



# Assessment of phosphogypsum waste use in plant nutrition

Kamila Stępień, Piotr Stępień\*, Urszula Piszcz, Zofia Spiak

Wroclaw University of Environmental and Life Sciences,  
Department of Plant Nutrition, Poland

\*Corresponding author's e-mail: [piotr.stepien@upwr.edu.pl](mailto:piotr.stepien@upwr.edu.pl)

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**Abstract:** Phosphogypsum (PG) – a waste material generated in enormous amounts, accumulates a wide range of pollutants and thus represents a major environmental problem. Among the proposed potential strategies for PG management, none has been implemented on a large scale up to date. At the same time, the rapid depletion of phosphorite resources, used to manufacture most commercial phosphorus (P) fertilizers, poses unprecedented challenges for future agriculture and environmental protection. The aim of this study was to assess the possibility of using PG as a source of P for fertilizing plants. The effect of PG fertilization on the dry mass accumulation, P and sulphur (S) contents in soil and in the above-ground parts of plants, as well as on the level of heavy metal contaminations, were studied in the experimental model consisted of 12 genotypes of three lupine species – *Lupinus angustifolius*, *Lupinus albus* and *Lupinus luteus*. The PG application increased the content of both the available and active P in the soil. The increased P bioavailability resulted in an elevated uptake and intracellular content of this nutrient in the studied plant species in a dose- and variety-dependent manner. The heavy metals present in the waste did not affect their accumulation in the plants. The results indicate the possibility of using P forms present in PG as an alternative source of this component in plant nutrition, at the same time allowing elimination of the waste deposited on huge areas, which will certainly contribute to improving the quality of the environment.

## Introduction

Phosphogypsum (PG) is a waste-product formed during the production process of phosphoric acid used in the manufacturing of phosphorus fertilizers, technical-grade phosphates, polyphosphates for household chemicals, as well as used in the food industry and as an animal feed additive (Grabas et al. 2018, Rothwell et al. 2020). The main raw material for the production of phosphoric acid is sedimentary rocks called phosphorites, which can be processed for this purpose using a wet or thermal method. For economic reasons, about 90% of the phosphoric acid is manufactured by the wet process, which generates a huge amount of waste product (Chernysh et al. 2021). The production of 1 ton of phosphoric acid results in formation of as much as 5 tons of PG (Al-Hwaiti and Al-Khashman 2015, Pliaka and Gaidajis 2022), thus leading to its annual global production of more than 200 million tons (Saadaoui et al. 2017, Grabas et al. 2018).

Phosphogypsum is a material containing a wide range of pollutants and thus presents a major problem in the phosphorus fertilizer industry. The most common practice of PG management all over the world, including Poland (Grabas et al. 2018), is its storage in the form of heaps located near

the phosphoric acid plant. These landfills have been classified as highly harmful to the environment, posing a serious threat due to the possibility of soil and groundwater contamination by rainwater flowing from the slopes of the heap and by infiltration of rainwater into the deeper layers of the landfill (Hentati et al. 2015, Saadaoui et al. 2017, Pliaka and Gaidajis 2022). Importantly, the heaps that are formed often reach up tens of meters in height and collect enormous amounts of contaminated material in one place (Grabas et al. 2018, Pliaka and Gaidajis 2022).

According to Rajković et al. (2000) up to 50 types of contaminants can be found in phosphogypsum. These are, among others, fluorosilicic acid, calcium, sodium and potassium fluorosilicates, and undecomposed phosphorus raw material. In addition, considerable contents of heavy metals are also present in PG, including cadmium (Cd) and lead (Pb) (Hentati et al. 2015, Grabas et al. 2018, Pliaka and Gaidajis 2022). The unfavorable and time-varying physicochemical properties of phosphogypsum are factors limiting the potential for reclamation of its heaps. The annually diminishing capacity of landfills to receive this waste creates an urgent pressure to find alternative uses for this by-product. Apart from serious environmental effects, the deposition of PG in heaps also

entails enormous economic consequences (Hentati et al. 2015, Chernysh et al. 2021).

Among the potential applications of PG, none has been implemented on a large scale and only about 15% of its global production is reused (Al-Hwaiti and Al-Khashman 2015, Pliaka and Gaidajis 2022). Phosphogypsum as a source of phosphorus (P), sulphur (S) and calcium (Ca) has long been the subject of research on the possibility of its use for industrial and agricultural purposes. The composition of PG shows that it might be potentially used for plant cultivation and soil improvement (Hentati et al. 2015, Chernysh et al. 2021, Pliaka and Gaidajis 2022). Over the last decade, not always justifiable concerns about the negative impact of waste on human health and environmental quality, have resulted in reluctant attempts to manage it, or even have been completely abandoned. It has been despite the fact that the positive effect of phosphogypsum has been proven in the cultivation of various types of plants (Hilton 2006, Hentati et al. 2015). However, further research is essential as so far efforts have not led to the development of specific guidelines that would facilitate to assess the suitability of waste of different origins for agricultural management and ensure its safety under changing environmental conditions (Chuan et al. 2017, Saadaoui et al. 2017, Pliaka and Gaidajis 2022).

The multilateral impact of PG on the quality of soils, characterized by extremely diverse properties, means that agriculture could become an important recipient of this problematic waste, which would not only bring great ecological benefits, but also huge economic income (Chuan et al. 2017). What is particularly important, the phosphogypsum landfills accumulate huge amounts of phosphorus (Cordell and White 2013, Pliaka and Gaidajis 2022, Tian et al. 2022), a component whose insufficient availability in soils is an increasingly serious challenge for agriculture in many regions of the world (Xu et al. 2020, Aslam et al. 2021). The total P content in PG is around 2.5–7.5% (Tian et al. 2022). It is estimated that about 700,000 Mg of unused P is dumped on global waste heaps every year, which is equal to almost a quarter of the annual consumption amount of this nutrient by 7 billion people (Cordell and White 2013). The P deficiency may cause a reduction in the growth of all arable crops in up to 67% of the world agricultural area (Dhillon et al. 2017) and in the near future, its availability, along with water and energy, may become the main factor limiting agricultural production globally (Rothwell et al. 2020, Aslam et al. 2021).

In modern agriculture, about 60% of phosphorus introduced into soil comes from mineral fertilizers (Elser and Bennett 2011). These days, it has been observed that the phosphorite resources for the phosphorus fertilizer production are depleted too fast, therefore finding alternative sources of this component and increasing its recycling rate has become one of the main priorities of global agriculture (Rothwell et al. 2020, Tian et al. 2022). In addition to this, it is necessary to find solutions to increase the use of phosphorus from those alternative sources by plants. One of the methods is to cultivate species, which have developed natural adaptations, enabling them to absorb this ingredient more efficiently under the conditions of its limited availability in the soil (Lambers and Plaxton 2015, Xu et al. 2020, Aslam et al. 2021). Among these adaptations, we can distinguish such which allow for increased absorption of

poorly soluble forms of phosphorus from soil, and such which allow for the efficient use of the absorbed resources and plant survival under the conditions of low P availability (Lambers and Plaxton 2015). In particular, lupins constitute a useful group of plants for this type of research (Xu et al. 2020, Aslam et al. 2021). The species exhibit an above-average ability to absorb phosphorus from poorly available resources, which has been confirmed in numerous studies (Egle et al. 2003, Funayama-Noguchi et al. 2015, Xu et al. 2020, Aslam et al. 2021). Moreover, lupins exhibit a wide interspecies diversity in terms of adjustment strategies (Egle et al. 2003, Lambers et al. 2013, Funayama-Noguchi et al. 2015, Dissanayaka et al. 2017). In line with the above, we decided to use various lupin species as model organisms for present investigation. We tested the hypothesis that phosphogypsum might be used as an efficient and safe source of phosphorus for plants, answering the following research questions: does the use of PG increase the concentration of P in soil and plants? Is the level of P accumulation in plant tissue species- and variety-dependent? How does the use of this waste affect the reaction and salinity of soil? Does PG supplementation carries a risk of the soil and plant contamination with heavy metals?

The specific aim of the study was to assess the possibility of using phosphogypsum waste for fertilizing the varieties of three lupin species – white lupin (*Lupinus albus* L.), yellow lupin (*Lupinus luteus* L.) and narrow-leaf lupin (*Lupinus angustifolius* L.). We evaluated the impact of PG on the dry mass accumulation in shoots and chemical composition of plants, with particular emphasis on their phosphorus supply, content of S and of two heavy metals (Cd and Pb). In addition, we examined selected physicochemical properties of soils after phosphogypsum supplementation, including pH and salinity, the content of active and soluble forms of phosphorus as well as Cd and Pb.

