

Phosphorus fractions in preferential flow pathways and soil matrix in hillslope soils in the Thuringian Forest (Central Germany)

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Abstract

Phosphorus (P) is primarily transported in soil through preferential flow pathways (PFP), which can rapidly move water and matter bypassing large portions of the soil. This study investigated the composition of P forms in PFPs and soil matrix in two profiles at a forested hillslope in the Thuringian Forest (Central Germany), in order to evaluate (1) the effect of PFPs on the distribution of P fractions in forest soils, and (2) how hillslope position influences P fractions and other chemical parameters. To characterize water and mass fluxes in the profiles, flow pathways were visualized using dye tracer experiments. Stained and unstained soil material was sampled to assess differences of chemical parameters in the PFPs and soil matrix, and tested for correlations between chemical parameters to determine the factors influencing P fractions in soils. The results revealed significantly higher P contents (total P and most P fractions) in the upslope profile compared to the downslope profile. This accumulation effect in the upper profile was also observed for C, N, Fe, and Mn. The distribution of flow patterns also differed between the two profiles with stronger vertical infiltration into mineral soil and more preferential flow along stones and roots in the upslope profile compared to the downslope profile. However, the observed difference could not be addressed to hillslope effects as both test plots were located in mid-slope position, but were strongly influenced by spatial heterogeneity (e.g., micro-relief). Furthermore, no statistically significant accumulation effect of P or other elements in PFPs compared to soil matrix was found. At the test site, the combination of high stone content with low potential for P sorption, and predominance of near-surface lateral flow, appears to have hampered the development of gradients in chemical parameters between PFPs and soil matrix.

Key words: phosphorus fractions / forest soil / hillslope processes / preferential flow / PFP

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1 Introduction

Water flow and solute transport in forest soils predominantly occurs along preferential flow pathways (PFP) and complex flow networks in the soil, bypassing large parts of the matrix (Uchida et al., 2005; Laine-Kaulio et al., 2015). Typical forms of PFPs include macropores, fingers, funnels, and hydrophobicity-induced flow paths (Noguchi et al., 1999; Beven and Germann, 2013), which are often a result of soil heterogeneity (Lin, 2010). At the hillslope scale, hydrological and biogeochemical dynamics are characterized by high spatial variability (Stieglitz et al., 2003; van Verseveld et al., 2009; Bachmair and Weiler, 2014). Further, subsurface flow occurs at the highly conductive zone between the bedrock surface and the adjacent saturated soil matrix (Hill et al., 1999; Buttle and McDonald, 2002; Weiler et al., 2005; Graham et al., 2010). The low mountain ranges in Central Europe are often overlain by periglacial cover beds which strongly influence subsurface runoff and perched water table development (Bachmair et al., 2012; Reiss and Chiffard, 2014). Such periglacial layers particularly differ in terms of texture, bulk density, and rock content (cf Sauer, 2002; Semmel and Terhorst, 2010). This results in higher infiltration capacities in the upper layer, but the

redirection of vertical percolating water into lateral fluxes at the basal layer (Chiffard et al., 2008).

The transport of nutrients in forest soils has been investigated by a number of tracer experiments, which have indicated the importance of PFPs in leaching processes (Bundt et al., 2001; van Verseveld et al., 2009; Bogner et al., 2012). For P, the study of Backnäs et al. (2012) primarily examined different P fractions in PFPs as compared to the soil matrix in a podzol under forest in Southern Lapland, Finland. Based on the results, Backnäs et al. (2012) determined that leaching of P through PFPs takes place primarily along stone surfaces, where PFPs are larger than PFPs related to coarse grains or roots. Thus, P sorption may be limited due to potentially faster water flow, weaker lateral mass exchange, and less sorption interaction than in smaller PFPs (Jarvis, 2007). By contrast, an accumulation of P might occur in small preferential pores that are characterized by reduced flow rates and a stronger interaction with the soil matrix. As a result, there is a higher potential for elevated P concentrations in export fluxes, especially when PFPs are stable over longer periods (Jensen et al., 1998).

