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Reducing nutrient loss in intensive agriculture – preliminary pot research

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Abstract: The maintenance of appropriate soil structure is critical for preventing soil degradation and mitigating nutrient losses that cause eutrophication of water bodies. An important challenge to combat eutrophication in the Baltic Sea is reducing phosphorus losses from agricultural land. Gypsum (CaSO₄·2H₂O) has been identified as a promising soil amendment that improves soil structure and reduces phosphorus leaching. However, it has not been widely used in Poland.

The article explains the importance of gypsum during the formation of a lumpy soil structure and in reducing phosphorus losses. A total of 18 samples were prepared, including three replicate samples without and with gypsum. Gypsum was added to each of the three pots based on the bulk density of the soil to correspond 4 Mg of gypsum per ha. The soil samples were analysed for total phosphorus, phosphates, available phosphorus, pH in water, KCl, and organic carbon.

The study presents findings of a laboratory pot test conducted on three soil samples from Southern Poland. The pot experiment indicated a decrease in turbidity of leachates from the soil samples treated with gypsum. Gypsum application did not significantly affect soil pH and total phosphorus content. Analysis of the soil samples before and after the watering showed that the total phosphorus concentration did not change. This was due to the low share of phosphorus released relative to the total phosphorus content in the soil.

Keywords: agricultural areas, gypsum, liming, phosphorus losses, soil condition

INTRODUCTION

The maintenance of the proper soil conditions depends largely on its structure, soil organic matter (SOM), and soil pH. These three factors not only affect yield but also govern key processes determining environmental impact (Fertilizers Europe, 2023). A stable and aggregated soil structure minimises erosion and leaching of nutrients, while enhancing soil aeration and water retention. Meanwhile, an appropriate soil pH is essential for effective nutrient uptake by crops and for limiting the absorption of heavy metals and aluminium by plants.

The geological origins of the most Polish soils create disadvantaged conditions for the development of a stable lump

soil structure, water retention, and availability of nutrients. In Poland, the agricultural landscape originates from the periods of glaciation. The Scandinavian glacier covered the present-day Polish territory three times, shaping the oldest soils in the southern part of the country (Mindel glaciations) and the youngest in the northern part of the country (Wurm glaciations). Approximately 56.6% of Polish soils are classified as light and highly permeable (FAO, 2003). Over 90% of the soils in Poland originate from sedimentary rocks, mainly loose materials brought by glaciers from Scandinavia. These soils have undergone intensive leaching of alkaline ions (Marks, 2005).

In Poland, light and very light soils predominate, consisting mainly of various types of sand with about 10% floatable

fractions. These soils are prone to dryness due to their low water retention. Moreover, they are characterised by a low content of nutrients and organic matter (Jadczyszyn and Smreczak, 2017). This type of soil is susceptible to acidification, which limits the absorption of nutrients by crops and increases the loss of nutrients through leaching, e.g. surface runoff (Kobus, 2017).

The optimal soil pH ranges from 5.5 to 8.0, depending on the crop, and is crucial for ensuring the availability of nutrients, mainly macro-components such as N, P, and K (Wójcik (ed.), 2014; Smreczak, Ochal and Siebielec, 2020). Soils with a pH below 5.5 require liming to reduce their acidity. Liming is typically carried out using quicklime (CaO), calcium carbonate (CaCO₃), or their mixture.

The glacial origin of the soil also contributes to significant moisture loss. According to the Institute of Meteorology and Water Management (Pol.: Instytut Meteorologii i Gospodarki Wodnej – IMGW-PIB) moisture content of 30–40% at a depth of up to 7 cm (top-soil) might be an indicator of a water deficit in the root zone (Balsamo *et al.*, 2009).

The content of organic matter, particularly humic acids, plays an important role in the formation of a stable lumpy soil structure. However, Polish soils typically have unsatisfactory levels of SOM. According to the Polish classification, the content of SOM between 1–2% classifies the soil as moderately abundant in organic carbon ($C_{org.}$), while SOM levels above 3.5% indicate high organic content. In contrast, according to European standards, soil moderately abundant in organic carbon should contain 3.44–10.0% SOM, which corresponds to 2.0–6.0% of $C_{org.}$ (Kuś, 2015). The characteristics of Polish soils described above exacerbate the leaching of nutrients from the soil. Periods of drought alternating with heavy rains intensify soil erosion.