## Materials and Methods

### Soil material and phosphogypsum properties

The soil material used during the experiment was slightly acidic ( $\text{pH}_{\text{KCl}}=5.68$ ), with salinity level (electrical conductivity) at  $47 \mu\text{S}\cdot\text{cm}^{-1}$ , a very low available phosphorus content determined by the Egner-Riehm method ( $3.20 \text{ mg}\cdot 100 \text{ g}^{-1}$ ) and very low active phosphorus ( $0.011 \text{ mg}\cdot\text{dm}^{-3}$ ). The sulphur content was at a level of  $12.8 \text{ mg}\cdot 100 \text{ g}^{-1}$ . The contents of toxic elements – cadmium (Cd) and lead (Pb) – were lower than the average natural contents reported in medium soils (Kabata-Pendias and Pendias 2001), and was  $0.014$  and  $8.6 \text{ mg}\cdot\text{kg}^{-1}$ , respectively.

Phosphogypsum was obtained from a heap belonging to the now-defunct WIZÓW Chemical Plant ( $51^{\circ}17'42''\text{N}$ ,  $15^{\circ}34'53''\text{E}$ ), Poland, which used to use apatite raw material for production. The waste was characterized by a total phosphorus content of 0.8%, with an acidic reaction ( $\text{pH}_{\text{H}_2\text{O}}=2.6$ ) and salinity at the level of  $4.67 \text{ mS}\cdot\text{cm}^{-1}$ .

### Plant material

In the pot experiment, 12 varieties of three lupin species were tested: *Lupinus angustifolius* (AU11257-19/1, LAE-1, Kalif, Oskar), *Lupinus albus* (Buttercup, Lucrop, Perkoz, Egipt), and *Lupinus luteus* (Mister, Lord, Perkoz, Taper). Of each of

the four varieties, two were highly efficient in the phosphorus absorption and transport under its deficiency in the soil, and two were characterized by low efficiency. The selection of those varieties was based on previous screening vegetation experiments, which tested the ability of 33 varieties and genotypes of lupins to accumulate phosphorus in above-the-ground parts. In this respect, a high efficiency was exhibited by such varieties as: *LAE-1*, *AU 11257-1/19*, Buttercup, Lucrop, Lord and Mister, and low efficiency by: Oskar, Kalif, Egipt, Pikador, Perkoz and Taper.

The plants were grown in the phytotron chamber under fully controlled conditions, including: 16-hour photoperiod (PPFD  $250 \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ), temperature of  $25/20^\circ\text{C}$  (day/night), and relative humidity of 55–65%. Throughout the experiment, the soil material water content (SWC) was maintained at 60% of the maximum water capacity. To estimate pot water capacity the fully water-saturated soil material was weighed and then dried to constant weight. The weight difference between water saturated and dried soil material was taken as weight of water needed to bring pots to pot capacity and lower SWC (% pot capacity) were calculated accordingly (Verheijen et al. 2019, Ogbaga et al. 2020). The plastic pots (14 cm height, 9.5 cm diameter) were filled with a mixture of 500g of soil collected from the arable layer of the farmland and 150 g of washed sand, and fertilized with basic nutrients:  $40 \text{ mg N}\cdot\text{kg}^{-1}$ ,  $60 \text{ mg K}\cdot\text{kg}^{-1}$ ,  $60 \text{ mg Mg}\cdot\text{kg}^{-1}$  soil. The selected lupin varieties were supplemented with PG doses corresponding to 20 and  $50 \text{ Mg}\cdot\text{ha}^{-1}$ . After germination, the substrate in the pots was inoculated with nitragine, according to the manufacturer's instructions (Biofood S.C., Wałcz, Poland). In the 4<sup>th</sup> week of vegetation, the plants were additionally fertilized with  $10 \text{ mg N}\cdot\text{kg}^{-1}$  and  $40 \text{ mg K}\cdot\text{kg}^{-1}$ .

The plants were harvested at the end of the flowering phase (BBCH 68), i.e., during the period of the greatest accumulation of phosphorus, and freshly weighted. The above-ground parts of lupins were dried at  $70^\circ\text{C}$  for 72 h and reweighed for determination of dry mass (DM). The samples were used for subsequent analytical procedures.

### Analyses of soil and plant material

The effects of phosphogypsum on soil material properties were assessed by analyzing the pH reaction and salinity, the content of soluble and active phosphorus, and two heavy metals: Cd and Pb, the presence of which in waste poses a serious environmental risk (Al-Hwaiti and Al-Khashman 2015). After harvesting the plants, the pot content was thoroughly mixed and a soil material sample was collected, dried to the air-dry state and sieved through a sieve with a mesh diameter of 1 mm. The soil pH was determined in  $1 \text{ mol}\cdot\text{dm}^{-3}$  KCl solution with the soil-to-solution ratio of 1:2.5. The measurement was carried out using the multifunctional pH meter (Elmetron, Zabrze, Poland). The salinity was determined by measuring the electrical conductivity of the soil material suspension in distilled water at 1:2.5 ratio with the conductivity meter (Elmetron, Zabrze, Poland). The available phosphorus content in soil material was determined by the Egner-Riehm method (PN-R-04023 1996), with the buffered calcium lactate being used as an extractant for 90 min. After development of the color complex, the phosphorus concentration was measured at 420 nm. The concentration of the active phosphorus was

determined calorimetrically (Watanabe and Olsen 1965) after extraction from the soil material with  $1 \text{ mM CaCl}_2$  at 1:5 soil-to-solution ratio and a short shaking time of 5 min (Fotyma et al. 1991). The Cd and Pb content was determined according to Yanai et al. (2000), by extracting the soil material with a mixture of  $0.25 \text{ mol}\cdot\text{dm}^{-3} \text{ NH}_4\text{Cl}$ ,  $0.05 \text{ mol}\cdot\text{dm}^{-3} \text{ HCl}$ ,  $0.2 \text{ mol}\cdot\text{dm}^{-3} \text{ CH}_3\text{COOH}$  and  $0.005 \text{ mol}\cdot\text{dm}^{-3} \text{ C}_6\text{H}_8\text{O}_7$  at  $\text{pH}=1.3$ .

The effect of applied phosphogypsum on the studied lupin varieties was assessed on the basis of the dry matter accumulation, the phosphorus content in the above-ground parts of plants, and the sulphur (S) content as the main constituent of PG. In addition, changes in the intracellular contents of Cd and Pb in response to PG application were assessed.

The dried plant material was dry mineralized in a muffle furnace at  $450^\circ$  and the ash was dissolved in  $1 \text{ mol}\cdot\text{dm}^{-3} \text{ HNO}_3$ . The P concentration was determined using the vanadate-molybdate colorimetry method at 400 nm. The Cd and Pb contents were determined by atomic absorption spectroscopy (AAS), with SpectrAA220FS spectrometer (Varian, Melbourne, Australia) maintaining the parameters specific to each element. The S content in plant material was determined by the Butters and Chenery method as modified by Bielecki and Kulczycki (2012). Briefly, the mineralization was started in concentrated nitric acid (V) and the binding of sulphur by heating with a solution of magnesium nitrate (V). Afterwards, the samples were mineralized in a muffle furnace (10 h,  $450^\circ\text{C}$ ), and the resulting ash was brought into solution by treatment with HCl. In the modified method, the barium reagent – a mixture of barium chloride and Tween-80 detergent, was used instead of barium chloride crystals during the preparation of solutions after mineralization. The quantification was performed with a Cecil spectrophotometer (Cecil Instruments, Cambridge, United Kingdom) at a wavelength of 400 nm.

In addition, the phosphorus utilization efficiency was calculated by two most commonly used methods:

$$(a) \text{ the RE method: } RE = (P_n - P_0)/D \times 100,$$

and

$$(b) \text{ the PNB method: } PNB = P_n/D \times 100,$$

where: RE – Crop recovery efficiency, PNB – Partial nutrient balance,  $P_n$  – phosphorus uptake by plants supplemented with phosphogypsum ( $\text{mg P}\cdot\text{pot}^{-1}$ ),  $P_0$  – phosphorus uptake by the control plants ( $\text{mg P}\cdot\text{pot}^{-1}$ ), D – phosphorus dose ( $\text{mg P}\cdot\text{pot}^{-1}$ ).

### Statistical analysis

All statistical analyses were performed with Statistica software version 13 (TIBCO Software Inc., Palo Alto, CA, USA, 2017). Where significance is indicated, a two-way ANOVA (analysis of variance) with the Bonferroni test was conducted at the significance level of  $p=0.05$ . Data points in the figures represent the means  $\pm$ SD.

## Results and discussion

### Effects of phosphogypsum on chemical properties of soil material

#### pH reaction and salinity

In the present experiment, the soil material became gradually acidified with an increasing phosphogypsum doses (Fig. 1). The  $\text{pH}_{\text{KCl}}$  values ranged from 5.23 for the plants supplemented with  $50 \text{ Mg PG}\cdot\text{ha}^{-1}$  to 5.75 for the control plants. Although the



difference in pH between the variants fertilized and unfertilized with PG did not exceed 0.5 units, an additional acidification of the soil material, which had already been characterized by a slightly acidic reaction before the beginning of the experiment, should be considered as an adverse phenomenon. Therefore, in the case of acidic soils, the combined use of PG with alkalinizing materials should be considered (Carmeis Filho et al. 2016, Bouray et al. 2020). The pH reaction of the soil material used in the control treatment remained at a similar level, indicating that the cultivation of individual lupin species and varieties did not significantly modify that parameter.