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The main sources of P in natural forest ecosystems are weathering from phosphate minerals (apatite) and the mineralization of organic matter. Weathering leads to very slow P release over long time periods, though highly weathered soils can become depleted in P (Walker and Syers, 1976; Fox et al., 2011). The labile P pool, which supplies P to the soil solution, is composed of adsorbed P, weakly soluble P compounds, inorganic P in plant residues, and some organic P forms (McDowell et al., 2001). Lookman et al. (1995) determined desorbable P pools in acid sandy soils, which can either immediately supply the soil solution or are desorbed more slowly (e.g., adsorbed P due to saturation and precipitation of Al and Fe oxides). Depending on pH value, adsorption and precipitation processes in soil solution can lead to the formation of weakly soluble (hydr)oxy metal phosphates (i.e., in presence of Al, Fe, and/or Mn at pH < 5.0), or di-Ca-phosphate under alkaline conditions in the presence of Ca (Morgan, 1997). These chemical processes and the uptake of inorganic P (P_i) by plants causes a decrease of P_i concentrations in soil solution with depth (e.g., Kaiser et al., 2003). Labile organic P (P_o) in soils is derived from orthophosphate monoesters (e.g., inositols, mononucleotides, sugar phosphates), orthophosphate diesters (e.g., phospholipids, teichoic acids, nucleic acids, and their degradation products), and phosphonates (Newman and Tate, 1980). In the soil solution in forests, P_o is often predominant over P_i (Kaiser et al., 2003). According to Backnäs et al. (2012), soluble phosphate (P_i) as well as labile monoesters and diesters (P_o) can be leached from the upper horizon, but P leaching is less likely to occur as labile organic forms in the subsoil due to the tendency of P_o to accumulate in stable forms. However, the previously mentioned studies refer to investigations with contrasting methods (i.e., *in-situ* measurements vs. chemical extractions) at different soils and sites, and under changing conditions, which makes general conclusions difficult to derive. To summarize, many factors influence the accumulation and transport of P in forest soils (e.g., soil development, management practices, rainfall characteristics, hillslope hydrology, antecedent moisture status, connectivity of flow pathways) and affect research results (in terms of sampling and analytical methods) (Heathwaite and Dils, 2000; Slazak et al., 2010; De Schrijver et al., 2012; Bol et al., 2016).

Although previous studies have indicated that PFPs are important pathways for P transport and that P accumulates in long-term stable PFPs, there is a lack of detailed studies reflecting the heterogeneity of P distribution in soils at forested hillslopes. Therefore, this study investigated the composition of P forms in PFPs and the soil matrix in two profiles at a forested hillslope, in order to evaluate (1) the effect of PFPs on the distribution of P fractions, and (2) the effect of hillslope position on P fractions and other chemical parameters in forest soils. Most of the factors affecting the accumulation and transport of P are similar for the two investigated plots. Due to the different positions at the hillslope (i.e., upslope and downslope), changing conditions in soil moisture and water fluxes may have a distinct effect on P distribution in horizontal and vertical directions reflecting differences in mass fluxes. As an indicator of the characteristics of water and mass fluxes in the profiles, the flow pathways were visualized using dye tracer experiments. Furthermore, stained and unstained soil materi-

al was sampled to assess possible differences of P compositions in soil matrix and PFPs. The correlations between P fractions and chemical parameters were tested to examine the factors influencing P fractions in the soils.

2 Material and methods

2.1 Site description

The study site is adjacent to the monitoring site Vessertal (EU-ICP Forests Level II Program) in the Thuringian Forest, Central Germany (N 50°36.26', E 10°46.20', 810 m asl). The mean annual precipitation is 1,200 mm and the mean annual temperature is 5.5°C. The soil type is a "Sauerbraunerde" (KA5), which is equivalent to a Dystric Cambisol (FAO-WRB). The bedrock is volcanic (trachyandesite), which is typically overlain by periglacial drift sediments. Accordingly, the upper layer (*Hauptlage*) is characterized by incorporation of airborne loess components, which results in a loam texture in the Ah-Bv and Bv horizon (Tab. 1). The estimated stone content of the topsoil is 10–25% and the Bv horizon contains 25–50% stones. The subsoil which has been formed from deeper periglacial layers (*Basislage*) is more affected by products of physical bedrock weathering. Thus, the subsoil horizons (IIbV-Cv and Cv horizon) are more sandy and have a higher stone content (> 50%). For soil properties in detail see Tab. 1. The vegetation is dominated by European beech (*F. sylvatica* L.) with a stand age of approx. 120 y.

