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Research Article

Phosphorus Sorption Kinetics in Reclaimed Lignite Mine Soils under Different Age Stands of *Robinia pseudoacacia* L. in Northeast Germany

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The objectives of the work were to study phosphorus (P) dynamics in postmining soils under short rotation coppices at different stages of *Robinia pseudoacacia* L. growth (2, 3, 4, and 14 years old). From the results obtained, the amount of total P, total organic P, plant available P, and P stock increased with increasing age of *R. pseudoacacia*. However, values were very low compared to that recommended for optimum plant growth, reflecting a general deficit in P. Additionally, the P sorption and desorption processes were investigated. The total P sorption capacity obtained from the laboratory experiments was on average, 2.5 times greater for soils under the oldest *R. pseudoacacia* than values measured at the younger sites. Values of P saturation factor (α) were comparatively lower compared to that reported in the literature. This may be attributed primarily to the less P saturation of the postmining soils, coupled with rather small contents of oxalate iron (Fe_{ox}) and aluminium (Al_{ox}) (sum of 47 mmol kg⁻¹). Results demonstrate significant difference between 2 and 14 years old *R. pseudoacacia*; thus establishing of short rotation coppice (SRC) on degraded marginal sites may be a valuable method of soil reclamations.

1. Introduction

Due to the open cast mining activities in Brandenburg large areas are left unproductive, where the cultivation of short rotation tree plantation (short rotation coppice SRC) was considered as a viable option for reclamation purposes [1]. In the Lusatia region of eastern Germany (about 100 km southeast of Berlin), amelioration and rehabilitation measures for a large scale open-cast lignite mining areas have been established since the 1950s. In this region an area of about 1000 km² has been degraded by mining activities [2]. The dominant land use management after mining in this area is focused on plant succession and the establishment of forest ecosystems. The reclaimed overburden sediment is often characterized by low nutrient status, lack of soil organic matter (OM), low water retention capacity, and small microbial populations [2–4].

The plant mainly used for the recultivation of these marginal sites is black locust (*Robinia pseudoacacia* L.), since

it has the ability to grow on the nutrient poor sandy substrate with low water holding capacity [5, 6]. Besides, as a $\rm N_2$ fixing tree, it can also improve soil fertility through increase in soil OM input and thereby greatly improve and increase nutrient content and availability [7–13]. The cultivation of *R. pseudoacacia* is considered as a good method for land reclamation [6, 11, 14–16]. It grows very fast especially during the young stages of development and it has been reported that on reclamation sites in the Lusatia region the aboveground growth rates were about 5.8 t ha⁻¹ year⁻¹ [5] and can reach up to 9.5 t ha⁻¹ year⁻¹ in the older plantation [17]. The establishment of the woody plantation on marginal sites can be a promising tool and may be beneficial not only from the ecological aspects but also for providing economic benefits such as the production of bioenergy [1, 5, 11, 18, 19].

Owing to the unfavourable biotic and abiotic properties of the overburden mining substrate, the biogeochemical processes associated with soil ecosystem development can be said to be in the initial phase. The substrate contains very

		Area	I	Dominant substrate			Fertilizer rates		
Study site	Established in	ha	Sand	Silt	Clay	N	P	K	
		IIa		%			$kg ha^{-1}$		
R2	2007	11.7	87.4	7.9	4.7	120	100	_	
R3	2006	8.6	87.3	8.7	4.0	120	100	_	
R4	2005	13.2	80.0	13.0	7.0	120	100	_	
R14	1994	0.75	74.6*	4.3*	20.3*	170	_	100	

TABLE 1: Description of the study sites located in the postlignite mining area, Welzow South.

low amount of nutrients, especially very low P content (nearly equal to zero). The efficiency of applied P fertilizer is one of the main problems in recultivation of this marginal site, since P fertilizer can be largely fixed by oxalate-extractable iron (Fe_{ox}) and aluminium (Al_{ox}), which makes it less available or effectively unavailable to plants [20–24]. Therefore, it is important to understand the kinetics of P sorption in this "initial soil" in order to describe the P bioavailability and P mobility.

Several studies have been carried out on soil P sorption and desorption kinetics in agroecosystems [25–43], and various techniques have been employed to investigate P (de)sorption from soils [29, 30, 32, 44, 45]. However, few studies [22, 46] concentrated on P sorption in mining soils. We hypothesized that *R. pseudoacacia* plantations of different ages would cause significant change in soil P dynamics over time. The objective of this study was therefore to determine and evaluate P sorption kinetics of postlignite mining soils at the early stages of development. Additionally, the degree of soil P saturation (an index of fertility component) as an environmental indicator for P management in mine soils was measured and calculated.

2. Materials and Method

2.1. Study Sites Descriptions. The field experiment with the fast growing tree species, R. pseudoacacia, was established on overburden substrates at the Lusatian lignite mining district in Welzow South (51°36′N, 14°18′E) in northeastern Germany. The mean annual temperature of the region is 9.4°C and the mean annual precipitation is 569 mm [5]. The substrates are mainly overburden sand partly with loamy sands and loams with varying amounts of lignite particles. The study sites have a low productivity and are currently used for the production of woody biomass for energy transformation purposes. The soil is inherently poor in nutrients such as phosphorus, potassium, and magnesium and therefore can be equated to soil at initial phase of development. The recultivated studied sites comprised R. pseudoacacia trees of different growth ages.

The trees were planted between 1995 and 2007 and at the time of sampling (November 2008), the *R. pseudoacacia* was 2, 3, 4, and 14 years old representing the following treatments: R2, R3, R4, and R14, respectively (Table 1).

The study sites R2, R3, and R4 are located within the same vicinity and were planted with the *R. pseudoacacia* in double rows with a distance of 180 cm between the rows, to allow

the use of harvesting machines. The distance between two tree rows within the double row is 75 cm and the distance between the plants is 85 cm. The average initial planting densities correspond to 9.200 trees ha $^{-1}$. Only in the year of planting mineral fertilizers were applied in the amount of $120\ kg\ N\ ha^{-1}$, $100\ kg\ P\ ha^{-1}$, and $80\ kg\ K\ ha^{-1}$ and ploughed up to the depth of $0.3\ m$.

The oldest site, R14, is located approximately 5 km south of R2, R3, and R4 sites. Site was established in spring 1994 and at the same time fertilized ones with 170 kg N ha⁻¹ and 100 kg K ha^{-1} , *R. pseudoacacia* was then planted in single row design with $1.9 \times 0.8 \text{ m}$ space among plants.

2.2. Sampling. Soils were sampled in November 2008. From each study site six independent replicates were taken; each replicate is a composite of five subsamples bulked together and represents one permanent monitoring plot. Each of the monitoring plots comprised 4 double rows with 19 trees in each row. Soil was sampled at three depths: 0–3 cm, 3–10 cm, and 10–30 cm using a 5 cm diameter auger. The sampled cores were put into a plastic container and homogenized, and roots were carefully removed. Portion of the soil was stored at 4°C to preserve moisture and the remaining was air-dried, sieved at 2 mm, and stored at room temperature for later chemical analyses.

2.3. Chemical Analyses. Soil pH was measured in 0.01 M $CaCl_2$ at weight (soil) to volume ($CaCl_2$) ratio of 1:2.5. The total organic carbon (TOC) and total nitrogen (TN) contents were analyzed by dry combustion using Vario EL III CNS Elemental Analyzer (Elementar Instruments, Hanau, Germany). Plant available P (Pav) was determined by the method of Olsen et al. [47]. The total organic P (TPo) was measured after loss on ignition followed by digestion with 0.5 M H₂SO₄ and P concentration in the filtrate was determined by using the standard ammonium molybdate method of Murphy and Riley [48]. In the ignition method all Po is converted into Pi [49]. The TPo is estimated by the difference between ignited and unignited samples. Soil microbial P (PMB) was determined in the fresh samples by the irradiation-extraction method, using microwave [50] and 0.5 M NaHCO₃ (pH 8.5) as extractant [51]. The P concentration of the filtered extract was quantified by the method of Murphy and Riley [48] using spectrophotometer (Uvikon) at 880 nm wavelength. The P_{MB} content was calculated by the difference between P

^{*} After Bungart and Hüttl [1].

