a given soils are indicated above the bars. Error bars ± SD.

#### 4.3.9. Nitrogen losses

Total nitrogen concentration in the leachate was at the highest level in the BA1 treatment in all soils. Unlike with total dissolved carbon, highest total dissolved N was leached in the GER soil, meanwhile it was at the equal level in FIN and SPA soils (Fig. 21). The BBFs leading to the highest total N input in soils was CPS (630 mg kg<sup>-1</sup> soil) but it caused far lower total N leaching than BA1 (total N input 505 mg kg<sup>-1</sup> soil), especially in GER and SPA soils. In FIN soils all organic or organo-mineral BBFs, except MO14 and MBC, increased N losses, whereas EPH was the only inorganic P source that increased N losses (Fig. 21).

Most of the N was lost as  $NO_3$ -N (Fig. 21), followed by organic N and  $NH_4$ -N (Fig. 21). Dissolved organic N concentration in BA1 treatments amounted to 4, 6 and 7% of the total dissolved N in FIN, GER and SPA soils, respectively (Fig. 22).

Only BA1 inreased NH<sub>4</sub>-N losses but the concentration was at the most 11 mg l<sup>-1</sup> in FIN soil and 3 and 5 mg l<sup>-1</sup> in the GER and SPA soils, representing only 2.4, 0.4 and 1.0% of the total N losses, respectively. In all other treatments NH<sub>4</sub>-N concentration accounted for about 0.1 mg l<sup>-1</sup>, except in MB1 treatment in SPA soil, where it was 0.4 mg l<sup>-1</sup>.



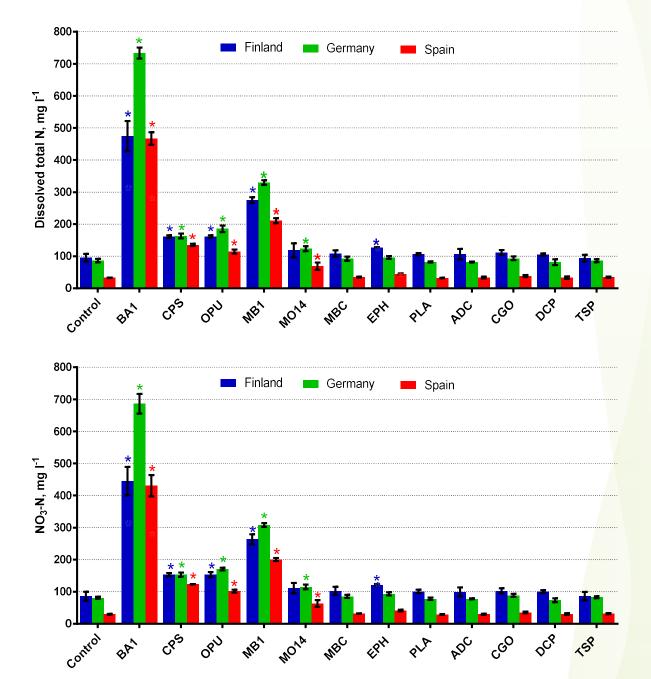


Figure 21. Dissolved total N (upper graph) and NO<sub>3</sub>-N concentrations (lower graph) in the percolating water in the rainfall simulation. Statistically significant differences (p < 0.05) as compared to control (\*) treatment in a given soils are indicated above the bars. Error bars ± SD.