According to PLC7 HELCOM data from 2020, agriculture is the main source of nutrients flowing into the Baltic Sea from Poland (66.41% N and 67.1% P). Phosphorus, in particular, is dangerous component responsible for eutrophication (HELCOM, no date; PGW Wody Polskie, 2020; Ollikainen *et al.*, 2024).

Poland has been a member of the HELCOM since 1992. Poland and other Baltic countries have declared to stop overfertilisation of the Baltic Sea by 2030. To this end, methods to reduce phosphorus losses should be developed by 2025, and their implementation planned for 2027. Studies on treatments that improve the soil structure and reduce nutrient losses are necessary for transforming Polish agriculture towards sustainable agriculture and meeting international obligations.

Research conducted over the past 25 years has confirmed the effectiveness of gypsum (calcium sulphate dihydrate, CaSO₄·2H₂O) as the soil amendment in reducing phosphorous losses (Kosenius and Ollikainen, 2019; Abdolvand and Sadeghiamirshahidi, 2024). Previous studies, mainly in USA and Finland, have shown many benefits of using gypsum, including reductions in phosphorus losses and organic carbon leaching (Ekholm *et al.*, 2012; Ekholm *et al.*, 2024; Yli-Halla *et al.*, 2023).

Liming is widely used to decrease soil acidity and this agricultural technique has been widely practiced in Poland. However, the gypsum application as a soil amendment, either alone or in combination with liming, is a novel approach for Polish farmers. This paper presents the results of a preliminary pot experiment performed on three Polish soils sampled from intensively farmed areas. Selected parameters of soil (total phosphorus, P-PO₄, organic carbon, pH, and electrical conduc-

tivity (*EC*)) and leachate properties (turbidity, pH, *EC*, total dissolved phosphorus (TDP), dissolved reactive phosphorus (DRP), and SO_4^{2-}) were compared between treatments with and without gypsum application.

MATERIALS AND METHODS

Soil samples were collected from three locations in Poland: two farms in the Szreniawa catchment area (Książnice Małe) (samples S2 and S3) and one farm located in Lower Silesia, near Wrocław (sample S1). Soil samples were collected in autumn 2019, after the main crop harvest, before the catch crop establishment and before autumn fertilisation.

The textural classes of soil samples were determined using the triangular diagram (Ferret's triangle) based on soil textural classification defined by the USDA (Casagrande, 1948), following the determination of particle size distribution using the Casagrande method. The sieved soils were analysed for dry matter, bulk density, and water-holding capacity (*WHC*). Bulk density was determined by measuring soil sample weight and volume when dried (at 100°C) using the metal ring method (PN-88/B-04481). Values of *WHC* were determined using the percolation method, where 50 cm³ of distilled water was poured on the 25 g soil samples, and the percentage of water retained by the soil measured (Nelson *et al.*, 2024). The parameters were used to ensure correct soil sample preparation for the pot experiment, without or with a calculated gypsum application.

A total of 18 samples were prepared, including three replicates, without and with gypsum application. Gypsum was added to each of the three pots based on the bulk density of soil at the rate of 4 Mg gypsum per ha (Ekholm *et al.*, 2012). Based on the *WHC*, the moisture content in the samples was maintained at 60% using the gravimetric method. The experiment was conducted at a room temperature and under a relatively constant humidity of 35–45%.

The soil samples were analysed for: 1) total phosphorus using the molybdate method after digestion in a mixture of HNO_3 and 60% $HClO_4$ (4:1 ratio), 2) phosphorus extraction using water (Dobrzański and Zawadzki (eds.), 1981; Piszcz, 2013), 3) available phosphorus (P-PO₄) using the Olsen method, 4) pH in water and KCl, and 5) organic carbon using the Tiurin spectrophotometric method.