Table 2: Tested kinetics equations for measured P (de)sorption kinetics.

Model	Equation	Parameters
Elovich	$q_t = 1/\beta * \ln(\alpha\beta) + 1/\beta * \ln t$	α —initial P (de)sorption constant [mg P kg ⁻¹ min ⁻¹] β —P (de)sorption rate constant [mg P kg ⁻¹]
Parabolic	$q_t = q_0 + k_p t^{0.5}$	k_p —diffusion rate constant
Exponential	$q_t = at^b$	<i>a</i> —P (de)sorption magnitude constant [mg P kg ⁻¹ min ⁻¹] <i>b</i> —(de)sorption rate constant

 q_0 and q_t are the amount of P (de)sorption (mg P kg⁻¹) at initial time and at time t, respectively.

concentration in irradiated and nonirradiated samples (based on dry mass) divided by a conversion factor of 0.40 used to convert the flow of P into microbial biomass [51]. The method of Schwertmann [52] and McKeague and Day [53] was used to determine the oxalate-extractable iron (Fe $_{\rm ox}$), aluminium (Al $_{\rm ox}$), and phosphorus (P $_{\rm ox}$) by extraction with acid-ammonium oxalate (pH 3) in the dark. The soil P stocks have been calculated from the P $_{\rm ox}$, [22, 54] (P $_{\rm ox}$ value accounts for up to 93% of total P). The P stock for each soil depth was estimated according the formula:

$$P_{\text{stock}}\left(\text{Mg ha}^{-1}\right) = X \times \text{BD} \times \text{th} \times (1 - S) \times 10^{-1},$$
 (1)

where X is the content of P_{ox} (g kg⁻¹), BD is the bulk density (Mg m⁻³), th is the thickness of the soil layer (cm), and S is the stones content.

2.4. Phosphorus Sorption and Desorption

2.4.1. Soil (De)Sorption Kinetics Theory. In the literature most commonly used equations to estimate P sorption capacity (PSC) in soils is a function of the sum of Fe_{ox} and Al_{ox} [22, 54]:

$$PSC = \alpha * (Fe_{ox} + Al_{ox}), \qquad (2)$$

where the saturation factor α has been estimated in various studies with the value of 0.5 [33, 34, 40, 54, 55]. Van der Zee [56] reported α values in the range of 0.4 to 0.6 (average of 0.5). This means that 1 mmol of the sum of Fe_{ox} and Al_{ox} sorbs a maximum 0.5 mmol of P [55]. The given equation represents the capacity of soil to sorb P and means that P is mainly associated with amorphous Fe and Al found in soils.

However, in this study P sorption was measured experimentally and values of total P sorption capacity (PSCt) were calculated as presented by Freese et al. [22]. The PSCt is expressed as the sum of $P_{\rm ox}$ and P sorption measured in the laboratory at different reaction time:

$$PSCt = P_{ox} + PS, (3)$$

where PSCt is the total P sorption capacity (mmol kg⁻¹), P_{ox} is the oxalate extractable P considered as the P initially sorbed by the soil (the already used P capacity), and PS is the actual measured P sorption of soil at different time intervals.

To fit the time dependent measured P (de)sorption data and describe the kinetics of P sorption the following equations were tested: Elovich equation, parabolic diffusion,

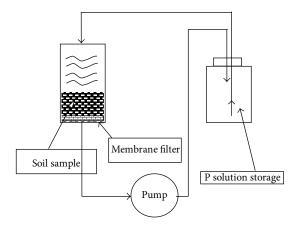


FIGURE 1: Adsorption experiment with a flow-through reactor.

and exponential equations (Table 2). All models were tested by the least-square regression analysis to determine which equations best describe the P (de)sorption kinetics of the investigated soils.

2.4.2. Phosphorus Sorption Kinetics. The P sorption kinetics of soil was measured in column experiment using the flowthrough reactor-setup described by Freese et al. [57]. The flow-through reactor method is an experimental setup with a closed loop arrangement, where the P-containing solution circulates continuously between the storage vessel and the soil-containing chamber. The scheme of a used model of a flow-through reactor technique is presented in Figure 1. The experiment was conducted by placing 5 g of air-dried soil samples in the reactor chambers made from plastic cylinders. The storage vessels and the reactors were filled with the 100 mL of 5 mg P L⁻¹ solutions of KH₂PO₄ with a background solution of 0.01 M CaCl₂. The solutions were continuously pumped by the multichannel peristaltic pump and the outflow of the reactor was fed back into the storage vessel. The pump permits the simultaneous use of 24 reactor chambers. The P solution was continuously circulated for 168 h, during the first 2 h at flow rates of 2.15 mL min⁻¹, followed by 1.14 mL min⁻¹ for the remaining duration of the experiment. The difference between the initial and finial P concentration at each time step was assumed to be sorbed by the soil. The P equilibrium concentration of the solution in the storage vessel was measured from the differences between the initial concentration of P in the applied solution and

Table 3: Soil chemical properties at 0-3, 3-10, and 10-30 cm layers under 2 (R2), 3 (R3), 4 (R4), and 14 (R14) years old *Robinia pseudoacacia* plantations. Different letters within columns indicate significant differences (P < 0.05, Holm-Sidak).

Study site	pH*	C:N	TOC^*	TN^*	P_{ox}	TPo	P_{MB}
Study site	pii	0.11	$\mathrm{gkg^{-1}}$		${ m mgkg^{-1}}$		
			0-3	cm			
R2	7.4a	21.3a	3.2c	0.15a	34.7b	17.7b	1.34a
R3	7.5a	20.6a	3.5c	0.17a	34.9b	24.4b	1.17a
R4	7.4a	21.3a	6.6b	0.31a	61.8b	24.9b	1.05a
R14	7.4a	15.3b	23.3a	1.52a	120.2a	85.5a	1.09a
			3-10) cm			
R2	7.4a	32.0a	3.2b	0.10b	31.4b	9.4b	1.06a
R3	7.5a	26.7b	3.2b	0.12b	30.7b	7.9b	0.87ab
R4	7.5a	26.7b	4.0b	0.15b	38.7b	12.8b	0.46b
R14	7.5a	21.9c	11.4a	0.52a	94.6a	35.9a	0.44b
			10-3	0 cm			
R2	7.5a	55.0a	2.2b	0.04c	22.1b	6.9b	0.92a
R3	7.6a	54.0a	2.7b	0.05bc	23.5b	8.7b	0.59a
R4	7.5a	33.6b	3.7b	0.11b	29.0b	9.4b	0.43a
R14	7.5a	27.4c	10.4a	0.38a	95.2a	24.0a	0.42a

^{*} After Matos et al. [14].

the final concentration of P in the storage vessel after time period of 2, 6, 24, 48, 96, and 168 h. P concentration in each sample was determined according to the method of Murphy and Riley [48]. P sorption isotherms were plotted using the amount of P sorbed (PS mmol kg $^{-1}$), at different reaction time (t).

2.4.3. Phosphorus Desorption Kinetics. The sorption experiment was followed by desorption measurements, where P was desorbed by using the Fe-oxide filer paper method [44]. To prepare the Fe-oxide filter paper strips, the filter paper circles (15 cm diameter, Whatman number 542) were immersed in FeCl₃ solution and then air dried for 1h and immersed in 2.7 M NH₄OH solution to neutralize the FeCl₃ and to form amorphous iron (hydr)oxide. Filter papers were rinsed with deionied water to remove adhering Fe-particles and after air drying was cut into strips of $10 \text{ cm} \times 2 \text{ cm}$. These stripes have a reactive surface area of 40 cm² with a BET-specific surface area of 1.5 m², as determined by N₂ gas adsorption, and contain approximately 120 $\mu \mathrm{mol}$ Fe [58]. The P desorption was evaluated by shaking one strip with 1 g of soil from the previous adsorption experiment in 40 mL 0.01 M CaCl₂ endover-end at 30 rpm for varying lengths of time with one filter paper in a fixed position. The Fe-oxide impregnated filter papers were replaced with fresh ones after 2, 6, 24, 48, and 96 h of desorption. The P retained on the strip was removed by shaking the strip with 40 mL of 0.1 M H₂SO₄ for 1 h and after neutralization P was measured by the method of Murphy and Riley [48] and expressed in mmol P kg⁻¹. To describe P release kinetics, the P desorption data were fitted to different equations.