MBC

EPH

BAI

ديم

ADC

PLA

DC8

TSP



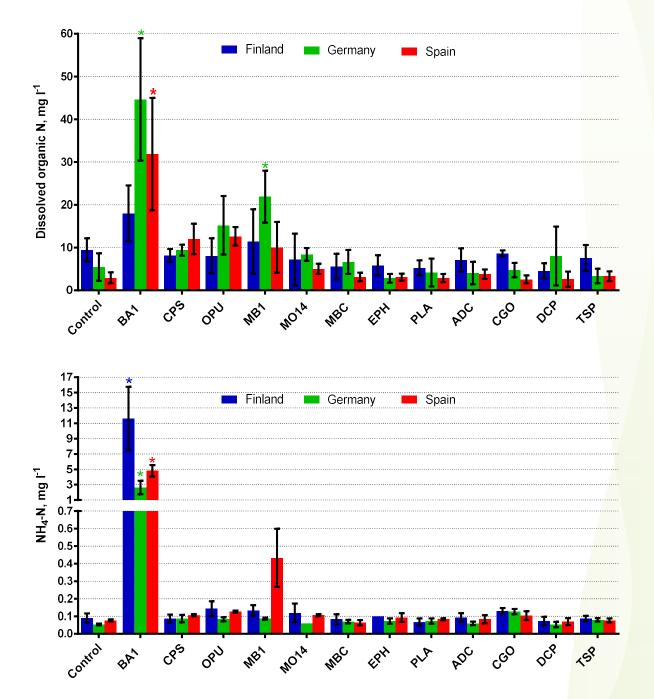


Figure 22. Dissolved organic N (upper graph) and  $NH_4$ -N concentrations (lower graph) in the percolating water in the rainfall simulation. Statistically significant differences (p < 0.05) as compared to control (\*) treatment in a given soils are indicated above the bars. Error bars ± SD.



# 5. DISCUSSION

# 5.1. Soil P test methods for predicting P losses

The selected experimental soils from Finland, Germany and Spain were selected based on results of local soil P test, indicating such a low P status that P fertilisation is recommended. However, according to the recent study of (Recena et al., 2022), Olsen-P values for soils originating from Finland and Germany would be unresponsive for P fertilisation. Also, soil testing method used in Finland, acid ammonium acetate, indicate that soil from Germany would in the Finnish classification system belong to the second highest P fertility class (seven classes) and P fertilisation would not be recommended. The calcareous soil from Spain would according to Finnish system belong to the second lowest P fertility class with P fertilisation recommendation of 26 kg ha<sup>-1</sup>. Calcium ammonium lactate, official soil P testing method in Germany, showed that soil from Spain had the highest soil test P value. This is probably due to solubilizing of (in a calcareous environment) non-soluble calciumphosphates in the acidic extraction solution. Results clearly showed poor correlation for P status interpretation of the studied soils when extracted with Olsen bicarbonate, acid ammonium acetate and calcium ammonium lactate methods.

Depending on soil properties, P leaching potential, especially of DRP, were dramatically different although Olsen-P values were same for FIN and GER soils. Results indicate that Olsen-P was not a perfect indicator for predicting P losses in acidic and neutral soils in this study, but may fit better for calcareous soils. Out of the tested three soil testing methods, acid ammonium acetate (pH 4.65) ranked the studied soils best according to the DRP losses. Furthermore, first extractant of Hedley fractionation, water extraction, predicted DRP losses well, as was also shown by (Sharpley & Moyer, 2000).

# 5.2. Soil properties affecting P losses from BBFs

Selected BBFs represent P fertilisers produced from various nutrient-rich side-streams and different production technologies, belonging to different product function categories (PFC) and component material categories (CMC) according to the Fertilising Products Regulation (2019/1009). Due to different chemical properties of the studied P sources, and of the soils used in this study, total P losses were varying from 5 (FIN soil) up to 9 (SPA soil) times higher between P sources. However, variability in DRP losses were even greater, variation of from 15 (GER soil) up to 30 (SPA soil) times in DRP losses were detected between different P sources. DRP losses were greatly affected by the soil properties. In acidic soil, P is mainly adsorbed on iron and aluminium oxides (Peltovuori, 2007). Soil pH has an effect on surface charge of the oxides and P sorption is decreased as soil pH increases (Hingston et al., 1967). In calcareous soils, P is sorbed onto CaCO<sub>3</sub> and metal oxides, and precipitated as non-soluble calcium phosphates (Frossard, 1995).