2.2 Dye tracer experiment

At the study site Vessertal, two test plots of 1 m² each were defined at different position of the hillslope in a line parallel to the slope (Ves1: 806 m asl, Ves2: 828 m asl). The slope is approx. 10° with a slightly lower gradient at Ves1, planar, and SE-exposed. The distances to trees around the plots were at least 2 m and the distance between the plots was approx. 60 m. During the tracer experiments, both areas were irrigated with a total amount of 30 L tracer-water solution containing 3 g L⁻¹ Brilliant Blue FCF within 1 h. The applied amount of irrigation water (30 L m⁻² h⁻¹) corresponds to a heavy rainfall event at the site and therefore should activate rapid flow paths (PFPs). Brilliant Blue dye was used due to its good visibility, retardation characteristics in soil, and its non-toxicity to the environment (Flury and Flühler, 1994; Weiler and Flühler, 2004). After the dye tracer irrigation, the plots were sprinkled with 2 L of water to wash off the dye residues from the organic layer, and then covered overnight (cf Backnäs et al., 2012). On the following day, the irrigated plots were excavated. Five vertical profile cuts per plot (1 m depth and 1 m width) were successively prepared in 20, 35, 50, 65, and 80 cm beginning from the plot border (see Fig. 1). Soil samples were taken from the three inner cuts at 35, 50, and 65 cm from dye-stained (flow region) and unstained (non-flow region) soil from all morphological horizons. For the forest floor (O-layer) it was not possible to distinguish between stained and unstained material because of the homogeneous distribution of the dye tracer by the irrigation. The Cv horizon was not stained in the upper profile (i.e., no PFP sampling in Cv at Ves2) and only one small pore was stained in the Cv

Table 1: Soil properties of two profiles at a hillslope at the Vessert site (Thuringian Forest, Central Germany) for PFP (preferential flow pathways) and Ma (soil matrix) samples, respectively. Ves1 is the downslope plot, Ves2 the upslope plot. Soil type is a “Sauerbraunerde” (KA5) corresponding to a Dystric Cambisol (FAO-WRB).

Test plot	Horizon	Depth (cm)	Texture	pH _{CaCl2} (–)	C (%)		N (%)		Al _{ox} (mg kg ^{–1})		Al _{di} (mg kg ^{–1})		Fe _{ox} (mg kg ^{–1})		Fe _{di} (mg kg ^{–1})		Mn _{ox} (mg kg ^{–1})		Mn _{di} (mg kg ^{–1})		P _{ox} (mg kg ^{–1})		TP (total P) (mg kg ^{–1})	
					PFP	Ma	PFP	Ma	PFP	Ma	PFP	Ma	PFP	Ma	PFP	Ma	PFP	Ma	PFP	Ma	PFP	Ma	PFP	Ma
Ves1	L-Of-Oh	+9–0		3.2	38.09		1.97		2383		1294		1034		1668		97		145		326		1105	
	Ah-Bv	0–4	Sandy loam	3.2	4.54	4.26	0.28	0.26	1835	1286	1180	973	2944	2330	5481	6470	94	97	243	212	195	177	439	418
	Bv	4–32	Sandy loam	4.2	2.35	2.19	0.15	0.15	7275	7960	5663	6006	5123	4980	7957	7757	317	307	445	459	357	418	516	545
	lIBv-Cv	32–65	Loamy sand	4.4	2.33	1.94	0.15	0.13	10500	9792	8170	7203	3995	3797	6280	5294	193	195	291	295	635	614	767	676
	Cv	65–100	Silty sand	4.3	1.76	0.38	0.12	0.03	9175	4563	7340	2440	2965	1095	5780	2415	131	115	239	282	529	329	635	251
Ves2	L-Of-Oh	+11–0		3.4	32.17		1.72		4114		1201		1276		1745		138		260		297		1145	
	Ah-Bv	0–3	Loam	3.0	7.15	7.83	0.43	0.46	2732	2762	1838	1529	3695	2594	7987	6923	108	57	204	152	538	525	860	809
	Bv	3–35	Loam	3.9	3.71	3.84	0.25	0.25	5958	7718	5358	6147	6777	6567	9260	10897	448	416	600	601	685	686	958	1048
	lIBv-Cv	35–65	Sandy loam	4.3	2.66	1.92	0.17	0.12	12215	11873	9753	8330	3868	3308	8710	8040	276	233	465	421	1056	901	1161	967
	Cv	65–100	Silty sand	4.1		0.37		0.03		4642		2831		589		5550		142	424		163		348	

horizon of the downslope profile (Ves1). In sum, 25 samples for Ves1 and 24 samples for Ves2 were taken, containing varying amounts of soil material because the thickness of soil horizons and stained/unstained parts per horizon differed considerably. The samples were sieved (< 2 mm), dried at 40°C, and then stored in plastic bottles until analysis. For the analysis of C, N, and total P the samples were finely ground.