2.5. Statistical Analysis. The data presented are mean values of six independent field replicates. One-way analysis of variance was used to test for the impact of different R. pseudoacacia age on P sorption kinetics and on other parameters. Person correlation and multiple linear regression analyses were also performed. Sigma plot (version 12.0, Jandel Scientific) was used for all analyses at significant level of P = 0.01 and P = 0.05.

3. Results and Discussion

3.1. General Soil Properties. The soils from all treatment were alkaline caused by intensive liming during initial reclamation, and there was no significant difference in pH values at R2 and R14 sites (Table 3). Growing of R. pseudoacacia on postmining soils had an effect on most soil properties. The TOC and TN content increased with plantation age at all investigated soil layers and were significantly the highest under the oldest R. pseudoacacia plantation (R14 site), with values of 23.3 and 1.5 g kg⁻¹ for TOC and TN, respectively, at the 0-3 cm depth (Table 3). Since these sites are in the initial stage of soil formation, the N input from the below and aboveground biomass is very low. Additionally, decrease in TOC and TN contents with increasing soil depth was observed; TOC and TN values averaged 10.4 and 0.38 g kg⁻¹, respectively, at the 10–30 cm. The growth of R. pseudoacacia affects the content of TN and TOC, which could be attributed to the N-fixing capability of the tree [13]. The increase of TOC and TN content with age of R. pseudoacacia growth has been reported by other researches [4, 59, 60]. The accumulation of TOC with time has been also reported by Pietrzykowski and Krzaklewski [59] of the reclaimed soils in sand mine.

However, it has been observed that the rate of TOC and TN accretion tends to slow down with time [60, 61]. Nevertheless, the obtained results on TOC and TN content were very low compared to the forest soils of the region. For example, Matos et al. [62] reported TOC and TN content of about 46.8 and 2.5 g kg⁻¹, respectively, at the 0-10 cm soil layer under traditional mixed pine-oak forest. It needs to be emphasised that factors as the rate of OM, TOC, and TN accumulation and thickness of the humus horizons are important indicators in soil formation process of postmining sites [14, 59, 63, 64]. At the investigated sites presence of litter layer was not (R2-R4 sites) or barely (R14 site) observed. At the R14 site the thickness of organic layer was around 2-3 cm; however it is expected that it will increase over time with increased litter additions. As shown in studies by Pietrzykowski and Krzaklewski [59] on reclaimed sand mine soils in Upper Silesia (Poland), the thickness of the organic layer increased with time and averaged 3.5 cm under 25 years old mixed pine and birch forest. The C:N ratio decreased with time and presented values at the 0-3 cm soil layer were 15 and 21 at the oldest R14 and youngest R2 plantations, respectively (Table 3). This suggests a high decomposition and turnover rate of OM. Nevertheless, detailed information on N content, C fractionation, and C sequestration of the discussed sites is presented by Matos et al. [14] and Quinkenstein et al. [15].

The TPo content increased significantly (P < 0.01) with age of R. pseudoacacia and decreased significantly (P < 0.01)with increasing soil depth (Table 3). The highest TPo values were observed for soil at the R14 site for all depths with the largest amount of 85.5 mg kg⁻¹ in the top soil, representing 79% higher compared to the youngest R2 plantation. Phosphorus is transformed from humus layer to mineral soil as biological activity increases. The young plantations were not well developed and thus biomass and litter production was very low with almost no litter layer; only at R14 plantation a thin layer of forest floor was observed. Therefore, the TPo content was the highest at the oldest plantation, where higher microbial activity and better decomposable litter occurred. We did not measure litter fall and no investigations on litter layers were performed. These conclusions are therefore based on the field observation. Nevertheless, it is expected that the organic layer will develop with time and needs to be considered for further investigation.

The average P_{MB} values at the R14 site varied from 0.42 to 1.09 mg kg $^{-1}$ (Table 3). At each site, the P_{MB} content decreased with increasing soil depth. No significant differences were observed for P_{MB} at the 0–3 cm layer among sites. At the subsequent soil depth, the lowest P_{MB} was found at R14 site and the highest at R2 site with values being significantly different. The highest P_{ox} , TPo, and P_{MB} were observed at the 0–3 cm layer across all study sites. Furthermore, significant increase in P_{ox} and TPo, with increasing trees age (P < 0.05) as well as significant positive correlation between P_{ox} and TPo (P < 0.05) was observed for all investigated soil depths (Table 4).

3.2. Soil P Forms. The soil P_{ox} content varied with age of R. pseudoacacia and soil layers. As reported by other authors [22, 29, 32, 54], P_{ox} constitutes approximately 93% of total P.

Table 4: Pearson correlation among available $P(P_{av})$, total organic P(TPo), microbial $P(P_{MB})$, oxalate extractable Fe (Fe_{ox}) , and Al (Al_{ox}) across reclamation sites with different age of *Robinia pseudoacacia* plantations.

1							
Varia	able for 0–3 cm	1	2	3	4	5	6
1	P_{av}	_					
2	TPo	0.92**	_				
3	P_{MB}	NS	NS	_			
4	P_{ox}	0.94**	0.92**	NS	_		
5	Fe _{ox}	0.84**	0.90**	NS	0.95**	_	
6	Al_{ox}	0.88**	0.96**	NS	0.99**	_	_
Varia	able for 3–10 cm						
1	P_{av}	_					
2	TPo	0.68^{*}	_				
3	P_{MB}	NS	NS	_			
4	P_{ox}	0.80^{**}	0.93**	NS	_		
5	Fe _{ox}	0.80^{**}	0.95**	NS	0.98**	_	
6	Al_{ox}	0.71**	0.89**	NS	0.96**	_	_
Varia	able for 10–30 cm						
1	P_{av}	_					
2	TPo	0.59*	_				
3	P_{MB}	NS	NS	_			
4	P_{ox}	0.70**	0.81**	NS	_		
5	Fe _{ox}	0.66*	0.82**	NS	0.99**	_	
6	Al_{ox}	0.60*	0.86**	NS	0.96**		

Values are correlation coefficients followed by significant level (P < 0.05 and P < 0.01, * and **, resp.; NS—not significant).

The P_{ox} content increased across sites, with the highest value of 120 mg kg⁻¹ found at the depth of 0-3 cm at R14 site and the lowest at R2 site, where values ranged from 22 to $34 \,\mathrm{mg}\,\mathrm{kg}^{-1}$ (Table 3). The P_{ox} content was not significantly different across the young sites (R2-R4) but was significantly higher at R14 site at each soil depth (P < 0.05, Table 3). This indicates that cultivation of R. pseudoacacia over 1year period has led to enrichment of P in the postmining soil. Nevertheless, Rahmonov [16] reported soil TP ranging from 70 to 100 mg kg⁻¹ under 20 years old R. pseudoacacia plantation established on reclaimed sand excavated site. It has been discussed that leguminous plants require more P than others plants for their root development and energy processes since it enhances their symbiotic N-fixation process [7, 60, 65]. However, Pox values observed in this study are comparatively lower than the values of 896 mg kg⁻¹ reported by Koopmans et al. [32] for the first 10 cm soil depth of grassland loamy sandy soil.