Acidic FIN soil contained the highest concentration of oxalate extractable iron and aluminium. Thus, it can be assumed that poorly crystalline Fe- and Al-oxides provide the major binding sites for P and thus depressing soluble P concentration in soil solution, whereas in calcareous SPA soil high CaCO<sub>3</sub> content reduced P solubility. However, in GER soil with low iron and aluminium concentration and no free CaCO<sub>3</sub>, solubility of P was probably least controlled by the soil properties. Although similar Olsen-P values in FIN and GER soils, Olsen-P extracted P pools from FIN soils that were not in equilibrium with the soil solution and provided lower DRP concentration to soil solution than in GER soil. Among BBFs, EPH increased soil pH in each of the experimental soil and decreased total P losses to the lowest level



among treatments. Together with pH effect, EPH increased electrical conductivity (EC) values of the leachate at the second highest level after BA1, further reducing particulate P losses as a result of less slaking in higher salt concentration of soil solution.

Phosphorus losses occurred mainly as particulate P, and from the FIN soil up to 93% of the total P losses occurred as particulate P in the control treatment, whereas in the coarser-textured GER soil this share was 60%. Regarding the effects on surface water quality, dissolved reactive P, i.e. inorganic P, is immediately bioavailable for algae, whereas particulate P needs to be detached from the soil particles to the soluble P pool before being bioavailable (Ekholm, 1998; Reynolds & Davies, 2001). Total P losses were lowest from calcareous SPA soil and this is probably related to high electrical conductivity caused by the soluble calcium salts. In the acidic clay soils in Finland, gypsum (CaSO<sub>4</sub>) has been shown to reduce P losses by decreasing break-up of clay aggregates due to increased electrical conductivity in soil solution (Uusitalo et al., 2012). Highest total P losses from FIN and GER soils were caused by mineral P fertiliser (TSP), whereas in SPA soil BA1 caused highest total P losses, followed by OPU, DCP, CPS and TSP, but differences among BBFs were not as large as in FIN and GER soils. Reason for the enhanced total P losses from calcareous soil by these organic BBFs may be due to decreased precipitation rate of calcium phosphates and causing decreased P adsorption. Although BA1 and OPU caused equal total P losses as DCP and TSP in calcareous soil, DRP losses were far higher in DCP and TSP treatments. This may be due to high organic P shares in BA1 and OPU and P losses occurred as particulate P. This is also supported by the higher organic P concentration in BA1 amended soil prior to rainfall simulation.

## 5.3. BBF properties affecting P losses

In acidic FIN soil, EPH caused lowest DRP losses probably due to low P solubility in EPH and P solubilizing was further suppressed by increased soil pH and EC. In GER soil MB1 reduced DRP concentration and the share of DRP of the total P losses most, even to a lower level than was detected in the control treatment. Also, in calcareous SPA soil MB1 depressed DRP losses to the lowest level among BBFs. This is probably related to low solubility of bone-based P in soils having pH above neutral (Ylivainio & Turtola, 2009). However, in acidic soil solubility of bone-based P increases and turns into plant available form over some years (Ylivainio & Turtola, 2009). Although MO14 is a plant based BBF, extra apatite was added to increase P content, causing one of the lowest DRP losses. Overall, BBFs with the highest share of acid soluble P (EPH, PLA, MO14 and MB1) caused lowest DRP losses. Compared to other ash-based BBFs (PLA, EPH) with about equal amount of acid soluble P, ADC increased DRP losses more. This may be due to the AshDec-process, which has shown to convert P into a more soluble mineral phase (Adam et al., 2009).