The issues concerning the impact of PG on the soils pH remain the subject of numerous discussions. It has been previously showed that PG may effectively mitigate the harmful effects of soil acidification (Crusciol et al. 2016) by increasing the calcium (Ca) content and reducing aluminium (Al) toxicity more rapidly than calcium carbonate (Hentati et al. 2015). Importantly however, the obtained effects depend on the type and properties of soil (Takasu et al. 2006, Blum et al. 2013). Reducing the negative impact of acidification on plants is not synonymous with the improvement of soil pH, and even if the waste demonstrates deacidifying effect under certain conditions, it is a substance far less effective than calcium carbonate (Bouray et al. 2020).

In contrast to pH, significant differences were observed during the present experiment in salinity, both in combinations supplemented with PG and in the control combinations (Fig. 1B). The level of salinity increased with increasing doses of PG, reaching a maximum of  $1129 \mu\text{S}\cdot\text{cm}^{-1}$ , whereas before the experiment, the value of this parameter was  $47.9 \mu\text{S}\cdot\text{cm}^{-1}$ . An increase in the salinity of soil material was also observed for the control plants, but that was most likely a consequence of the mineral fertilizer application prior to the experiment. On average, the lowest salinity levels were recorded in the combinations with white lupins, and the highest levels in the soil material samples collected from the pots where yellow lupin varieties were cultivated. After phosphogypsum was applied at a dose equivalent to  $20 \text{ Mg}\cdot\text{ha}^{-1}$ , a threefold increase in salinity was observed, and after application of  $50 \text{ Mg PG}\cdot\text{ha}^{-1}$ , the salinity level rose almost 4.5 times.

The results obtained here are in line with some previous reports, where the use of phosphogypsum contributed to an increase in the soil salinity (Elrashidi et al. 2010, Elloumi et al. 2015, Smaoui-Jardak et al. 2017, Ochmian et al. 2021). That may result in the inhibition of plant growth and ionic imbalance limiting the availability of certain ingredients, including phosphorus (Elrashidi et al. 2010). In the present experiment, despite more than the fourfold increase in salinity levels after applying a PG dose equivalent to  $50 \text{ Mg}\cdot\text{ha}^{-1}$  (Fig. 1B), an increase in the phosphorus content in the above-ground parts of lupins (discussed later in detail) was observed (Fig. 3). Elloumi et al. (2015) reported the negative effect on yield in sunflower cultivation, most likely due to an increase in the salt concentration in the substrate, in response to phosphogypsum application equal to 5% of the soil weight (approx.  $150 \text{ Mg}\cdot\text{ha}^{-1}$ ). On the contrary, the waste of 2.5% (approx.  $75 \text{ Mg}\cdot\text{ha}^{-1}$ ) had a positive effect on plant growth, even though the soil conductivity value reached  $2400 \mu\text{S}\cdot\text{cm}^{-1}$ . Smaoui-Jardak et al. (2017) demonstrated that the inhibiting effect of PG on tomato yield occurred only after applying

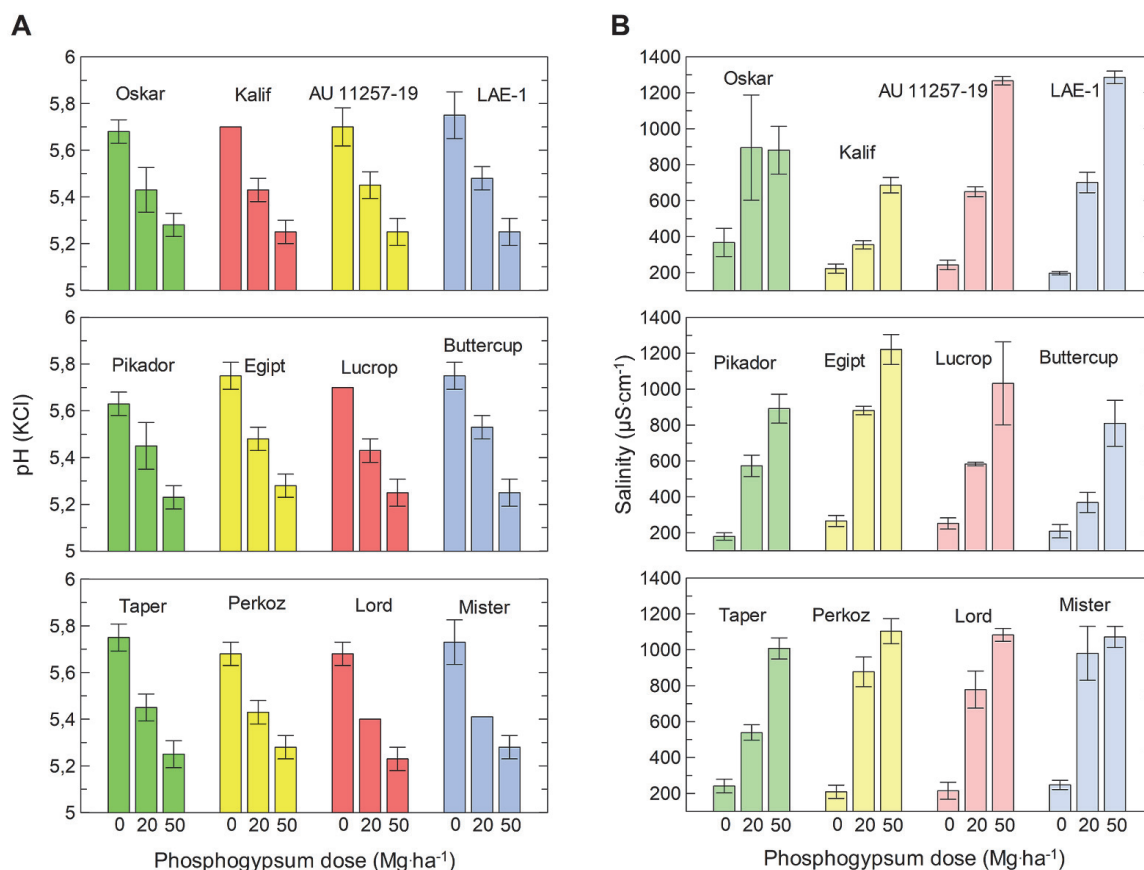
a dose corresponding to 20% of the soil weight, with the conductivity being increased to  $2650 \mu\text{S}\cdot\text{cm}^{-1}$ . In the course of our experiment, the conductivity level did not exceed  $1300 \mu\text{S}\cdot\text{cm}^{-1}$  (Fig. 1B), which allowed the soils to be classified as unsalted ( $0\text{--}2000 \mu\text{S}\cdot\text{cm}^{-1}$ ), and the effect of salinity on plant growth was considered negligible (Shahid and Rehman 2011). Nevertheless, the obtained results indicate that this parameter must be subject to strict control.