After adding gypsum to the soil samples, the impact of watering on phosphorus leaching was compared between gypsum-treated and control pots. Each pot was watered with 300 cm³ of distilled water, applied in three sessions of 100 cm³ each. Two-week intervals were maintained between watering, during which the soil moisture was maintained at 60% of its WHC. The leachates were collected and analysed for: 1) potential of hydrogen (pH) - WTW Xylem Analytics Brands, 2) electrical conductivity (EC) - WTW Xylem Analytics Brands, 3) turbidity (NTU) - Turb* 430 IR, 4) total dissolved phosphorus (TDP) analysed after filtration of leachates using syringe filters hydrophilic polyethersulphone (PES) membrane and mineralisation, pore size: $0.2 \ \mu m \ \phi = 33 \ mm (Macherey-Nagel), 5)$ dissolved reactive phosphorus (DRP) - analysed after filtration using soil filters type 132, with low phosphate and potassium content, dedicated to seed and soil analysis, 6) sulphate ions were analysed using the spectrophotometry technique via precipitation method; the detection was done (at 430 nm) using $BaCl_2$ to produce sparingly soluble barium sulphate. Phosphate ions content was analysed using the colorimetric technique using the molybdenum blue method and photometer Slandi LF 300 (PUH Meritum).

The soil amendment used was a high-grade mineral sulphur-calcium fertiliser, "Agro-Wapń EKO-ZEC", produced by the Kozienice Power Plant. The gypsum is a solid, loose, powdered material with an amorphous structure. Its appropriate moisture content prevents dustiness. The gypsum is obtained from the desulphurisation of fuel gases.

According to its certificate, the gypsum contained 22.43 $\pm 1.4\%$ w/w Ca and 17.12% ± 1.5 w/w S. It bears the European "EC fertiliser" mark, and its utility value is validated by Certificate No. 13/16, confirming compliance with mineral fertiliser quality standards, issued by the Institute of New Chemical Syntheses in Puławy, Poland.

RESULTS AND DISCUSSION

CHARACTERISTICS OF THE SOILS

The texture analysis showed that the soil near Wrocław (S1) was loamy sand, whereas both samples from Książnice Małe (S2) and (S3) were silt loam (Tab. 1). The pH values measured in a KCl solution were 4.43, 7.56, 6.34, respectively. The highest pH before the experiment were measured for sample S2 (7.56) in the KCl solution. Total phosphorus concentrations were 0.04, 0.03, and 0.35% for samples S1, S2 and S3, respectively. The content of available phosphates was determined using the Olsen method. Phosphate concentrations determined by this method were 68.7, 12.2 and 297.5 mg·kg⁻¹ for samples S1, S2, S3, respectively. Additionally, the fraction of water-leachable phosphates, including mobile and highly soluble forms, were measured (Dobrzański and Zawadzki (eds.), 1981; Piszcz, 2013). The values of this parameter were 7.85 mg·kg⁻¹ (S1), 0.19 mg·kg⁻¹ (S2), and 53.26 mg·kg⁻¹ (S3).

After the three following watering sessions which ended the experiment, the soil samples were analysed again (Tab. 2).

Turbidity, pH, EC, TDP, DRP and SO_4^{2-} were determined in leachate samples collected after following three repeated watering sessions. The mean values of parameters measured with standard deviation are shown in Table 3.

All the three soil samples tested had a low organic carbon content (<1%). The average concentration of phosphorous (P_{total}) in arable soils in Poland ranges from 0.007 to 0.266%. Thus, the P_{total} values 0.04% for soil samples S1 and S2 can be considered typical for Polish soils (Tab. 1). Sample S2 showed the lowest concentration of mobile phosphates (0.19 mg·kg⁻¹, water extraction) and available phosphates (12.2 mg·kg⁻¹, Olsen method) as shown in Table 1.

In contrast, sample S3 had a high phosphorus content, amounting to 0.35%, 53.26 mg·kg⁻¹ of mobile phosphates, and 297.5 mg·kg⁻¹ of available phosphates. The organic carbon content in sample S3 was slightly higher than in the other samples (Tab. 1).