Each profile cut was photographed and digitally analyzed. The digital image analysis applied geometric correction (spatial distortion and lens aberration) and color correction (chromatic aberration and white balance) using the Software DxO Optics Pro9. Further, the program Gimp 2.8.14 was applied to adjust the pixel to cm relation (1 cm corresponds to 15 pixels), transform the RGB color space to CMYK, and finally to extract the cyan channel of CMYK. This channel was selected on the basis of previous tests which showed that the cyan channel provides a good representation of the dye color utilized (results not shown). The resulting images were coded as binary images (black: stained; white: unstained) and imported into the statistical tool R (version R i386 3.1.0, R Foundation, 2014) using the TIFF-package. Following, a matrix algorithm was applied to filter and remove objects (stained areas) smaller than 2 x 2 pixels. Further, the dye coverage curves (*i.e.*, the percentage of stained pixels per depth) for all profile cuts and the stained path width (SPW) of the detected flow pathways were calculated (*cf Weiler and Flühler, 2004*). The SPWs were classified into three groups: < 20 mm, 20–200 mm, and > 200 mm. Based on the SPW classification and the share of each SPW class per depth, five types of flow processes were derived: for (1) homogeneous and (2) heterogeneous matrix flow, and macropore flow with (3) low, (4) mixed, and (5) high interaction with the soil matrix. Here, the macropore flow types explicitly differ in the width of stained objects with long and narrow shapes for type (3) and broader objects in types (4) and (5), which also have increasing interaction (*i.e.*, lateral water flow) into the adjacent soil matrix (*Weiler and Flühler, 2004; Gimbel et al., 2015*).

2.3 Chemical analysis

The soil samples were extracted sequentially using the Hedley fractionation method (*Hedley et al., 1982, modified by Tiessen and Moir, 2008*). With this method, increasingly strong extractants are used to determine P forms with differing availability for plants. The samples of stained and unstained material per horizon of the three profile cuts per plot were separately treated in the further analyses. All samples were extracted with one replicate. Additionally, two soil standards (WEPAL-ISE 865 and 884) and blank samples were treated equally for quality control of the extraction procedure.

In the first step of the fractionation procedure, a subsample of 0.5 g soil was shaken in distilled water containing an anion exchange resin (Dowex 22, 16–50 mesh, Sigma-Aldrich, Germany) in netting bags (PP-405/230–41, Bückmann, Germany) (*Sibbesen, 1977*). The following extractants used were: 0.5 M sodium bicarbonate (NaHCO₃-P_i), 0.1 M sodium hydroxide (NaOH-P_i), 1 M hydrochloric acid (HCl_{di}-P), hot concentrated 3.5 M hydrochloric acid (HCl_{conc}-P_i), and finally acid digestion of the residual P fraction (residual P). A detailed description