#### *Phosphorus content in soil material*

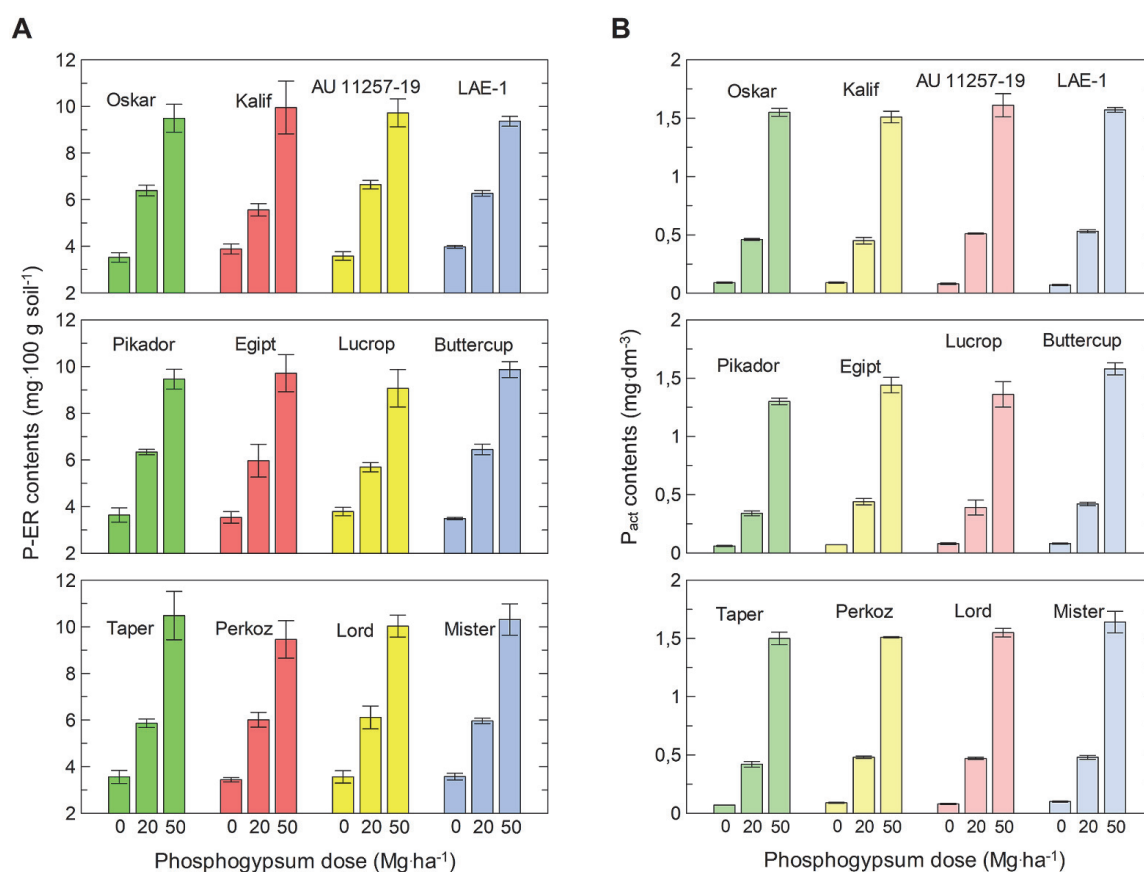
In this study, the available P content determined in the soil material by the Egner-Riehm method after the completion of plants vegetation, each time was higher than before the experiment (Fig. 2A). It was indicated that in the unfertilized soil material it ranged from  $3.49$  to  $3.97 \text{ mg P}\cdot 100 \text{ g}^{-1}$ , after applying phosphogypsum in an amount equivalent to  $20 \text{ Mg}\cdot\text{ha}^{-1}$ , it ranged  $5.69\text{--}6.64 \text{ mg P}\cdot 100 \text{ g}^{-1}$ , and in an amount equivalent to  $50 \text{ Mg}\cdot\text{ha}^{-1}$ , it ranged  $9.46\text{--}10.48 \text{ mg P}\cdot 100 \text{ g}^{-1}$ . On average, the highest P content in the control and fertilized soil material at a PG dose equivalent to  $20 \text{ Mg}\cdot\text{ha}^{-1}$  was obtained after the cultivation of narrow-leaf lupins, lower in the soil material where white lupin was grown, and the lowest after the cultivation of yellow lupin. However, after a PG dose of  $50 \text{ Mg}\cdot\text{ha}^{-1}$ , the highest amounts of available phosphorus were found in the soils material where yellow lupin was grown. The application of phosphogypsum also contributed to a significant increase in the concentration of active P in the soil material, corresponding to the phosphorus concentration in soil solution (Fig. 2B). The determined concentration of this phosphorus form in the control soil material ranged from  $0.06$  to  $0.10 \text{ mg P}\cdot\text{dm}^{-3}$ , and after the use of waste in an amount of  $20 \text{ Mg}\cdot\text{ha}^{-1}$ , it ranged from  $0.34$  to  $0.53 \text{ mg P}\cdot\text{dm}^{-3}$ . The application of a PG dose equivalent to  $50 \text{ Mg}\cdot\text{ha}^{-1}$  resulted in an increase in active P to  $1.30\text{--}1.61 \text{ mg P}\cdot\text{dm}^{-3}$ . As with the available P content, the highest concentration of active phosphorus was found in the soil materials where narrow-leaf and yellow lupins were grown. Despite the diverse capacity of the studied varieties for P absorption and transport in tissues, there were no significant differences in the content of two designated forms of this component ( $\text{P-ER}$  and  $\text{P}_{\text{act}}$ ) within individual species.

Analyzing the above results in the context of using PG as an alternative source of phosphorus, it should be noted that already after the use of waste in an amount equivalent to  $20 \text{ Mg}\cdot\text{ha}^{-1}$ , the available P content increased by 60%. This effect was further enhanced after application of  $50 \text{ Mg}\cdot\text{ha}^{-1}$  phosphogypsum, with the available P being increased by up to 200%, as compared to the initial soil content before the experiment (Fig. 2A). The concentration of active phosphorus also increased significantly (Fig. 2B). While the concentration of this P form in the fertilized soil used in agricultural plots should range from  $0.3$  to  $3.0 \text{ mg P}\cdot\text{dm}^{-3}$  (Piszcz 2013), the mean concentration determined in the soil material samples collected from the most phosphogypsum-fertilized combination was as high as  $1.5 \text{ mg P}\cdot\text{dm}^{-3}$ .

The literature abounds in various opinions on the effects of phosphogypsum on the content of phosphorus compounds bioavailable to plants in the soil. Many authors point out that PG properties, such as the acidic reaction, high salinity, as well as high calcium content are factors that can significantly limit



**Fig 1. (A) Soil pH (KCl) and (B) soil salinity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )**



**Fig. 2. (A) Content of available phosphorus determined by the Egner-Riehm method (P-ER) and (B) concentration of active phosphorus ( $P_{\text{act}}$ ) in soil**

the availability of this component to plants (Delgado et al. 2002, Elrashidi et al. 2010, Ekholm et al. 2011, Nayak et al. 2011, Quintero et al. 2014, Bouray et al. 2020). The hitherto studies on the possibility of using PG for fertilizing arable crops have often demonstrated that the use of this waste does not contribute to an increase in the available phosphorus forms in the soil and P content in plants (Elrashidi et al. 2010, Ekholm et al. 2011, Nayak et al. 2011, Quintero et al. 2014). The authors give two reasons for this phenomenon. Firstly, PG is a source of poorly soluble phosphorus (Al-Karaki and Al-Omouh 2002, Ekholm et al. 2011). Secondly, large amounts of Ca are introduced together with waste into the soil, which results in increased phosphorus sorption, especially precipitation in the form of Ca-P complexes (Al-Karaki and Al-Omouh 2002, Delgado et al. 2002). On the other hand, in the studies by Yakovlev et al. (2013), PG level at 1.1% of soil mass (approx. 20 Mg·ha<sup>-1</sup>) increased the content of the available form of this component in the soil by about 23.5%. In the studies by Blum et al. (2014), even after the use of this waste in an amount equal to 9 Mg·ha<sup>-1</sup>, the P content in soil increased by about 15%. In the studies by Elrashidi et al. (2010), the content of this component increased by up to 30%, but only after the use of waste in an amount of 50% of soil mass. The highest reported content was obtained in the studies by Vyshkopolsky et al. (2008). The authors, after applying phosphogypsum in an amount equivalent to 8 Mg·ha<sup>-1</sup>, obtained a 62% increase in the available forms of P, yet notably, in that case the studies were conducted on soils with an extremely high magnesium content. In the studies by Bouray et al. (2020) and Tian et al. (2022), PG also had a positive effect on the phosphorus availability.

The increase in the content of P forms available to plants, as demonstrated in this study, was therefore higher than that given by other authors, thus proving that PG can be a significant source of this nutrient for plants. Simultaneously, an elevated P content in the control combinations in comparison to the initial soil content indicates that the cultivation of lupins under the low P supply contributes to the mobilization of phosphorus from other soil resources, which confirms the long-known theory of the high pre-crop value of these species (Lambers et al. 2013, Dissanayaka et al. 2017, Ding et al. 2021).

#### *Cadmium and lead content in soil material*

The presence of heavy metals in phosphogypsum is one of the main reasons why attempts at agricultural PG management have been reluctant (Al-Hwaiti and Al-Khashman 2015, Chabchoubi et al. 2021, Chernysh et al. 2021). The solubility of the phosphogypsum impurities is mainly determined by the pH reaction (Chabchoubi et al. 2021) and hydration level of the landfilled waste as well as its organic and inorganic ligand content (Ammar et al. 2013, Chabchoubi et al. 2021). At the same time, many components found in PG may form various types of compounds and complexes with each other, which are characterized by limited solubility (Bouray et al. 2020). According to Kassir et al. (2012), larger amounts of heavy metals are collected in hardly soluble waste fractions.

Under the conditions of this experiment, each time a dose of phosphogypsum modified the Pb content in soil material, and the direction of changes depended on the studied species and variety (Tab. 1). At the same time, the amount of a waste dose did not significantly affect the Cd content. That parameter

was indeed dependent on the cultivated lupin genotype. For most varieties of narrow-leaf and white lupins, after the use of phosphogypsum equivalent to 20 Mg·ha<sup>-1</sup>, the content of both studied heavy metals decreased in relation to the control combination. In contrast, after cultivation of yellow lupin, the Cd and Pb content in the soil material increased significantly at a waste dose of 20 Mg·ha<sup>-1</sup> and it decreased only after a higher dose corresponding to 50 Mg·ha<sup>-1</sup>. The average content of two tested components in the fertilized material was the highest after the cultivation of narrow-leaf lupin. There was no association between the efficiency in absorption and transport of phosphorus in tissues of the studied varieties and the Pb and Cd soil material content (Tab. 1).