P-PO₄ in Bulk P-PO₄ Silt Clay Sand (50-Soil texture water density of EC Soil Corg-Ptotal (Olsen) (2-50 µm) 2000 µm) (<2 µm) (USDA/ pH_{H2O} pH_{KCl} extract dry sample (%) (mS·m^{−1}) (mg·kg⁻¹ sample (%) (mg·kg⁻¹ of FAO) $(g \cdot cm^{-3})$ of soils) soil) % **S**1 1.45 16 80 loamy sand 5.70 0.07 4.4 7.85 0.04 68.7 4 4.43 S2 1.15 20 59 21 silt loam 7.78 7.56 0.05 16.4 0.19 0.04 12.2 **S**3 1.15 12 74 14 silt loam 6.55 6.34 0.71 34.6 53.26 0.35 297.5

Explanations: EC = electrical conductivity, S1 = reference sample (before watering) of soil from Wrocław, S2, S3 = reference samples (before watering) of soil from Książnice Małe.

Source: own study.

Table 2. Results of soil analysis after 3^{rd} watering (end of experiment)

Soil sample	Gypsum amendment	P-PO ₄ in water extract (mg·kg ⁻¹ of soil)	P-PO ₄ (Olsen) (mg·kg ⁻¹ of soil)	P _{total} (%)	рН _{н2О}	pH _{KCL}	C _{org.} (%)	EC (mS·m ^{−1})
61	no	14.64	40.119	0.04	5.99	4.61	0.45	2.5
51	yes	6.01	41.915	0.04	5.20	4.51	0.35	37.4
	no	1.71	9.583	0.03	8.24	7.41	0.50	9.3
82	yes	0.27	9.009	0.03	7.79	7.31	0.60	53.3
	no	114.37	195.902	0.33	6.94	6.03	0.98	8.9
53	yes	75.02	188.744	0.33	6.66	6.08	1.18	31.0

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Explanation: *EC* = electrical conductivity. Source: own study.