General P deficit was reflected in the very low P_{av} content at the top 0–3 cm layer with values ranging from 2.5 to 8.0 mg kg⁻¹ (Figure 2). This very low P_{av} content is typical for mine soils and comparable to that reported by Vetterlein et al. [66] for noncarboniferous mine spoils form the Lusatia (ranges between 3 and 11 mg kg^{-1}) and was well within the ranges observed by Wilden et al. [67] for postlignite mining

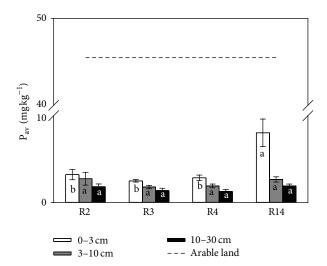


FIGURE 2: The P_{av} at 0–3, 3–10, and 10–30 cm soil depth under 2 (R2), 3 (R3), 4 (R4), and 14 (R14) years old *Robinia pseudoacacia* plantations and in arable soil at 0–10 cm depth. Error bars represent standard deviations of the mean values; different letters indicate significant difference among the sites (P < 0.05, Holm-Sidak).

reclamation sites. Martínez et al. [46] found comparable values of P_{av} (lower than $10\;mg\,kg^{-1})$ for mine sandy loam soils in Spain, and Rahmonov [16] reported vaulues of 3- 6 mg kg^{-1} for sand mine reclamation site planted with R. pseudoacacia. The results demonstrate higher Pav at R2 site, despite being not significant in comparison to R3 or R4 sites. This may be probably due to fertilizer application a year before soil samples were collected. Similar increase in P_{av} after P fertilizer application was also noted by Grünewald [68]. At all the investigated sites, P_{av} decreases with increasing soil depth and could be ascribed to plant uptake of P from soils and translocation to plant pool over the years [69] and as a result of P retention by soil. Considering the top 0-3 cm layer, Pav was 60% higher at R14 compared to R2 site. Nevertheless, it should be emphasised that no cultural practices (e.g., ploughing) took place and thus P distribution over time was not influenced by such process. As suggested by Gillespie and Pope [7], growing of R. pseudoacacia greatly improves soil P_{av} and as discussed by Lee et al. [9], fast decomposition of R. pseudoacacia leaves and flowers significantly increases P in soil and consequently benefits plant in the growing season, when nutrients demands are increasing. The greater litter fall of R. pseudoacacia at R14 site (data not shown) and its rapid decomposition could support rapid P cycling at this site. Additionally, litter of R. pseudoacacia is relatively rich in nutrients [16] and the decomposition rate of leaves has been discussed as a fast process [13]. Moreover, as discussed by Matos et al. [14] long term cultivation of R. pseudoacacia contributed to the increase of more stable and highly recalcitrant C fraction, which accounted for 70% of soil TOC. Matos et al. [14] reported that heavy C fraction was 5 times higher at the R14 site compared to the young R2 site. It is known that humic substances affect the P solubility [39]; therefore, plant P_{av} was significantly enriched at the R14

plantation, where mixture of soluble P with OM significantly increases plant $P_{\rm av}$ content.

Moreover, as reported by Tingxiu and Guofan [70], Pav in soil appears to be one of the main factors, which influence R. pseudoacacia growth. Thus, growing of R. pseudoacacia enriches the soil with nutrients essentially in the top soil layer. On the other hand, the higher content of P_{av} in the top soil layer could be explained by the higher P uptake by plants at R14 site, which could result in translocation of this ion. Moreover, to overcome P limitations, plants have developed complex adaptation, for example, changes in root architecture [71]. On the other hand, studies of Gillespie and Pope [7] suggest that rhizosphere acidification by R. pseudoacacia can affect the P content by increasing phosphates solubility and consequently cause greater quantities of nutrient supply and greater nutrient uptake. As P moves to the tree roots by diffusion process, the impact of soil acidity on P_{av} is limited to the rhizosphere. Plants in response to low P conditions secrete phosphohydrolases into the rhizosphere, which convert organic phosphate into inorganic soluble phosphate, for example, acid-phosphatase [72].

According to work of Liu and Deng [65] P is one of the factors affecting N-fixation of R. pseudoacacia, and therefore more soil P is likely to be utilized during tree growth and translocated into the aboveground plant P pool. Additionally, the soil texture of R14 site indicates greater proportion of clay content (20%) than soils of the younger sites (around 5% of clay) and therefore may lead to a greater ability to hold nutrients in their plant available forms [73]. Furthermore, the largest difference among depths was found at R14 site, which declined significantly (P < 0.01) by 67% from the 0–3 cm layer to the 3–10 cm layer. This could result in the formation of calcium-phosphates that are hardly soluble [74]; however no significant differences were observed across sites at the 3–10 and 10–30 cm soil depths.

In contrast, the results of Böhm [75] showed higher P_{av} content (6.6 mg kg⁻¹) at a nearby arable site than at the R2 site (2.5 $\mbox{mg}\,\mbox{kg}^{-1}).$ However, this was only noticed at the top 0– 10 cm layer, and at the deeper soil depth (up to 60 cm) the P_{av} was higher under SRC than in arable soil [75]. Nevertheless, the results of the young R. pseudoacacia plantations (R2-R4) concur with the findings of Böhm et al. [76], who did not find any relevant differences in P content 4 years after establishment of R. pseudoacacia plantation at postmining sites. When considering the traditional agricultural cultivated soil [77], the content of P_{av} for the top soil layer was over 5 times lower at mine soils under R14 site than at arable soils (Figure 2). The presented P_{av} was determined by the method of Olsen et al. [47]. However, in Germany the common method to examine the P availability in soils is the double lactate (DL) method, where P is extracted with Ca-lactate [78]. Therefore, P_{av} (Figure 2) were recalculated according the equation by Schick et al. [79] and then compared with values typical for the region. Consequently, P availability of the arable soils, presented in Figure 2, reached 63 mg P kg⁻¹ (P content by DL method). This soil is characterized by optimal supplied of P and falls into class C for soils in Brandenburg [80], whereas postmine soils deficient in P are far below it.

Table 5: Oxalate extractable Fe, Al and P, P sorption maximum (PS_{max}), α values measured from P sorption (α_{sorp}), and initial values (α_{initial}) at 0–3, 3–10, and 10–30 cm soil layers under 2 (R2), 3 (R3), 4 (R4), and 14 (R14) years old *Robinia pseudoacacia* plantations. Different letters within columns indicate significant difference among the sites (P < 0.05, Holm-Sidak).

	Fe _{ox}	Al_{ox}	PS _{max}	P _{ox}	$lpha_{ m sorp}$	$lpha_{ m initial}$
Study site	а	b	с	d	e = (d+c)/(a+b)	f = d/(a+b)
		mmo	ol kg ⁻¹			
			0-3 cm			
R2	13.10bc	5.65b	1.37c	1.12b	0.13	0.06
R3	9.81c	4.88b	1.19c	1.13b	0.16	0.08
R4	17.92b	6.91b	1.85b	2.00b	0.15	0.08
R14	33.35a	12.32a	2.57a	3.88a	0.14	0.09
			3-10 cm			
R2	12.07b	5.10b	1.19c	1.01b	0.13	0.06
R3	9.85b	4.87b	1.28c	0.99b	0.15	0.07
R4	13.64b	6.31b	1.49b	1.25b	0.14	0.06
R14	35.53a	12.68a	2.76a	3.05a	0.12	0.06
			10-30 cm			
R2	10.34b	4.28c	1.14c	0.71b	0.13	0.05
R3	9.03b	3.88c	1.10c	0.76b	0.14	0.06
R4	11.90b	5.88b	1.80b	0.94b	0.15	0.05
R14	37.14a	13.63a	2.87a	3.07a	0.12	0.06

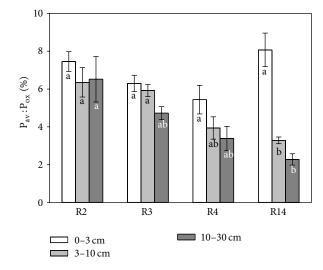


FIGURE 3: The ratio of P_{av} and P_{ox} in mineral soil at 0–3, 3–10, and 10–30 cm depth under 2 (R2), 3 (R3), 4 (R4), and 14 (R14) years old *Robinia pseudoacacia* plantations. Error bars represent standard deviations of the mean values; different letters indicate significant difference among the sites (P < 0.05, Holm-Sidak).