The results obtained here are in line with the report of Enamorano et al. (2009), who concluded that increasing doses of PG did not contribute in proportion to the increased content of heavy metal. The more recent studies further support an insignificant effect of phosphogypsum on the content of these toxic elements in soil (Campbell et al. 2006, Kassir et al. 2012, Al-Hwaiti and Al-Khashman 2015, Tian et al. 2022). According to Enamorano et al. (2009), the actual level of toxic elements, which may be dispersed and/or uptaken by plants from soils fertilized with PG, does not exceed 1% of their total waste content. Most heavy metals react with different soil components to form poorly soluble complexes. Presumably, in the present study, the immobilization of Pb, which occurred after the use of phosphogypsum, was a result of the introduction, along with waste, of a large amount of Ca, S and P, causing its precipitation in poorly soluble forms (Kabata-Pendias and Pendias 2001).

On the other hand, the species- and variety-dependent effect of PG on the heavy metal contents observed in our experiment might be explained by different strategies being developed in various lupin species to efficiently extract phosphorus, and thus contributing differently to the modification of conditions in the rhizosphere (Pearse et al. 2006, Lambers et al. 2013, Ding et al. 2021, Aslam et al. 2021, Monei et al. 2022). However, a complete explanation of this phenomenon requires a more thorough analysis and goes beyond the scope of this work.

## **Effects of phosphogypsum on dry mass accumulation and the plant chemical composition**

### ***The dry mass accumulation***

Under the conditions of low abundance of the available phosphorus, the accumulation of dry matter varied significantly with regard to both species and variety (Tab. 2). The average biomass accumulation increased by species in the order such as: *Lupinus angustifolius* < *Lupinus luteus* < *Lupinus albus*. Increasing the dose of phosphogypsum did not significantly modify the lupine biomass. Of all the studied species, the narrow-leaved lupin was the only one which in each case responded with a significant increase in biomass after the application of phosphogypsum. The average biomass of white lupin remained at a similar level after the use of waste in the amount of 20 Mg·ha<sup>-1</sup> and was significantly reduced at the dose of 50 Mg·ha<sup>-1</sup>. The Lucrop variety was an exception. In the case of yellow lupine, growth reduction was observed after the use of a lower dose of the waste.

**Table 1.** Content of lead and cadmium in soil collected after vegetation, mg·kg<sup>-1</sup>

| Species                                    | Variety         | Cd                                      |             |             | Pb                                      |             |             |
|--------------------------------------------|-----------------|-----------------------------------------|-------------|-------------|-----------------------------------------|-------------|-------------|
|                                            |                 | Phosphogypsum dose, Mg·ha <sup>-1</sup> |             |             | Phosphogypsum dose, Mg·ha <sup>-1</sup> |             |             |
|                                            |                 | 0                                       | 20          | 50          | 0                                       | 20          | 50          |
| <i>Lupinus angustifolius</i> L.            | Oskar           | 0,17                                    | 0,11        | 0,17        | 4,70                                    | 3,65        | 4,05        |
|                                            | Kalif           | 0,12                                    | 0,19        | 0,10        | 3,58                                    | 4,58        | 3,28        |
|                                            | AU 11257 – 19/1 | 0,17                                    | 0,13        | 0,19        | 5,03                                    | 3,73        | 4,20        |
|                                            | LAE – 1         | 0,18                                    | 0,12        | 0,21        | 4,90                                    | 3,55        | 4,50        |
|                                            | <b>Mean</b>     | <b>0,16</b>                             | <b>0,14</b> | <b>0,16</b> | <b>4,55</b>                             | <b>3,88</b> | <b>4,01</b> |
| <i>Lupinus albus</i> L.                    | Pikador         | 0,14                                    | 0,10        | 0,20        | 4,78                                    | 3,33        | 4,48        |
|                                            | Egipt           | 0,14                                    | 0,13        | 0,20        | 4,33                                    | 4,03        | 4,00        |
|                                            | Lucrop          | 0,11                                    | 0,20        | 0,009       | 3,55                                    | 4,65        | 3,35        |
|                                            | Buttercup       | 0,17                                    | 0,12        | 0,17        | 4,68                                    | 3,55        | 3,93        |
|                                            | <b>Mean</b>     | <b>0,14</b>                             | <b>0,14</b> | <b>0,16</b> | <b>4,33</b>                             | <b>3,89</b> | <b>3,94</b> |
| <i>Lupinus luteus</i> L.                   | Taper           | 0,14                                    | 0,14        | 0,15        | 4,00                                    | 4,70        | 3,45        |
|                                            | Perkoz          | 0,13                                    | 0,19        | 0,08        | 3,70                                    | 4,65        | 3,15        |
|                                            | Lord            | 0,11                                    | 0,19        | 0,07        | 3,60                                    | 4,45        | 3,08        |
|                                            | Mister          | 0,15                                    | 0,14        | 0,12        | 4,13                                    | 4,70        | 3,48        |
|                                            | <b>Mean</b>     | <b>0,13</b>                             | <b>0,17</b> | <b>0,10</b> | <b>3,86</b>                             | <b>4,63</b> | <b>3,29</b> |
| <b>Mean for lupin</b>                      |                 | <b>0,14</b>                             | <b>0,15</b> | <b>0,14</b> | <b>4,25</b>                             | <b>4,13</b> | <b>3,74</b> |
| LSD <sub>0,05</sub> for dose               |                 | n.s.                                    |             |             | 0,123                                   |             |             |
| LSD <sub>0,05</sub> for lupin variety      |                 | 0,0125                                  |             |             | 0,244                                   |             |             |
| LSD <sub>0,05</sub> for interaction I × II |                 | 0,0219                                  |             |             | 0,417                                   |             |             |

**Table 2.** Dry matter yield in lupin varieties, g D.M.

| Species                                    | Variety         | Phosphogypsum dose, Mg·ha <sup>-1</sup> |             |             |
|--------------------------------------------|-----------------|-----------------------------------------|-------------|-------------|
|                                            |                 | 0                                       | 20          | 50          |
| <i>Lupinus angustifolius</i> L.            | Oskar           | 0,90                                    | 0,99        | 0,99        |
|                                            | Kalif           | 0,54                                    | 0,75        | 0,86        |
|                                            | AU 11257 – 19/1 | 0,89                                    | 0,98        | 0,94        |
|                                            | LAE – 1         | 0,66                                    | 0,96        | 1,05        |
|                                            | <b>Mean</b>     | <b>0,75</b>                             | <b>0,92</b> | <b>0,96</b> |
| <i>Lupinus albus</i> L.                    | Pikador         | 1,67                                    | 1,83        | 1,73        |
|                                            | Egipt           | 1,88                                    | 1,68        | 1,52        |
|                                            | Lucrop          | 1,50                                    | 1,62        | 1,73        |
|                                            | Buttercup       | 1,51                                    | 1,38        | 0,91        |
|                                            | <b>Mean</b>     | <b>1,64</b>                             | <b>1,62</b> | <b>1,47</b> |
| <i>Lupinus luteus</i> L.                   | Taper           | 1,17                                    | 0,91        | 0,87        |
|                                            | Perkoz          | 0,95                                    | 0,82        | 1,24        |
|                                            | Lord            | 0,90                                    | 0,84        | 0,97        |
|                                            | Mister          | 1,21                                    | 1,21        | 1,22        |
|                                            | <b>Mean</b>     | <b>1,06</b>                             | <b>0,94</b> | <b>1,07</b> |
| <b>Mean for lupin</b>                      |                 | <b>1,15</b>                             | <b>1,16</b> | <b>1,17</b> |
| LSD <sub>0,05</sub> for dose               |                 | n.s.                                    |             |             |
| LSD <sub>0,05</sub> for lupin variety      |                 | 0,108                                   |             |             |
| LSD <sub>0,05</sub> for interaction I × II |                 | 0,190                                   |             |             |



Lupins constitute a highly diverse group in terms of habitat requirements (Gresta et al. 2017). In general, white lupin has the highest yielding potential, narrow-leaf lupin has a lower one, and yellow lupin the lowest, but it can be subject to significant fluctuations. The results from previous studies exhibited a high variability of this parameter depending on different growth conditions, in particular climatic and soil conditions (Gresta et al. 2017, Abraham et al. 2019). Moreover, they also pointed to a significant variation in yields, both between different lupin species and their varieties and even populations (Gresta et al. 2017). That is in accordance with the results of the current experiment, where, under the conditions of low available phosphorus, the accumulation of dry matter varied significantly with regard to both species and variety (Tab. 2). The average biomass accumulation increased by species in the order such as: *Lupinus angustifolius* < *Lupinus luteus* < *Lupinus albus*.