Mineral P fertiliser (TSP) contained highest share of water-soluble P<sub>i</sub> and TSP increased DRP losses most in GER soil, probably due to lower P retention capacity (low metal oxide and carbonate content) as compared to FIN and SPA soils. However, water-soluble P content of BBFs was not the only determinant for explaining DRP concentration in the leachate. Acid soluble P fraction constituted 68% of the total P in DCP, but it increased DRP concentration in leachate to a higher or equal level than the BBFs (BA1, CPS, OPU) with higher share of water-soluble P. On the contrary, CGO contained 77% of acid soluble P, but still it increased water-soluble Pi concentration in the experimental soils to the highest level among P sources prior to rainfall simulation. However, this was not translated into high DRP losses. On the contrary, DRP losses from the CGO were at a lower level than in DCP, TSP and CPS treatments. This may be caused by the fact that DCP was in a form of powder whereas BA1, OPU and CGO were small pellets and CPS was only sieved through 6 mm sieve. Therefore, DCP had a higher



surface area to react with soil and soil solution to enhance P solubilization. Pelletized, less soluble P sources may have remained partly intact during the incubation period but grinding of BBF containing soil samples prior to Hedley fractionation increased surface area of struvite and enhanced dissolution during 16 h extraction period. Similar phenomenon may have occurred with EPH, MBC and ADC as well. All BBFs were mixed with the soil without prior milling to evaluate their P leaching potential as such and mimic fertilisation practices on the field. In case DCP would be processed to granular form, P leaching potential may be different than observed in this study.

Organic BBFs might provide means for carbon storage into a soil and to avoid direct carbon release back to atmosphere as CO<sub>2</sub>. Depending on the production technologies, the BBFs chemical composition and physical stability may differ drastically from one product to another. Also, organic matter can have an effect on P solubility in soils as it can block P adsorption sites and sustain P in a soluble form (Siddique & Robinson, 2003; Ylivainio et al., 2021) or decrease P precipitation rate into a insoluble calcium phosphates. This may have occurred with CPS in all soils. Although CPS provided far more total carbon (14900 mg kg<sup>-1</sup> soil) than BA1 (3900 mg kg<sup>-1</sup> soil) and OPU (2300 mg kg<sup>-1</sup> soil), DOC concentration in the leachate was increased more by BA1 and OPU in GER and SPA soils. In the acidic FIN soil relative increase of DOC concentrations in BA1 and OPU treatments was less than in GER and SPA soils, indicating that mineralization of organic matter was enhanced more in soils with higher pH. Furthermore, an increase in DOC concentration at a higher pH may be due to a shift to smaller-sized organic molecules as a result of decoupling of inter-molecular hydrogen bonds in high pH, and  $Ca^{2+}$ ion effect on DOC stability (Andersson et al., 2000). Although high DOC concentration may decrease P adsorption (Weng et al., 2012), DRP losses in GER and SPA soils caused by BA1 and OPU were much lower level than in TSP treatments, but particulate P concentrations were at a higher level. This may indicate that organic P fractions were not yet mineralized or P bound to colloids were leached as such. Although potential gaseous ( $CO_2$ ) losses during the incubation period prior to rainfall simulation were not determined, easily degradable carbon content of CPS was probably already degraded during the digestion and composting process and more recalcitrant carbon mineralized at a lower rate during the three-week incubation period. MBC contains only recalcitrant carbon compounds and the same low level of DOC losses than in the control treatment was observed.

This study showed that BBFs produced lower P losses than common mineral P fertiliser in all experimental soils representing different soil properties in the EU. Especially in soil with low P adsorption capacity BBFs produced lower P losses, both total P and DRP losses, the latter one being immediately available for algal growth and causing eutrophication of surface waters in its full extent (Iho et al., 2023). The same phenomenon was observed in calcareous soil as well, supporting the targets for replacing mineral fertilisers with BBFs for better environmental performance. In acidic soil only CPS produced higher DRP losses than TSP, but for total P the opposite was observed. These results support the view that the studied BBFs are safe fertilisers when considering P losses to surface waters.





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