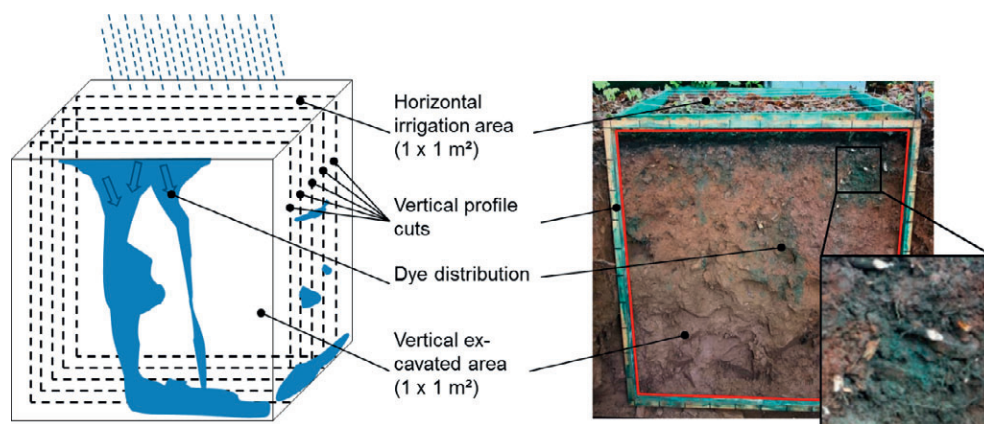


Figure 1: Scheme of tracer experiments (left): Dye application at the soil surface (1 m^2), covering overnight, and excavation of five vertical (1 m^2) profile cuts (example on the right). The red frame shows the spatial distortion of photographed images which has to be corrected for further analyses. The black framed enlargement shows staining of flow pathways along roots and stone surfaces.

of the procedure is given in *Tiessen and Moir (2008)*. As a modification of the above mentioned method, we used 25 mL solution for the extraction and 3 mL concentrated nitric acid for the digestion of the residual P. For the determination of total P (TP) in NaHCO_3 , NaOH and HCl_{conc} , the extracts were oxidized in an autoclave using ammonium persulfate. Organically bound P (P_o) was calculated as the difference between TP and P_i in the extracts (*Tiessen and Moir, 2008*). The P concentrations in all extracts were measured colorimetrically with a spectrophotometer (UV-mini 1240, Shimadzu) based on the method of *Murphy and Riley (1962)* and *O'Halloran and Cade-Menun (2008)*. The total P contents of all samples were determined by extraction with concentrated nitric acid and measurement with ICP-OES (SPECTRO).

Following the concept of the Hedley fractionation (*Hedley et al., 1982; Tiessen and Moir, 2008; Crews and Brookes, 2014*), the different P fractions represent (1) surface-adsorbed readily available P, (2) strongly-bonded or adsorbed moderate available P, and (3) very strongly-bonded or inaccessible mineral P with very low availability. Therefore, P forms were classified for further analysis as labile P (resin- P_i + NaHCO_3 -P), moderately labile P (NaOH-P + HCl_{dil} -P), and stable P (HCl_{conc} -P + residual-P) (cf *Negassa and Leinweber, 2009*).

Total C and N contents were determined after dry combustion with a CN analyzer (Vario EL III Elementar GmbH, Hanau, Germany) of ground samples. The soils contained no inorganic C, thus, soil organic C (SOC) equals total C. Concentrations of C in PFPs were not corrected for added C as part of the Brilliant Blue dye. The C content of the dye is 56% and the amount of total added C in the experiments was 50 g C m^{-2} . *Hagedorn and Bundt (2002)* conducted comparable experiments with a dye-derived addition of 75 g C m^{-2} and found a maximum increase of SOC in PFPs by 2.5% in 0–9 cm depth, and by 3.5% in 50–100 cm depth. In the current study, less dye was applied to the plots. Thus, the change in C content in PFPs is expected to be very low.

The amorphous metal sesquioxides (Al_{ox} , Fe_{ox} , Mn_{ox}) and P_{ox} were determined after extraction with acid 0.2 M ammonium oxalate (100 mL added to a subsample of 2 g). Dithionite-extractable metals (Fe_{di} , Al_{di} , Mn_{di}) were analyzed with 50 mL Na-citrate-dithionite in a subsample of 0.5 g (modified after *Holmgren, 1967*). The measurement of element contents in the extracts was conducted with ICP-OES (SPECTRO).

2.4 Statistical analysis

The statistical significance of differences between P contents of different chemical fractions in flow pathways and matrix, and between the two test plots were tested using the R software package (version R i386 3.1.0, R Foundation, 2014). Given that most of the data sets exhibited non-normal distributions (tested by Shapiro–Wilk test and q-q-plots using R), the non-parametric Wilcoxon rank-sum test was used to statistically compare mean values (significance level of $p = 0.05$). The statistical tests were conducted pair-wise at horizon level due to the hierarchical structure of the data (2 plots, each 3 cuts, each 5 horizons). Because no paired data for PFP and soil matrix were available for the O-layers and Cv horizons (see section 2.2), data of these layers were excluded in the Wilcoxon rank-sum test. Thus, the test was conducted for the three mineral horizons with three repetition (cuts) for PFP and soil matrix, respectively, and separately for the two profiles.