 Table 1. Results of soil analysis prior to the pot experiment

a old sumplemeanSDmeanSDmeanSDmeanSDmeanSDmeanSD 1^{v} warering 011 1.8 1.721 31.10 21.58 5.35 0.131 1.26 0.56 0.31 $1.112.50$ 23.57 1^{v} warering 011 5.38 1.17 27.677 11.06 4.71 0.101 1.26 0.32 $0.112.50$ 2.08 2^{w} warering 011 1.80 0.451 $2.06.33$ 7.37 4.44 0.06 1.44 0.011 1.38 0.07 2.59 $0.112.50$ $2.66.3$ 2^{w} warering 111 1.80 0.52 $2.66.33$ 7.37 4.44 0.06 1.44 0.011 0.13 0.07 2.59 $1.12.50$ $2.66.3$ 2^{w} warering 112 5.89 0.72 $2.86.33$ 2.910 2.910 2.910 0.73 0.07 $2.92.9$ $1.12.50$ 2^{w} warering 112 5.89 0.82 2.930 9.41 0.26 0.26 0.26 0.26 0.26 0.26 0.22 2^{w} warering 112 5.99 0.92 0.210 0.212 0.21 0.212 0.212 0.212 0.22 2^{w} warering 112 9.101 9.24 0.220 0.212 0.212 0.212 0.22 0.223 0.223 2^{w} warering 112 0.210 0.212 0.212 0.212 0.212 0.212 0.212 0.223 2^{w} warering 112 0.210	Leachate from	Turbidit	y (NTU)	EC (m	nS•m ⁻¹)	Hq	(-)	TDP (m	ng·dm ⁻³)	DRP (n	ng·dm ⁻³)	SO_4^{2-} (n	ıg·dm ⁻³)
	a soil sample	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
	1 st watering 0L1	41.80	17.71	31.10	21.58	5.35	0.13	1.26	0.56	1.35	0.31	14.30	7.93
2nd watering 0.14.140.453.2171.915.430.091.400.111.380.072.5891.102nd watering 1.11.800.52256.337.374.440.061.140.110.430.06991.112063nd watering 1.15.890.501.545.302.015.410.061.440.120.752.021.172053nd watering 1.15.890.621.88.732.9004.630.140.0810.870.096.54.441.341nd watering 1.25.890.621.88.732.90055.227.440.280.810.290.060.006.4.491.341nd watering 1.240913.4212.96055.527.440.280.910.290.060.007.58.332.522nd watering 1.240913.4312.60055.527.440.280.910.077.58.332.522nd watering 1.29.219.212.6001.31467.830.140.810.120.060.007.58.332.522nd watering 1.29.219.212.6001.31467.837.310.210.250.060.007.58.342.592nd watering 1.29.219.218.137.618.137.618.130.220.140.120.060.007.59.449.512nd watering 1.29.146.139.218.14 <td>1st watering 1L1</td> <td>5.38</td> <td>1.17</td> <td>276.67</td> <td>11.06</td> <td>4.71</td> <td>0.10</td> <td>1.27</td> <td>0.08</td> <td>0.65</td> <td>0.03</td> <td>1,112.50</td> <td>268.49</td>	1 st watering 1L1	5.38	1.17	276.67	11.06	4.71	0.10	1.27	0.08	0.65	0.03	1,112.50	268.49
2^{nd} watering 1L1180 0.52 $2.36.33$ 7.37 4.44 0.06 1.14 0.11 0.43 0.06 991.11 206 3^{nd} watering 0L1 767 1.54 3.300 2.01 5.41 0.09 1.42 0.50 1.61 0.02 20.22 1.13 3^{nd} watering 0L1 5.89 0.62 1.9873 2.990 4.63 0.14 0.28 0.90 0.00 63.44 1.14 $1''$ watering 0L2 2.961 2.966 5.32 7.44 0.28 0.91 0.28 0.00 57.33 26.2 $1''$ watering 0L2 2.901 3.421 $2.63.3$ 3.101 7.63 0.14 0.28 0.901 0.78 0.75 4.73 $1''$ watering 0L2 9.911 3.421 2.943 5.722 7.44 0.28 0.911 0.06 0.00 75.33 26.2 2^{nd} watering 0L2 9.911 3.421 2.673 2.74 0.28 0.911 0.76 0.912 0.06 0.00 75.33 26.2 2^{nd} watering 0L2 9.911 9.246 0.212 0.241 0.241 0.241 0.267 0.267 29.34 29.34 2^{nd} watering 0L2 7.14 2.943 2.914 0.212 0.241 0.241 0.261 0.261 0.202 0.202 20.22 1.14 2^{nd} watering 0L2 7.14 2.944 7.84 0.241 0.241 0.241	2 nd watering 0L1	4.14	0.45	32.17	1.91	5.43	0.09	1.40	0.11	1.38	0.07	25.89	1.07
3^{vit} watering 0.11 7.67 1.54 3.300 2.01 5.41 0.09 1.61 0.02 2.02 1.1 3^{vit} watering 1.11 5.89 0.62 188.73 29.90 4.63 0.14 1.24 0.18 0.09 0.00 634.44 1.34 1^{vit} watering 0.12 $2.2.61$ 2.966 85.83 3.01 7.63 0.15 0.24 0.06 0.00 4.778 $40.$ 1^{vit} watering 0.12 4.091 3.421 2.9600 55.52 7.44 0.28 0.91 0.06 0.00 758.33 $22.$ 2^{vit} watering 0.12 9.01 9.21 9.85 13.46 7.86 0.24 0.21 0.05 0.06 0.00 758.33 $24.$ 2^{vit} watering 0.12 9.21 9.85 13.46 7.86 0.24 0.81 0.29 0.06 0.00 79.33 $24.$ 2^{vit} watering 0.12 9.21 9.85 7.44 0.28 0.24 0.29 0.06 0.00 79.33 $24.$ 2^{vit} watering 0.12 7.14 0.92 0.24 0.81 0.29 0.06 0.00 29.24 29.7 2^{vit} watering 0.12 7.14 0.24 0.24 0.24 0.24 0.24 0.26 0.06 0.00 29.24 $24.$ 2^{vit} watering 0.12 7.14 6.34 7.84 0.81 0.29 0.24 0.26 0.06 0.00 29.24 24	2 nd watering 1L1	1.80	0.52	236.33	7.37	4.44	0.06	1.14	0.11	0.43	0.06	991.11	206.67
3^{vid} watering 111 5.89 0.62 198.73 2990 463 0.14 1.24 0.18 0.90 0.00 634.44 1.34 1^{w} watering 012 22.61 29.68 85.83 3.01 7.63 0.15 0.81 0.28 0.06 0.00 4778 $40.$ 1^{w} watering 112 34.01 34.21 260.00 55.52 7.44 0.28 0.90 0.12 0.06 0.00 75.33 22.4 2^{vid} watering 112 39.01 34.21 59.53 13.44 7.86 0.24 0.24 0.06 0.00 758.33 22.4 2^{vid} watering 112 39.01 94.81 7.86 0.24 0.24 0.12 0.06 0.00 739.44 $487.$ 2^{vid} watering 112 7.14 0.343 94.30 75.43 84.30 7.83 0.24 0.94 0.06 0.00 739.44 $487.$ 3^{vid} watering 112 7.14 0.343 94.30 75.44 7.80 0.24 0.24 0.06 0.00 739.44 $487.$ 3^{vid} watering 113 7.14 0.343 92.40 75.44 7.80 0.94 0.22 0.06 0.00 739.44 $487.$ 3^{vid} watering 112 7.14 0.343 92.41 7.80 7.83 0.24 0.24 0.06 0.00 0.00 0.00 3^{vid} watering 113 14.95 5.34 2.47 0.87 0.42 <	3 rd watering 0L1	7.67	1.54	33.00	2.01	5.41	0.09	1.42	0.50	1.61	0.02	20.22	1.71
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	2 nd watering 0L3	26.57	5.36	119.57	16.96	6.37	0.06	5.23	0.47	27.65	3.57	29.11	1.17
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3^{1d} watering IL3 2.66 0.92 269.67 10.60 6.10 0.08 24.60 11.65 19.50 0.12 613.33 40.10 11.65 19.50 0.12 613.33 40.10 11.65 10.12 10.1	3 rd watering 0L3	40.16	23.09	64.70	36.93	6.50	0.18	37.85	12.40	29.98	3.75	23.50	2.59
	3 rd watering 1L3	2.66	0.92	269.67	10.60	6.10	0.08	24.60	11.65	19.50	0.12	613.33	40.55