#### Phosphorus content and uptake in plant material

During the present experiment, the differences in the intracellular P content within individual lupin species were more distinctive than the differences in the P content in soil material samples collected after cultivation of lupin varieties. On average, the highest amount of phosphorus in plants, regardless of the dose of phosphogypsum, was found in narrow-leaf lupin varieties (Fig. 3), and the lowest in white lupin varieties. The varieties that contained high phosphorus concentrations in the absence of the PG supplementation did not always have the highest P content after the use of the waste. The maximum phosphorus content of  $7.5 \text{ g P} \cdot \text{kg}^{-1}$  was recorded in plants of the Kalif variety (narrow-leaf lupin).

Despite the low level of the available phosphorus in the soil material used in the studies ( $\text{P-ER} = 3.20 \text{ mg} \cdot 100 \text{ g}^{-1}$ ), the content of this component in the aboveground parts of all the studied varieties of narrow-leaf lupin and yellow lupin (Fig. 3) was higher than the critical content necessary to obtain 90% of the maximum yield of the grain. According to Bolland et al. (1997), before flowering it should amount to  $2.2 \text{ g P} \cdot \text{kg}^{-1} \text{ DM}$  for white lupins, and  $2.3 \text{ g P} \cdot \text{kg}^{-1} \text{ DM}$  for yellow lupins and narrow-leaf lupins.

Under the conditions of the conducted experiment, after a lower dose equivalent to  $20 \text{ Mg} \cdot \text{ha}^{-1}$ , a significant increase in the intracellular P content was observed in the *Lupinus albus* and *Lupinus luteus* varieties as compared to the control level (Fig. 3). This value exceeded  $3.0 \text{ g P} \cdot \text{kg}^{-1}$ , which proved that the plants were well nourished with phosphorus, and at the same time it indicated that they could effectively use the poorly available forms of this nutrient. However, a significant increase in the P concentration in the aboveground parts in most varieties of *Lupinus angustifolius* was observed only after a higher dose of PG. In the aboveground parts of white lupin and yellow lupin, the observed increase in the intracellular P content due to increasing doses of phosphogypsum was more steady. The Lord variety was an exception in this respect, as the P content in its tissues increased significantly only after the use of the waste in an amount equal to  $50 \text{ Mg} \cdot \text{ha}^{-1}$ .

The mean P uptake of all studied varieties ranged from  $3.7$  to  $6.5 \text{ mg P} \cdot \text{pot}^{-1}$  (Fig. 3). Except for AU 11257-1/19 and Buttercup, increasing amount of the PG supplementation resulted in an increased P uptake in lupins. On average, the highest increase in phosphorus uptake after the highest dose of

waste in relation to the control values was recorded for narrow-leaf lupins, however that differed in variety-dependent manner. The highest absolute P uptake was observed in white lupins, which resulted from high biomass accumulation. Regardless of the applied PG dose, the average P uptake remained very similar in narrow-leaf lupins and yellow lupins, despite a significant difference in the amount of biomass accumulated by both species. Similar to the intracellular P content, the varieties characterized by highest P uptake in the control combination, did not necessarily demonstrate high uptake of this nutrient after the application of the waste.

As already mentioned, in the previous reports on the possibility of using PG for fertilizing arable crops, it has often been demonstrated that the use of this waste does not contribute to an increase in the available P in the soil or its content in plants (Ekholm et al. 2011, Nayak et al. 2011, Quintero et al. 2014). The results from our experiment, however, are in line with other authors, according to whom PG can be a significant source of phosphorus for plants (Vyshpolsky et al. 2008, Yakovlev et al. 2013, Bouray et al. 2020). At the same time, we observed a significant species- and variety-dependent trends in phosphorus uptake and content. As previously reported by Pearse et al. (2006) and Abdolzadeh et al. (2010), individual species of lupins are characterized by significant differences in the P content in tissues. Pearse et al. (2006) observed that under the conditions of limited availability of this nutrient, the highest concentration in aboveground parts decreased in the order such as: yellow lupins > narrow-leaf lupins > white lupins. Similarly, Brennan and Bolland (2003) studying two species of lupins indicated that they had a similar phosphorus content in aboveground shoots, but yellow lupins contained more of it in seeds. According to the authors, the higher efficiency of yellow lupin in P acquisition was due to the fact that the plants were grown on acidic soil, which could contribute to a better growth of its roots, and thus promote a better utilization of this component than in the case of narrow-leaf lupins. Funayama-Noguchi et al. (2015) observed that under the P-deficiency conditions, the concentration of this nutrient in the roots and shoots of white and narrow-leaf lupin remained at a similar level, while it was significantly higher in the leaves of narrow-leaf lupin. Importantly, however, the indicated differences may have been a consequence of different sampling dates, differences in the growth conditions of the studied plants (Pearse et al. 2006), but also the different reaction of individual varieties (Chen et al. 2013).

Furthermore, the varieties that during our experiment efficiently accumulated phosphorus at cellular level under the conditions of its limited availability, did not always have the highest P content under the PG supplementation conditions (Fig. 3). Presumably, the efficiency of the developed P-acquisition strategies in various lupin species may depend on a number of external factors, as previously pointed out by other authors (Cheng et al. 2014, Dissyanaka et al. 2017, Aslam et al. 2021). The use of PG, which contributes to the modification of soil conditions, may affect a number of other properties in rhizosphere and modify ability of lupins to uptake this component. It has been well-documented that individual species and even varieties differ significantly not only in terms of the P content in tissues, but also can vary significantly in terms of sensitivity to changing environmental factors, and hence the



variable effectiveness of the strategies used (Egle et al. 2003, Chen et al. 2013, Lambers et al. 2013, Aslam et al. 2021).

### Phosphorus utilization factor

Despite many years of research to improve the P availability to plants, this issue remains one of the main challenges in the scope of agriculture (Dhillon et al. 2017). Compared with the efficiency of nitrogen and potassium utilization, which is 50% and 40% respectively (Smaling et al. 2006), the efficiency of phosphorus utilization in the year of its application rarely exceeds 25%, and more often is only equal to 10–15% of the applied P dose (Roberts and Johnston 2015, Dhillon et al. 2017). The efficiency of the nutrient utilization can be calculated in several ways. The RE method (*Crop recovery efficiency*) is the most common and widely used approach for evaluating nutrient utilization efficiency. However, Syers et al. (2008) proved that the phosphorus recovery values obtained by this method may often be heavily underestimated, indicating that P is utilized inefficiently, and thus they recommend the PNB method (*Partial nutrient balance*). Therefore, in the present study, the phosphorus use efficiency was estimated according to both methods.

During our experiment, the efficiency factors of phosphorus utilization for the RE method ranged from -0.89% to 6.04%, and for the PNB method from 5.19% to 14.12% (Tab. 3). The estimated values of the factors were significantly dependent on both the applied PG dose as well as the species and variety of lupin. On average, the highest phosphorus efficiency factors were recorded for white lupins, especially after a PG dose equivalent to 20 Mg·ha<sup>-1</sup>. The mean P recovery recorded for white lupins at a dose of 50 Mg·ha<sup>-1</sup> was more

similar to that estimated for yellow and narrow-leaf lupins. According to Roberts and Johnston (2015) the phosphorus recovery values estimated by the RE method usually do not exceed 10–15% in the first year of cultivation, while by the PNB method they often range from 50 to 70%. The efficiency factors of phosphorus utilization estimated by both methods were significantly lower.

The P uptake is influenced by a number of factors that need to be taken into account when interpreting the phosphorus use efficiency factors (Roberts and Johnston 2015, Dhillon et al. 2017). Notably, the highest phosphorus use efficiency recorded for white lupin was mainly due to the highest dry mass production by this species (Tab. 2) rather than the highest P content in tissues (Fig. 3). On the other hand, the relatively low efficiency of phosphorus utilization estimated in this experiment was not only a consequence of the application of a poorly soluble P source for fertilization, i.e., phosphogypsum, but also resulted from the short duration of the experiment. That points out to the necessity to conduct more studies aimed at assessing the long-term efficiency of phosphorus utilization from PG.