With the exception of the top of 0–3 cm soil layer of R14 site, the P_{av} : P_{ox} ratio decreased with increasing time for all soil layers (Figure 3). Simultaneously, the α -values, which express the degree of phosphate saturation, slightly increased (Table 5) and correspondingly, the P_{ox} values increased over time in all soil layers. Consequently, the ratio between P_{av} and P_{ox} shifted more to unavailable forms of P in soil. However,

it is important to also consider that, during the first years of establishing R2–R4 plantations, the effect of the initial applied P fertilizer has declined. Nevertheless, the availability of the applied P is also controlled by the sorption/desorption processes in the soil. As discussed by Borggaard et al. [21], Freese et al. [22], Maguire and Sims [81], McDowell and Condron [82], and Schoumans [40], P can be largely fixed by Fe_{ox} and Al_{ox} and thereby making P less available for plants uptake. From the obtained results Fe_{ox} and Al_{ox} showed a strong positive correlation with P_{av} and P_{ox} for all soils depths (P < 0.01, Table 4). Moreover, most of P added to soil as fertilizer was sorbed by the soil resulting in P forms, which are not readily available, thus leading to very low P_{av} concentrations in the soil solution (measured values of $0.2 \, \mathrm{mg} \, \mathrm{L}^{-1}$).

The P stock estimated for the depth of 0–30 cm showed evidence of significant increase of P stock in the soil with increasing age of plantation (*P* < 0.05), with the largest value of 0.50 Mg ha⁻¹ at the R14 site and lowest value of 0.12 Mg ha⁻¹ at R2 site (Figure 4). No significant difference in P stock was observed among young R2–R4 plantations. However, the difference in P stocks between R2 and R14 sites suggests that, after 12 years of establishing *R. pseudoacacia* plantation on postmining soil, accumulated P at 0–30 cm depth averaged 0.38 Mg ha⁻¹, amounting to P accumulation rate of about 32.0 kg ha⁻¹ year⁻¹. Böhm et al. [76] found higher P stocks under *R. pseudoacacia* plantation compared to arable lands established on mining soils, suggesting that establishment of SRC at postmining sites appears to be a promising recultivation strategy in terms of P enrichment in soil. Studies of Berthold et al. [83] on 35–50 years old

Table 6: Coefficient of determination (r^2) for the kinetics equations of the measured P (de)sorption at the 0–3, 3–10, and 10–30 cm soil layers
under 2 (R2), 3 (R3), 4 (R4), and 14 (R14) years old Robinia pseudoacacia plantations.

			Coefficient of do	etermination— r^2			
Study site	Sorption			Desorption			
	Elovich	Parabolic	Exponential	Elovich	Parabolic	Exponential	
			0-3 ст	m			
R2	0.97	0.83	0.96	0.98	0.85	0.94	
R3	0.92	0.71	0.9	0.99	0.91	0.98	
R4	0.95	0.84	0.94	0.99	0.93	0.97	
R14	0.98	0.83	0.98	0.99	0.96	0.98	
			3–10 c	m			
R2	0.97	0.83	0.97	0.99	0.88	0.95	
R3	0.94	0.82	0.93	0.98	0.94	0.98	
R4	0.91	0.69	0.89	0.99	0.95	0.97	
R14	0.85	0.59	0.82	0.99	0.96	0.98	
	10–30 cm						
R2	0.97	0.88	0.96	0.99	0.91	0.98	
R3	0.93	0.75	0.87	0.99	0.87	0.95	
R4	0.96	0.82	0.95	0.99	0.91	0.96	
R14	0.92	0.71	0.92	0.99	0.94	0.96	

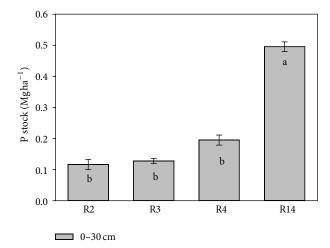


FIGURE 4: Total P (TP) stocks in mineral soil at 0–30 cm depth under 2 (R2), 3 (R3), 4 (R4), and 14 (R14) years old *Robinia pseudoacacia* plantations. Error bars represent standard deviations of the mean values. Different letters indicate significant difference among the sites (P < 0.05, Holm-Sidak).

R. pseudoacacia sites established on sandy Cambisols in Hungary reported P stock of 2.6 Mg ha⁻¹, which is 5 times greater, compared to the investigated mining soils. Moreover, they found significantly high accumulation of P stocks in organic layer at *R. pseudoacacia* sites. This may lead to the conclusion that optimal P level in postmining soils might be reached approximately after additional 20 years of *R. pseudoacacia* growth.

On the other hand, a number of studies report the effects of P deposition from the atmosphere in temperate systems and its impact on the nutrient status of ecosystems [84–86]. Major sources of P input include soil particles, pollen, burning of plant material, coal, and oil [85]. According to studies by Tipping et al. [86] in the southeast region of Germany, P desorption rate of 0.07 g m⁻¹ a⁻¹ has been calculated. Transforming this value to per ha basis gives 0.7 kg ha⁻¹ a⁻¹ which is only 2.2% of the measured annual rate of P stock enrichment of the R14 site. To obtain the net gain or loss, both P inputs and P emissions should be considered by taking into account atmospheric transport of P on ecosystems [86]. Nevertheless, the P input by P depositions into soils is very small and therefore not relevant for the investigated sites.

3.3. Soil P Sorption Kinetics. The proposed three equations (Table 2) have been fitted to measured P sorption data and evaluation of the calculated correlations coefficients of determinations (r^2) has been presented in Table 6. The highest correlations coefficients r^2 was observed for the Elovich equation (0.85–0.98). Hence, this equation is the most suitable model for the measured P sorption and well described the data of all investigated soils (Figure 5). Other researchers reported that the Elovich equation describes the P sorption data very well [25, 28, 39, 87]. The parabolic and exponential equations also describe the data satisfactory. However, the parabolic diffusion equation is not as adequate as the Elovich equation, as can be seen from the lower r^2 values (0.59–0.88, Table 6). The prediction of sorbed P by

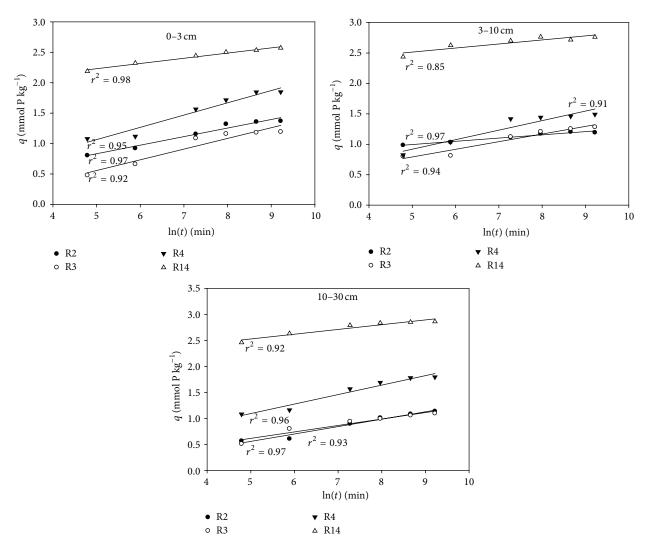


FIGURE 5: Fit of the Elovich equation to P sorption data for the 0-3, 3-10, and 10-30 cm soil depths under 2 (R2), 3 (R3), 4 (R4), and 14 (R14) years old *Robinia pseudoacacia* plantations; q is the amount of sorbed P (mmol P kg⁻¹) at time t.

the Elovich equation is between 91 and 97% (except for R14 at 3–10 cm layer) of the experimentally measured P sorption.