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leachates from soil sample S3 without gypsum, 1L3 = sample of the leachates from soil sample S3 with gypsum, S1, S2 and S3 = as in Tab. 1.

Source: own study.

Soil samples were re-analysed after the third watering (Tab. 2). In the case of active acidity measurement (pH measured in water), the three consecutive watering sessions increased the pH, from 0.29 to 1.35 in all three soil samples not treated by adding gypsum (Tab. 2), compared to the pH value before the test (Tab. 1). Samples treated with gypsum showed a slightly decreased pH values ranging between 0.01–0.5.

The potential of hydrogen measurement in KCl solution reflects exchangeable acidity, which represents hydrogen ions absorbed by the sorption complex. Therefore, no significant changes in pH were observed during subsequent waterings. In the case of samples without gypsum, pH values varied before and after watering from 0.13 to 0.29, while for samples with gypsum, the range was 0.08 to 0.31.

An increase in the organic carbon content was observed after the third watering, especially in soils treated with gypsum (0.35, 0.60 and 1.18% for samples S1, S2 and S3, respectively) as shown in Table 2. This could be compared to the soil prior to the experiment, which showed the organic carbon content of 0.07, 0.05 and 0.71% for samples S1, S2 and S3, respectively (Tab. 1).

The total phosphorus content in the soil samples, with and without gypsum, remained unchanged after three rounds of watering (Tab. 2). However, a decrease in phosphate ion leaching was observed in samples treated with gypsum, along with a decrease in the concentration of phosphorus available as measured using the Olsen method. These effects may result from the immobilisation of phosphate ions in chelate compounds formed after gypsum application, particularly in the presence of humic acids (Hartono, Indriyati and Selvi, 2013; Konewka, 2014).

It is likely that phosphate ions bound in complex compounds are more difficult to extract using sodium bicarbonate employed in the Olsen method. For example, in the determination of available phosphates in sample S3, 195.9 mg·kg⁻¹ of P-PO₄ was detected in the sample without gypsum, compared to 188.7 mg·kg⁻¹ in S3 sample with gypsum.

Figure 1 shows the comparison of the changes in the content of phosphorus washed out by water and available phosphorus, determined by the Olsen method.

The results were compared with parameters measured for the reference sample prior to the experiment.