### The effect of phosphogypsum on the sulphur content in lupins

PG is a waste containing approximately 24–34% of CaO and even around 48–58% of SO<sub>3</sub> (Saadaoui et al. 2017). The introduction of the waste containing a high sulphur concentration may result, under certain conditions, in the ionic imbalance in the soil (Bouray et al. 2020). In the course of the current experiment, no significant increase was observed in the S content in aboveground parts of plants, even after the

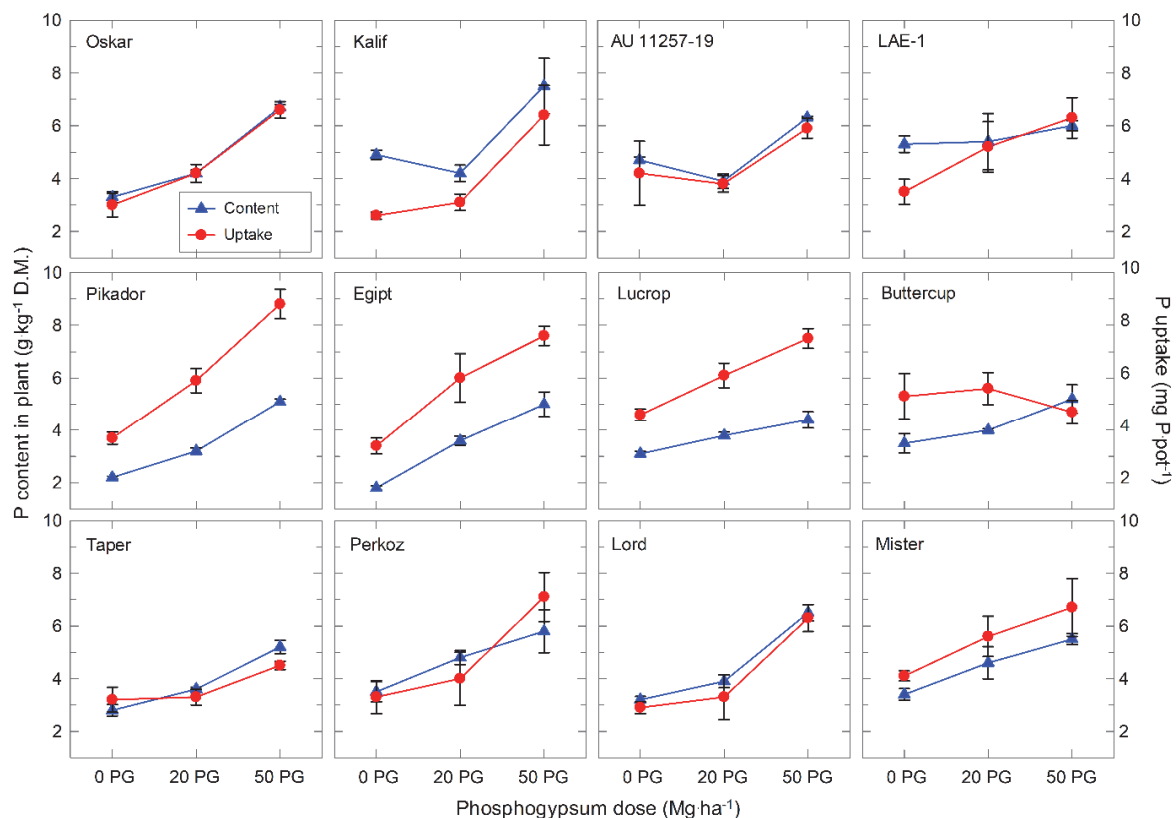


Fig. 3. Phosphorus content (g.kg<sup>-1</sup>) and uptake (mg.pot<sup>-1</sup>) in lupin varieties

application of the highest PG dose (Fig. 4). Individual lupins accumulated this nutrient in different ways, however, no link was found between the varied capacity of varieties to mobilize and transport P and S in plant tissues. The recorded intracellular sulphur concentration ranged from 0.4 to 3.2 g S.kg<sup>-1</sup>. On average, it was demonstrated that the studied lupin species responded with an increased S content after the application of PG at a dose of 20 Mg·ha<sup>-1</sup>, and remained at a similar level when fertilized with the PG dose of 50 Mg·ha<sup>-1</sup>. The results here are consistent with previous findings in other species, including maize and lucerne, where no excessively high S content was observed in response to phosphogypsum supplementation (Caires et al. 2004, Blum et al. 2013 and 2014, Bouray et al. 2020). According to the authors, it is due to the fact that PG is a waste that dissolves gradually, and thus gradually releases this component. This process is particularly evident in clay soils, which additionally retain part of the released sulphur on colloidal surfaces (Blum et al. 2014).

#### Cadmium and lead content in plant tissue

Due to the high environmental durability of heavy metals and their high tendency to bioaccumulate (Grochowska et al. 2021, Lopez-Chuken et al. 2021), their content in PG has to be controlled (Chabchoubi et al. 2021). That is especially important for plants that accumulate heavy metals in large quantities. According to many authors, the highest risk to the environment and human health resulting from the use of the waste is associated with a relatively high Cd content (Enamorado et al. 2009, Al-Hwaiti and Al-Khashman 2015, Elloumi et al. 2015, Smaoui-Jardak et al. 2017). Cd inhibits plant growth by interfering with processes such as cell division, photosynthesis, nutrient uptake, as well as enhancing oxidative stress and disrupting hormonal homeostasis (Manzoor et al. 2022, Ouyang et al. 2022). As demonstrated by Kassir et al.

(2012), despite only a slight increase in the Cd soil content after the application of PG, both the roots and leaves of the cultivated chicory (*Cichorium intybus* L.), which acts as a heavy metal accumulator, contained much more Cd than the level of tolerance for this plant.

The lupin species studied in the present experiment demonstrated a high diversity in the intracellular Cd and Pb concentration (Tab. 4) in aboveground parts. Each time yellow lupin contained the highest amount of Cd, while narrow-leaf lupin of Pb. It was also observed that the content of all studied elements decreased in *L. angustifolius* after the PG application. In *L. luteus* and *L. albus*, the waste supplementation contributed to a decrease in Pb content compared to the control plants, but had no limiting effect on Cd accumulation. The intracellular Pb concentration in most of the varieties was reduced already after the application of PG at a dose of 20 Mg·ha<sup>-1</sup>. The Cd concentration in both species, irrespective of the applied dose, remained at a similar level. During the experiment, the variety-dependent ability to accumulate Cd and Pb in aboveground parts was also observed within individual lupin species, but it did not coincide with different abilities of varieties to absorb and transport phosphorus.

The results obtained here are in line with previous studies on the accumulation of heavy metals in lupins. Brennan and Bolland (2003), studying two lupin species demonstrated that regardless of the source and dose of P, each time yellow lupin contained 4–25 times more Cd than narrow-leaf lupin. Römer et al. (2000) demonstrated that the content of this component in the shoots of narrow-leaf lupin was at least several times higher than that of white lupin. In addition, in the case of *L. albus*, the authors observed a high genotype-dependent variability of this parameter. In the studies by Trejo et al. (2016), the cadmium content recorded in narrow-leaf lupin was up to 344% higher than in white lupin.

**Table 3.** Phosphorus use efficiency estimated by the balance method (PNB) and the difference method (RE), %

| Species                         | Variety         | Phosphorus use efficiency (%) |             |              |             |
|---------------------------------|-----------------|-------------------------------|-------------|--------------|-------------|
|                                 |                 | RE                            |             | PNB          |             |
|                                 |                 | 20 PG                         | 50 PG       | 20 PG        | 50 PG       |
| <i>Lupinus angustifolius</i> L. | Oskar           | 2,88                          | 2,78        | 9,70         | 7,63        |
|                                 | Kalif           | 1,20                          | 3,82        | 7,24         | 7,44        |
|                                 | AU 11257 – 19/1 | -0,76                         | 2,41        | 8,88         | 6,85        |
|                                 | LAE – 1         | 3,88                          | 1,30        | 11,98        | 7,29        |
|                                 | <b>Mean</b>     | <b>1,80</b>                   | <b>2,58</b> | <b>9,45</b>  | <b>7,30</b> |
| <i>Lupinus albus</i> L.         | Pikador         | 5,08                          | 3,29        | 13,68        | 10,14       |
|                                 | Egipt           | 3,49                          | 1,60        | 14,12        | 8,66        |
|                                 | Lucrop          | 6,04                          | 1,85        | 13,87        | 8,79        |
|                                 | Buttercup       | 0,52                          | -0,89       | 12,83        | 5,44        |
|                                 | <b>Mean</b>     | <b>3,78</b>                   | <b>1,44</b> | <b>13,63</b> | <b>8,26</b> |
| <i>Lupinus luteus</i> L.        | Taper           | 0,03                          | 1,43        | 7,52         | 5,19        |
|                                 | Perkoz          | 1,52                          | 3,67        | 9,13         | 8,23        |
|                                 | Lord            | 0,92                          | 3,55        | 7,51         | 7,31        |
|                                 | Mister          | 3,31                          | 1,25        | 12,85        | 7,67        |
|                                 | <b>Mean</b>     | <b>1,44</b>                   | <b>2,48</b> | <b>9,25</b>  | <b>7,10</b> |
| <b>Mean for lupin</b>           |                 | <b>2,34</b>                   | <b>2,17</b> | <b>10,78</b> | <b>7,55</b> |