The sorption isotherms of soil from the investigated sites showed that the rate of P adsorption increased with an increase in time but at certain point; approximately after 48 h the sorption of P became almost constant and the sorption capacity was reached (Figure 6). The P sorption tended to be rapid for the first few hours and slowed down in the subsequent days for all investigated soils. The P sorption increased rapidly with time until about 48 h reaction time and continued for a longer time, even though the sorption rates became slower. This sorption behaviour is typical and is well reported in the literature [26, 34, 88].

When comparing the amount of adsorbed P among the plantations, it was evident that soil under older plantations (R14) had higher PS than the soils from younger plantations (R2–R4) (Figure 6), most probably caused by increase in Fe $_{\rm ox}$ and Al $_{\rm ox}$ and soil OM.

The time dependent P sorption PS(t) for the top soil ranged from 0.48 to 2.57 mmol kg^{-1} (PS_{2h} and PS_{168h}, resp., Figure 6) and was related to the age of *R. pseudoacacia*, that is, the sorption increased with increasing time of soil development. The maximum amount of sorbed P after 168 h of the sorption experiment was found for soils at the oldest R14 site $(2.9 \text{ mmol kg}^{-1})$ and the lowest at R3 site $(1.1 \text{ mmol kg}^{-1})$ at the 10-30 cm depth. There were no significant differences in the time dependent sorption between the two young sites (R2 and R3). However, PS(t) values for each soil depth showed significant differences between the young R2-R4 sites and the oldest R14 site (P < 0.01). The capacities of PS were consistent with the age of the plantation and the poor development of the investigated soils. Nevertheless, the P sorption values were definitely lower than in other soils from northern Europe, where Freese et al. [22] reported values around 10–117 mmol kg⁻¹. Furthermore, Börling et al. [27] reported values in the range of 31–103 mmol kg⁻¹, and

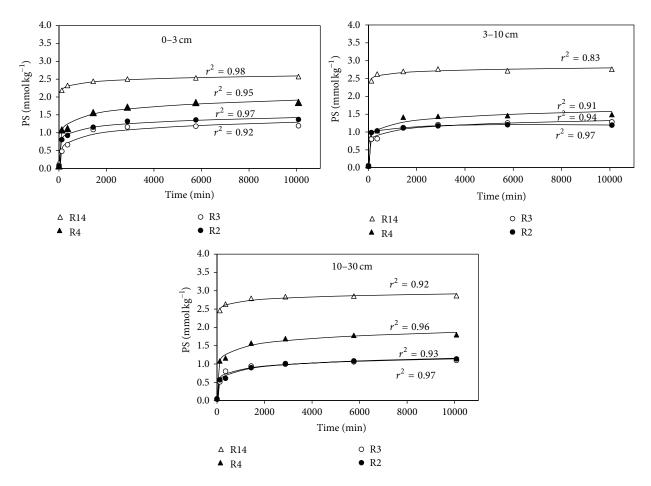


FIGURE 6: Time-dependent P sorption [(PS(t))] for the 0–3, 3–10, and 10–30 cm soil depths under 2 (R2), 3 (R3), 4 (R4), and 14 (R14) years old *Robinia pseudoacacia* plantations. Lines were fitted by using the Elovich equation: $q = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t$, where q is the P amount sorbed in time t and α and β are constants for a given sorption process.

Leinweber [33] reported PS values of 21 and 35 mmol kg⁻¹ for arable and grassland soils, respectively, in northwest Germany, whereas Peltovuori [38] observed values in the ranges of 66–169 mmol kg⁻¹ in weakly developed soil.

Values of PSCt were calculated based on formula (3), where PSCt is expressed as a sum of P_{ox} and measured P sorption under laboratory conditions at different reaction time. The amounts of PSCt for the R14 site ranged between 5.5 and 6.5 mmol kg⁻¹, whereas the younger sites R2-R4 showed only values in between 1.7 and 4.4 mmol kg⁻¹. On the average PSCt of the oldest site R14 is 2.5 times higher as compared to R2-R4 sites. It was found that at the 0-3 cm soil depth at the young R2, R3, and R4 sites, the PSCt was approximately 25% higher compared to that of the deeper layer (10–30 cm), whereas for the R14 site the difference between the depths was only 8%. The greater differences between top- and subsoil layers of R2-R4 may be due to the P fertilizer application before establishing these plantations, which was not the case for R14 site. The fertilizer in amount of 100 kg ha⁻¹ was only applied on the soil surface of R2-R4 sites, without any further soil mixing. Therefore, it is assumed that the application of P fertilizer has an impact on the PSC for the top soil layer of the young SRC sites.

Based on the α saturation factor calculated from formulae (2) and (3), the α values can be determined as

$$\alpha_{\text{sorp}} = (PS + P_{\text{ox}}) * (Al_{\text{ox}} + Fe_{\text{ox}})^{-1}.$$
 (4)

In this study measured $\alpha_{\rm initial}$, when only $P_{\rm ox}$ is consider, were in the range of 0.05–0.09 for all sites (Table 5). These values are far below values of agricultural and forest soils reported in literatures [22, 32, 34, 54, 55] and reflect the fact that the initial P content expressed with $P_{\rm ox}$ values of the postmining soils is very low. In addition, the very low α values of the younger sites (R2–R4) were accompanied by lower $Fe_{\rm ox}$ and $Al_{\rm ox}$ (only 50% compared to R14 site) and lower $P_{\rm ox}$ values (approximately 30%). In particular, this fact is of interest even if one assumes an increase of sum of $Fe_{\rm ox}$ and $Al_{\rm ox}$ over time, by advancing soil development (weathering). Additionally, with no further P increase this would lead to decreasing α values. According to van der Zee [54], the α value may depend on experimental conditions such as equilibrium time and initial P concentration and soil physical and chemical

characteristics including OM content, pH, and the particle size distribution [46, 89]. Freese et al. [22] reported mean α values of 0.43 and 0.48 for German agricultural soils for reaction times of 4 and 40 days, respectively, and Koopmans et al. [32] reported vales around 0.42 for grassland loamy sandy soil. The values of PSC calculated from formula (2), with the assumption that α = 0.5, were much higher compared with experimentally measured ones ($P_{\rm ox}$ + PS). It should be emphasised that obtained α values ($\alpha_{\rm sorp}$) were lower than 0.15, but significantly higher than $\alpha_{\rm initial}$. Therefore, the obtained results suggest that PSC is better defined when sorption is measured experimentally than being calculated from the fixed α factor, which is in line with work by Maguire et al. [34].

The measured P sorption is controlled by the Fe_{ox} and Alox, which have a high affinity for P. On one site, the amount of Fe_{ox} and Al_{ox} increased over time and therefore the sorption capacity, assuming that Feox and Alox are the main P sorption components. The PSCt of R3, R4, and R14 sites showed significant positive correlations (P < 0.05) with Fe_{ox} + Al_{ox} for all sorption times longer than 24 h. No significant correlation was found for the youngest R2 site. Nevertheless, soils with the highest PSC have the highest sum of Fe_{ox} and Al_{ox} contents (Figure 7). Comparable correlations of PSC with Fe_{ox} and Al_{ox} have been reported in the literature [24, 27, 33, 46, 54, 87, 89-92]. Numerous studies [22, 29, 46, 89, 93] have shown that the most important parameters that determine the P sorption are Fe_{ox} and Al_{ox}. The strong correlations between Fe_{ox} and Al_{ox} as well with the sum of Fe_{ox} + Al_{ox} as noted by Freese et al. [22] make it difficult to assess the single importance of one of these fractions for P sorption by means of regression analysis. Studies by Borggaard et al. [21] on sandy Danish soil confirm that the Fe_{ox} and Al_{ox} significantly influenced P sorption. Moreover, Singh et al. [93] and Lair et al. [91] observed that P sorption depends on Fe_{ox} and Al_{ox} contents with the highest P sorption for soils containing high amounts of Feox and Alox and the lowest in soils with the lowest content of Feox and Alox. On the other hand, Lookman et al. [94] suggest that Al_{ox} might be associated with soil OM. Thus, the difference in OM content across the study sites and its associations with Alox may further explain the variation of PS of the investigated soils.