LEACHATE ANALYSIS

A graphical comparison of the selected parameters was prepared based on the measurements during the analysis of leachate over three consecutive watering rounds, as presented in Table 3. The measurements include turbidity, TDP, and DRP concentration for leachate collected from samples with and without gypsum.

Figure 2 compares the turbidity measured in leachates from samples with gypsum and without gypsum. In the case of leachates from samples S1 and S3, a decrease in turbidity was observed after the application of gypsum. However, in sample S2, cracking of soil samples or very strong capping was observed, leading to very high *SD* values, which may have obscured the gypsum effect on turbidity.

Two phosphorus fractions were analysed in the leachates. TDP was analysed following filtering the samples using PES 0.2 μ m syringe filters and after mineralisation, while DRP was determined after filtering with coarser soil filters. A decrease in TDP concentration was observed in leachates L1 and L2 after the



Fig. 1. Differences in phosphorus concentration in soil samples after extraction using: a) water, b) via the Olsen method at the end of experiment; S1, S2, S3 = as in Tab. 1; source: own study



Fig. 2. Comparison of turbidity measured in leachates collected from soil samples with and without gypsum in consecutive waterings; 0L1, 1L1, 0L2, S2, 1L2, 0L3, 1L3ad in Tab. 3; source: own study

second and third watering rounds, as well as in leachate L3 after the first and third watering, compared to the control sample (Tab. 3). The comparison of DRP concentration in the leachates from samples L1, L2 and L3 is shown in Figure 3.

The concentration of DRP in leachates from gypsumamended samples S1 and S3 (1L2 and 1L3 in Fig. 3) was lower in each subsequent watering than in their corresponding unamended counterparts (0L1 and 0L3). However, no differences in DRP concentration were observed between samples 0L2 and 1L2. The lack of changes in DRP concentration due to gypsum between samples 0L2 and 1L2 can be explained by a low level of phosphorus in soil S2 and its substantial liming.



Fig. 3. The comparison of dissolved reactive phosphorus (DRP) concentration in leachates collected from soil samples S1 and S3 after consecutive waterings; 0L1, 1L1, 0L2, S2, 1L2, 0L3, 1L3ad in Tab. 3; source: own study

The results confirm that gypsum amendments effectively reduce the leaching of dissolved phosphorus, indicating that phosphorus is bound in a form less susceptible to being washed out by water. In addition, turbidity measurements suggest a reduction in particulate phosphorus as well. These results align with those from other studies.

Research conducted in Finland indicates that gypsum application can reduces phosphorus release to surface water bodies by up to 50% (Ollikainen *et al.*, 2020). In a study of surface water bodies within a catchment area where gypsum was applied, results showed a 55% reduction in the load of bound particulate phosphorus and a 25% reduction in dissolved phosphorus within three years of gypsum treatment (Ekholm *et al.*, 2012).

Studies conducted in Brazil have shown the beneficial effects of simultaneously using lime and gypsum amendments on corn crops. The combined introduction of both additives led to the increased availability of orthophosphates, ammonium, and nitrate nitrogen, while reducing the availability of micronutrients (Bossolani *et al.*, 2020).

The processes influencing the immobilisation of phosphate in soil, while maintaining its availability to plants, include stronger adsorption of phosphate due to increased ionic strength and the formation of chelate complexes between humic acids, calcium ions, and phosphate groups. Additionally, the presence of humus and calcium ions plays a critical role in the formation of lumpy soil structures, which helps reduce erosion processes.

Appropriate agricultural practices, such as shallow ploughing, crop rotation, and mulching of catch crops, increase the organic matter content in the soil. Calcium ions can be supplied to the soil through liming or gypsum application. The main purpose of liming is to regulate soil pH, whereas gypsum application does not change soil pH but improves its structure and limits phosphorus leaching.

Liming is typically performed using quicklime, calcium carbonate, or a mixture of both. Gypsum applications, on the other hand, involve the use of calcium sulphate dihydrate. When gypsum is applied, the effect of calcium ions in soil is observed more quickly compared to liming, as calcium ions from calcium sulphate dihydrate dissolve faster in the soil solution than those from liming additives.