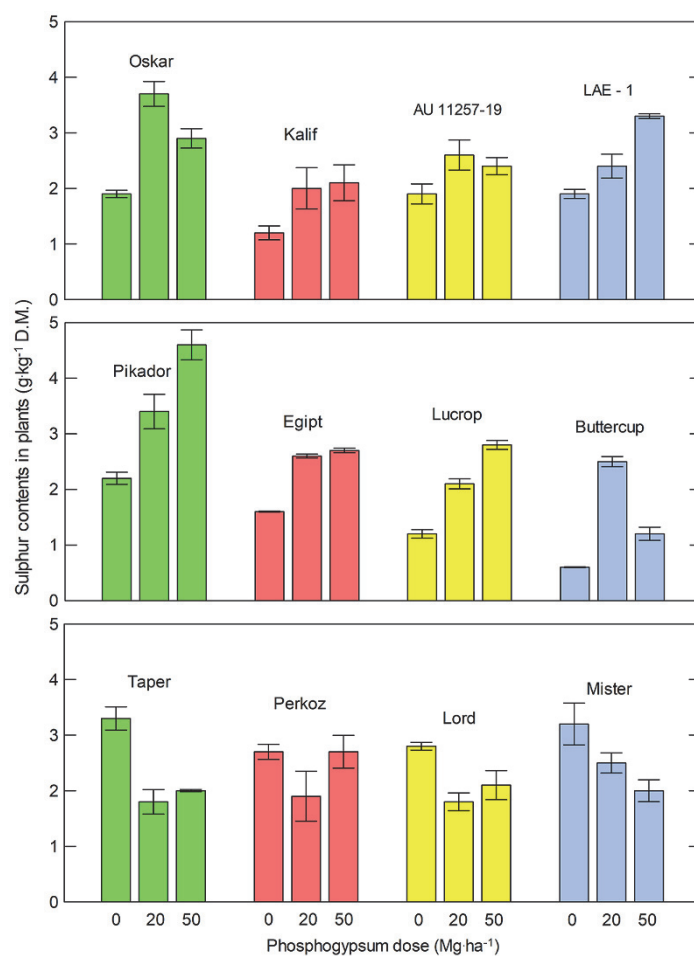


Fig. 4. Sulphur content in lupin varieties (g·kg<sup>-1</sup>)

Table 4. Content of lead and cadmium in plant, mg·kg<sup>-1</sup>.

| Species                                    | Variety         | Cd                                      |      |      | Pb                                      |      |      |
|--------------------------------------------|-----------------|-----------------------------------------|------|------|-----------------------------------------|------|------|
|                                            |                 | Phosphogypsum dose, Mg·ha <sup>-1</sup> |      |      | Phosphogypsum dose, Mg·ha <sup>-1</sup> |      |      |
|                                            |                 | 0                                       | 20   | 50   | 0                                       | 20   | 50   |
| <i>Lupinus angustifolius</i> L.            | Oskar           | 1,44                                    | 1,59 | 1,46 | 14,1                                    | 10,5 | 5,5  |
|                                            | Kalif           | 1,66                                    | 1,05 | 1,26 | 14,6                                    | 5,2  | 5,6  |
|                                            | AU 11257 – 19/1 | 1,08                                    | 1,58 | 1,32 | 13,3                                    | 11,1 | 4,7  |
|                                            | LAE – 1         | 1,26                                    | 1,81 | 1,19 | 19,9                                    | 10,8 | 4,8  |
|                                            | Mean            | 1,36                                    | 1,51 | 1,30 | 15,5                                    | 9,4  | 5,1  |
| <i>Lupinus albus</i> L.                    | Pikador         | 0,60                                    | 0,40 | 0,55 | 5,1                                     | 2,7  | 2,6  |
|                                            | Egipt           | 0,59                                    | 0,43 | 0,59 | 4,6                                     | 2,7  | 2,8  |
|                                            | Lucrop          | 0,73                                    | 0,50 | 0,49 | 5,9                                     | 2,4  | 2,7  |
|                                            | Buttercup       | 0,56                                    | 0,75 | 0,76 | 6,3                                     | 6,8  | 4,1  |
|                                            | Mean            | 0,62                                    | 0,52 | 0,60 | 5,5                                     | 3,6  | 3,0  |
| <i>Lupinus luteus</i> L.                   | Taper           | 1,91                                    | 1,68 | 2,13 | 8,8                                     | 4,6  | 5,0  |
|                                            | Perkoz          | 2,11                                    | 1,97 | 2,04 | 11,8                                    | 4,8  | 3,4  |
|                                            | Lord            | 1,85                                    | 2,03 | 1,94 | 9,6                                     | 4,4  | 4,8  |
|                                            | Mister          | 1,49                                    | 1,79 | 2,21 | 7,3                                     | 4,3  | 3,5  |
|                                            | Mean            | 1,84                                    | 1,87 | 2,08 | 9,4                                     | 4,5  | 4,2  |
| Mean for lupin                             |                 | 1,27                                    | 1,30 | 1,33 | 10,11                                   | 5,85 | 4,13 |
| LSD <sub>0,05</sub> for dose               |                 | n.s.                                    |      |      | 0,426                                   |      |      |
| LSD <sub>0,05</sub> for lupin variety      |                 | 0.175                                   |      |      | 0,758                                   |      |      |
| LSD <sub>0,05</sub> for interaction I × II |                 | 0.308                                   |      |      | 1,320                                   |      |      |

The decrease in Cd and Pb content in aboveground parts of the studied lupin species (Tab. 4), in particular in narrow-leaf lupin, observed here as a result of the PG application, might be explained in two ways. Firstly, the introduction of an additional pool of phosphorus into the soil may contribute to an increased production and secretion of organic acids from roots, which under certain conditions can chelate toxic elements, and thus limit their availability to plants (Römer et al. 2000, Monei et al. 2022). The released citrate can complex up to 85% of Cd, but this effect is highly dependent on the type of soil (Römer et al. 2000). Secondly, as indicated by Campbell et al. (2006), the presence of certain components in phosphogypsum, such as calcium and sulphur, can contribute to reducing heavy metal mobility and leaching, thereby reducing their availability in rhizosphere. Notably, the Cd content in plants determined here (Tab. 4) was higher than the average found in plants from unpolluted regions, which, according to Kabata-Pendias and Pendias (2001), range from 0.05 to 0.2 mg Cd·kg<sup>-1</sup>. However, despite the introduction of high PG doses, they were still at least half the level considered phytotoxic for the most sensitive plant species (Kabata-Pendias and Pendias 2001, Ouyang et al. 2022).

## Conclusions

The PG application in lupin cultivation effectively increased the content of both available and active P in the soil material. The concomitant acidification of the soil material with an increasing dose of this waste, however, indicates that PG should be used in the cultivation of plant species tolerant to acidic reaction, or together with the materials that exhibit an alkalizing effect. The increase in the available P forms in the soil material elevated the intracellular content and uptake of this nutrient in the studied plant species. However, the level of P accumulation depends not only on the applied PG dose but is clearly variety-dependent, as evidenced by the calculated phosphorus utilization factor. Importantly, the heavy metals, Pb and Cd, present in phosphogypsum did not affect their accumulation in the aboveground parts of the cultivated plants. The obtained results indicate the possibility of using P forms contained in PG as an efficient and safe source of this component in plant nutrition, at the same time eliminating heaps of this waste deposited on huge areas, which will contribute to improving the quality of the environment.

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## Ocena zastosowania odpadu fosfogipsu w żywieniu roślin

**Streszczenie:** Fosfogips (PG) to materiał odpadowy wytwarzany w ogromnych ilościach i zawierający szeroką gamę zanieczyszczeń, stanowiąc w ten sposób poważny problem środowiskowy. Spośród proponowanych strategii potencjalnego zagospodarowania PG, żadna nie została jak dotąd wdrożona na szeroką skalę. Następujące w tym samym czasie szybkie wyczerpywanie się zasobów fosforytów, wykorzystywanych do produkcji większości komercyjnych nawozów fosforowych (P), stawia bezprecedensowe wyzwania dla przyszłego rolnictwa i ochrony środowiska. Celem pracy była ocena możliwości wykorzystania PG jako alternatywnego źródła P do nawożenia roślin. Wpływ suplementacji PG na akumulację suchej masy, zawartość P i siarki (S) w glebie i nadziemnych częściach roślin oraz poziom zanieczyszczeń metalami ciężkimi badano w modelu doświadczalnym złożonym się z 12 genotypów trzech gatunków łubinu – *Lupinus angustifolius*, *Lupinus albus* i *Lupinus luteus*. Suplementacja PG zwiększyła zawartość zarówno dostępnego, jak i aktywnego P w glebie. Zwiększona biodostępność P skutkowała zwiększonym pobraniem i wewnątrzkomórkowym stężeniem tego składnika w badanych gatunkach roślin w sposób zależny od dawki i odmiany. Obecność metali ciężkich w odpadzie nie wpłynęła na ich zwiększoną akumulację w tkankach roślinach. Wyniki wskazują na możliwość wykorzystania P obecnego w fosfogipsie jako alternatywnego źródła tego składnika w żywieniu roślin, pozwalając jednocześnie na eliminację odpadów PG zalegających na ogromnych powierzchniach, co z pewnością przyczyni się do poprawy jakości środowiska.