Nevertheless, the concentration of Fe_{ox} and Al_{ox} was very low in all investigated soils and increase significantly (P < 0.01) with age of SRC for all soil depths (Table 5). The Fe_{ox} and Al_{ox} content at the oldest R14 site was about three times higher than at the youngest R2 site. At all sites the content of Fe_{ox} was two times higher than Al_{ox}, with Fe_{ox} and Al_{ox} values of 34 mmol kg⁻¹ and 12 mmol kg⁻¹, respectively, at R14 site. This significant increase in Fe_{ox} and Al_{ox} with the development of mine soils reflects a growing potential for increasing soil P and its stabilization over time, as indicated by the strong relationship between Fe_{ox} and Al_{ox} and TP content (P < 0.01, Table 4). Moreover, it has been observed that an increase in Fe_{ox} and Al_{ox} content during initial soil formation were two times higher after 55-60 years of soil development [95], although in this study it may take a much longer period until optimum values are reached.

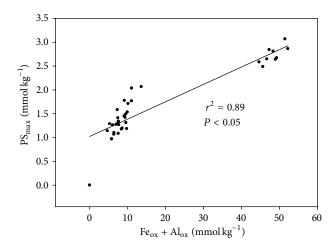


FIGURE 7: Relationship between the P sorption maximum (PS_{max}) and sum of oxalate extractable Fe and Al content ($Fe_{ox} + Al_{ox}$) of mining soils under *Robinia pseudoacacia* plantations.

3.4. Soil P Desorption Kinetics. Desorption of phosphates from soils following long term fertilizer application periods has been well studied in the last decades, especially, for soils with high P accumulation [32]. However, very little attention has been given to soils of postmining areas. Therefore, a better understanding of the P kinetics in the postmining soils is very important to establish good recultivation management practices as well as P fertilizer management. To assess P desorption in the investigated soils, the specific method of Feoxide impregnated filter paper was used. The advantages of the method are its simplicity and accuracy, easy preparation of the filter papers, and its applicability to all soil types [58]. Moreover, by using a sink with concentration gradient, the desorption process is forced, and it is independent of extraction solution. However, the desorption amount based on this technique may tend to overestimate the initial desorbed P or underestimate the quantitative progression of desorption, leading to the impression that desorption stability level is reached after some time [96]. Additionally, the adhesion of fine soil particles to the paper strips can cause adsorption errors. Using the Fe-oxide impregnated filter paper, van der Zee et al. [58] assumed that 20 h of desorption process could be a good estimator of the amount of P reversibly bound to the surfaces of reactive particles. As presented in work of Daly et al. [29] the highest P desorbed values were presented by using the method of Fe-oxide impregnated filter paper compared to the other desorption tests.

While measuring the P desorption the same soil samples were used for the sorption experiment. To describe the P desorption kinetics the three presented equations were tested (Table 2). From the equations, P desorption was describe by using equation with the highest values of correlation coefficient, which was the Elovich equation (0.98-0.99), followed by the exponential equation (0.94–0.98). The detailed information on the coefficient of determinations of the studied kinetics equations is presented in Table 6. The Elovich equation provided an excellent data fit and was fitted to P

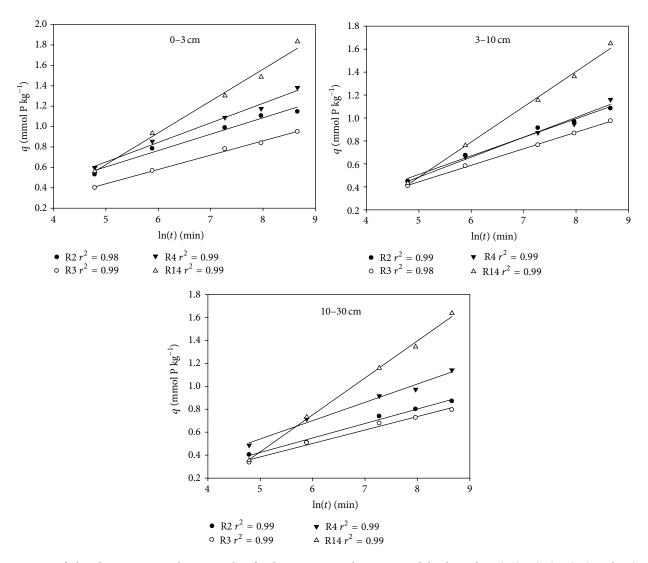


FIGURE 8: Fit of Elovich equation to P desorption data for the 0–3, 3–10, and 10–30 cm soil depths under 2 (R2), 3 (R3), 4 (R4), and 14 (R14) years old *Robinia pseudoacacia* plantations; q is the amount of desorbed P (mmol P kg⁻¹) at time t.

desorption data (Figure 8). As a suitable model for describing P desorption data, Elovich equation has been employed in numerous studies [36, 37, 97–102].

The goodness of fit of the Elovich equation to the desorption data is shown it Figure 9, where the P desorption curves are a function of time for all investigated sites. The investigated initial soils in this study were characterized by very low P sorption capacity and low P desorption values, followed by the low soil P concentration compared to traditional agricultural soil. Nevertheless, it was found that, with increasing age of *R. pseudoacacia* plantation, the P desorption amount increased. The amount of P desorbed from soil at R14 site ranges between 1.64 and 1.83 mmol kg⁻¹, with the highest value at the 0–3 cm soil depth. Consequently, R14 site showed significantly higher P desorption compared to the other R2–R4 sites, with values at the R14 site approximately 50% higher than that of R3 site. The lowest amount of P desorbed was found at R3 site, with values of 0.80 and 0.95 mmol kg⁻¹ at

the 10–30 and 0–3 cm soil depth, respectively. However, no significant differences were observed among the young R2–R4 sites as well as among soil layers within sites, with P desorbed values ranging between 0.80 and 1.38 mmol kg⁻¹.

As shown in the Figure 9 the rates of P desorption decreased with time. Soil P desorption from all investigated sites was initially faster, followed by a continuous slow release, which is a typical behaviour of P release from soil [26, 32, 36] and may be associated to fast and easy desorbable P and slow more strongly bound P, respectively. Desorption curves of soils at young R2–R4 *R. pseudoacacia* sites appeared to be similar, while chemical and physical properties of these soils were similar. The greater P release from soil at R14 site compared to that under the young plantations may likely be associated with the Fe $_{ox}$ and Al $_{ox}$ phases in the soils. It was previously reported that the desorbable soil P was related to Fe $_{ox}$ and Al $_{ox}$ in sandy soil [27, 29, 93, 103]. Moreover, study of Daly et al. [29] and Nafiu [36] indicated that the sum of Fe $_{ox}$

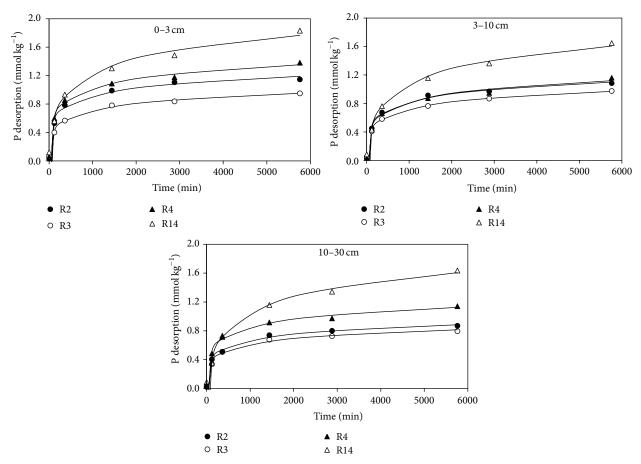


FIGURE 9: Time-dependent P desorption measured for the 0–3, 3–10, and 10–30 cm soil depths under 2 (R2), 3 (R3), 4 (R4), and 14 (R14) years old *Robinia pseudoacacia* plantations. Lines were fitted by using the Elovich equation: $q = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t$, where q is the P amount desorbed in time t and α and β are constants for a given desorption process.

and Al_{ox} was the most important soil properties influencing the rate of P desorption.