The presence of humic acids and calcium ions in the soil facilitates the formation of chelate complexes with calcium and orthophosphate ions, known as humic-calcium compounds (Konewka, 2014). Humic acids can also form chelates with metals such as Al and Fe. Tan (1998) described the mechanisms of phosphate group $PO_4^{3^-}$ binding through carboxyl groups (-COOH) and polyvalent cations. Phosphorus can be bound directly via ligand exchange between OH⁻ and $PO_4^{3^-}$ or by co-adsorption using metal bridging with Al and Fe, or bonded via calcium bridging (Hartono, Indrivati and Selvi, 2013).

Complex connections prevent phosphorus from precipitating as sparingly soluble calcium phosphates $(Ca_3(PO_4)_2)$ or being leached away. Therefore, humic acids, together with calcium ions, contribute to the immobilisation of phosphate ions while ensuring their availability to plants and their release under suitable conditions (Konewka, 2014).

Calcium ions also promote the formation of larger soil aggregates. Soil colloid particles typically carry a negative charge, which is surrounded by a layer of counterions (cations), forming an electrical double layer (Buszewski and Pomastowski, 2015). Charged particles repel each other, leading to dispersion. The application of gypsum into the soil increases the ionic strength of the colloid solution, which compresses the electrical double (diffusion) layer. This compression promotes the microaggregation of soil particles (Kotwica, 2005).

Moreover, an increase in the concentration of Ca^{2+} can help overcome the dispersion effects by Mg^{2+} or Na^+ ions, thereby promoting flocculation and the development of soil structure in dispersed soils (Chen and Dick, 2011). The formation of larger soil aggregates in the presence of calcium ions and the dispersion process of soil colloid particles influenced by the presence of Na^+ and Ca^{2+} ions are shown in Figure 4.



Fig. 4. Gypsum as soil amendment to improve soil physical properties: a) the presence of Ca^{2+} ions promotes aggregation of soil colloids, b) the presence of hydrated ions Na^+ promotes dispersion; source: Chen and Dick (2011), modified

An additional benefit of gypsum application is its ability to bond aluminium ions with sulphate ions. The dissociation of gypsum in soil solution releases Ca^{2+} and SO_4^{2-} ions. The presence of Ca^{2+} promotes the displacement of toxic aluminium from the soil solution. Al³⁺ ions combine with SO_4^{2-} ions forming aluminium sulphate, a coagulant that promotes the aggregation of soil particles (AroSulCa, 2019; Shruthi *et al.*, 2024). Research on gypsum and phosphogypsum is conducted at laboratory scale, pilot scale (in experimental plots), and full field scale in collaboration with farmers.

CONCLUSIONS

The expected effect of gypsum addition, a decrease in the leaching of phosphorus from the soil, was observed in two out of the three samples, both of which were moderately to highly enriched in phosphorus. The unresponsive sample had the lowest concentration of phosphorus and a high $pH_{\rm KCl}$. An analysis of soil samples

before and after watering showed no change in total phosphorus concentration. This outcome is attributed to the low share of released phosphorus relative to the total phosphorus content in the soil.

After the pot experiment was completed, soil analysis showed a lower phosphate (mobile phosphates) extraction with water in samples treated with gypsum compared to those without gypsum. Therefore, it can be concluded that the gypsum amendment effectively limited phosphate leaching.

Available phosphorus concentrations measured using the Olsen method in samples S1 and S2 before and after the pot experiment were comparable. However, a significantly lower concentration of available phosphorus in sample S3 after the experiment suggests that the effects of gypsum are more pronounced in soils with higher total phosphorous concentrations. In sample S3, gypsum amendment likely caused the binding of phosphates into forms that are more difficult to extract using NaHCO₃.

Moreover, leachate analyses confirmed the effectiveness of gypsum in reducing dissolved phosphorus leaching. While a decrease in TDP was observed in leachates, this reduction was not consistent across all waterings.

Our results confirmed previous findings that gypsum amendment does not significantly alter soil pH.

The low content of soil organic matter (SOM) in the tested samples prevented the observation of the improvement in organic matter content noted in the literature. Further research is needed to elucidate which factors influence the effect of gypsum on Polish soils.

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CONFLICT OF INTERESTS

All authors declare that they have no conflict of interests.

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