According to Koopmans et al. [32] kinetics of P desorption could be a limiting factor to plant growth, where the maximal desorption rate and the actual plant uptake rate are expected to be rather similar. However, they suggest that the calculated maximal desorption rate will not be reached for soil aggregates that are not in direct contact with the roots, and for a fine root density the actual plant uptake rate is consistently lower than the maximal desorption rate. Moreover, the maximal desorption kinetics depends also on physical characteristic (e.g., water content). For the investigated soils the maximum desorption rate was not reached, as can be seen from the rather small slope of isotherms and relatively small decrease in the amount of sorbed P, especially for the youngest initial soils with P desorption rates of 0.80 to 1.14 mmol kg⁻¹ at the 10–30 cm soil depth (Figure 9).

This implies that the total amount of P removed is dependent on the reaction time.

The relative P desorption curves for the investigated initial soils are presented in Figure 10. The relative P desorption was calculated according the formula:

$$(P \text{ desorption}) * (PS_{\text{max}} + P_{\text{ox}})^{-1},$$
 (5)

as a ratio between the actual desorbed amount of P and the sum of maximum amount of P measured by the sorption experiment and P_{ox}. In this study the relative desorbed P decreased with increasing age of R. pseudoacacia plantation and did not differ significantly between soil layers within the site (Figure 10). The relative P desorption varied for the different R. pseudoacacia plantations, ranging from 28 to 49% after 6000 minutes of desorption time, and increased in the order R14 < R4 < R3 < R2. The R2 sites desorbed almost 50% of the initial sorbed P in contrast to R14 site, which desorbed 28% (Figure 10). The relative amounts of desorbed P at the R14 site were significantly different (P < 0.01) from R2–R4 sites at all soil depths. It was observed that, at R14 site, only 28% of sorbed P was desorbed at all soil depths after 96 h of experiment, whereas for soil at R2 site 40% was already desorbed after 24 h, implying that for soil at R14 site longer period is expected to complete the desorption process. The differences between sites in P desorption ratio were probably caused by variations in soil properties such as amorphous content and affinity for P. Therefore, the lower P release rate at the R14 site may be attributed to higher Fe_{ox} and Al_{ox} content.

The data on relative P desorption were fitted to the Elovich equation (Figure 11), which describes very well the

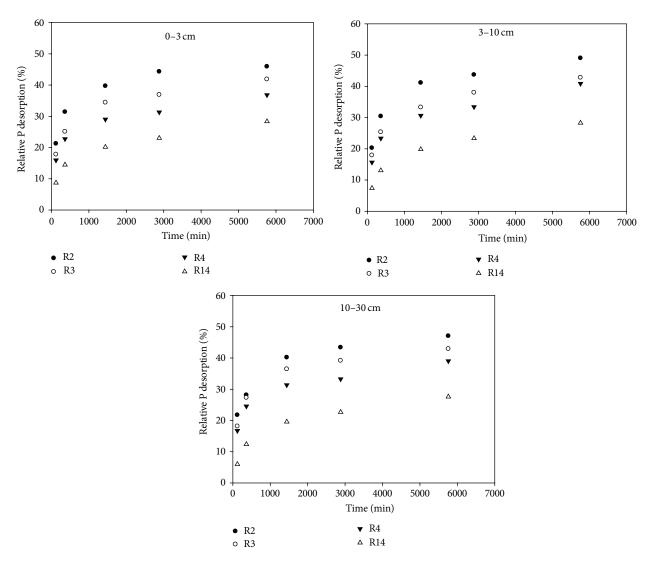


FIGURE 10: Time-dependent relative P desorption calculated from P desorbed in time and oxalate P (P_{ox}) and maximum P sorption (PS_{max}) measured for the 0–3, 3–10, and 10–30 cm soil depths under 2 (R2), 3 (R3), 4 (R4), and 14 (R14) years old *Robinia pseudoacacia* plantations.

data of all investigated soils, with very high coefficient of determination (0.98-0.99).

The longer desorption time may lead to the conclusion that a high proportion of P_{ox} was desorbable within the period of 4 days for soils at R2–R4 sites. In contrast, for soil under R14 plantation longer period is expected to complete the desorption process. As noted by Lookman et al. [96], for sandy soils with low sum of Fe_{ox} and Al_{ox} , the P desorption attains more than 90% of P_{ox} on a long time scale (200 days). The Spearman correlation shows significant (P < 0.01) negative correlation between all investigated sites and the Fe_{ox} and Al_{ox} . This suggests that with increasing amounts of oxalate forms the relative P desorption decreases (Figure 12). Nevertheless, the relationship between P desorption and sum of Fe_{ox} and Al_{ox} is not surprising, since amorphous oxides are known to present large surface area for P retention [102].

The results indicated that the investigated mine soils required more P fertilizer application in order to restore the

optimal P uptake for optimum plant growth. Therefore, further managements practices should involve the application of P with OM or mineral P fertilizer. Study by Vetterlein et al. [66] on the postmine spoil substrates from the Lusatian area indicated that application of P with compost or sewage sludge resulted in lower P recovery (as part of P would be bound in organic molecules) than with mineral P fertilizer; consequently organic P application could overcome P immobilisation and increase P availability for plants.

4. Conclusion

The data suggest that establishing *R. pseudoacacia* plantation on this initial postmining soil with very low P content can lead to the incorporation of significant amount of P into the soil in 14 years. Significant increase in P_{av} and P stocks in soils with increasing age of *R. pseudoacacia* plantation was observed, with the highest values at the oldest R14

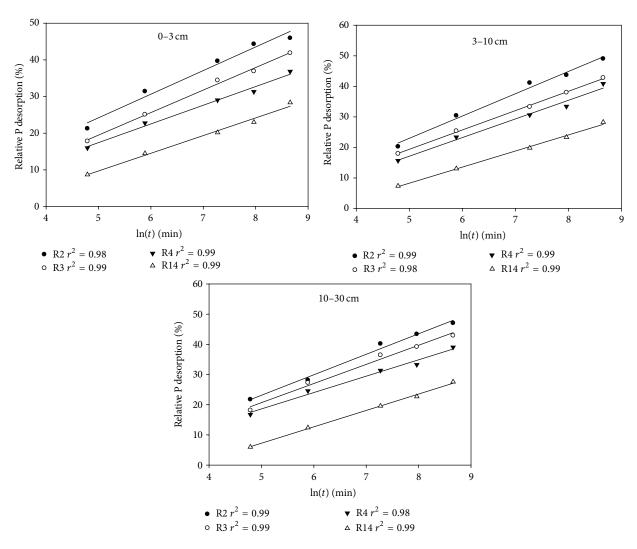


FIGURE 11: Fit of the Elovich equation to the time-dependent relative P desorption data for the 0–3, 3–10, and 10–30 cm soil depths under 2 (R2), 3 (R3), 4 (R4), and 14 (R14) years old *Robinia pseudoacacia* plantations.

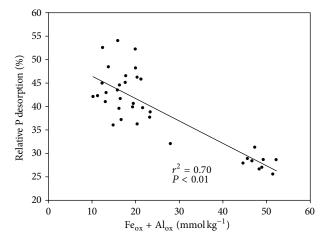


FIGURE 12: Relationship between the maximum of relative amounts of P desorbed and sum of oxalate extractable Fe and Al content (Fe $_{ox}$ + Al $_{ox}$) of mining soils under *Robinia pseudoacacia* plantations.

site. Similarly, the greatest P sorption capacity was found at the oldest R14 site. To characterize further development of the postlignite mine soil and the importance of using *R. pseudoacacia* plantation in reclamation process, additional research is needed mainly on the long-term scale. Particularly, further analysis of P sorption capacity and nutrient (NPK) status would be highly significant with regards to obtaining a comprehensive knowledge on how the age of the plantations influences soil P distribution over time.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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