For correlations between measured soil parameters and P fractions, the Spearman's rho correlation coefficients were calculated and tested for significance. Here, all analyzed data of the two plots ($n = 49$) were included. A scatterplot matrix, Spearman's rho correlation coefficients and p -values are provided in Fig. 2.

coverage of this layer compared to the mineral soil (Fig. 3). The occurrence of PFPs in the mineral soil horizons was very heterogeneous leading to highly variable dye coverage functions for the five cuts within both profiles. In the downslope profile (Ves1), the dye coverage strongly decreases in the first 10 cm of the soil to 27% in the Bv horizon and to < 10% in layers below 32 cm depth. This decrease was lower in the upslope profile (Ves2), where more stained areas in the subsoil were observed compared to Ves1. The Bv horizon in Ves2 had a mean dye coverage of 37% and the values reached < 10% in a depth of 47 cm. The SPWs in the mineral soils of both plots were predominantly narrow (< 20 mm), demonstrating that water is mainly seeping through small pathways. Following the classification of Weiler and Flühler (2004), the dominating flow type at the site was macropore flow with low interaction with the adjacent soil matrix.

However, the strong decrease of the stained area with soil depth and the light staining of the pathways in the mineral horizons indicate that vertical seepage is not the major flow component, but lateral flow is the predominant process at the investigated plots. This is confirmed by the (visual) observation of lateral translocations of tracer solution along the hillslope in the upper soil during excavation of the soil pits. The high importance of lateral subsurface flow in the O-layer and adjacent mineral soil, known as biomat flow (Sidle et al., 2007), was shown recently by Gerke et al. (2015) for forested hillslopes in Japan. They divided two key flow mechanisms: (1) lateral subsurface flow due to a permeability contrast between the O-layer and underlying mineral soil, and (2) hydrophobic soil layer between biomat and mineral soil. The O-layer at the Vessertal site is very porous with a diffuse boundary between the O-layer and the underlying mineral soil. The topsoil horizon is thin (3–4 cm), stony, and has a high root density in both profiles. Here, the biomat flow is probably occurring in both the organic and topsoil horizon. Below the topsoil, flow mechanisms are characterized by vertical-oriented pathways along stone surfaces and sporadically also along roots. In the upslope profile Ves2, a higher portion of vertical flow into the subsoil compared to the downslope

profile could be observed. Thus, less water flows laterally in Ves2 which may enhance vertical infiltration through PFPs. This was surprising, as an increase in vertical flow downslope was expected due to a slight decrease of the hillslope gradient at Ves1. However, both plots are located approximately in the middle of the entire hillslope, which ranges from 880 m asl at the hilltop to 680 m asl at the slope toe (ca. 1200 m length). Here, local differences (e.g., micro-relief or vegetation cover) are obviously having a greater impact on soil water flow than the hillslope position. Nevertheless, the subsurface flow regime of both test plots has a predominant lateral component within the O-layer and the topsoil horizon (“biomat flow”). Infiltration into the mineral soil occurs through PFPs along root channels and stone surfaces, which partially lead water into the subsoil. The preferential flow was considerably reduced in the IIBv-Cv horizon (dense periglacial basal layer with very high stone content) and has usually not reached the Cv horizon. Lateral flow in deeper soil horizons (above the dense periglacial basal layer or at the interface between mineral soil and bedrock) was not observed in the tracer experiments. The observed dye patterns in the subsoils may indicate that the amount of water applied was insufficient to induce preferential flow with a strong enough vertical component to reach the bedrock layer.

3.2 Phosphorus fractions in the soil profiles

The results of the chemical P fractionation shown in Fig. 4 represent the mean values of the three vertical cuts per profile. As mentioned in section 2.2, there are no data for unstained ‘Matrix’ in the O-layers and for ‘PFP’ in the Cv horizon of Ves2. The P fractionation results for Ves1-PFP in the Cv horizon is based on only one sample. The coefficients of variation of the analytical repetitions were < 15% for all P fractions, except resin-P_i. Very low P concentrations in the resin-P_i fraction increased the analytical uncertainty up to 18%. The variability of measured data for the three profile cuts per plot was clearly higher than the analytical uncertainty showing the high spatial heterogeneity within the soil profiles (Tab. 2). The total P contents of all samples were compared to the summa-

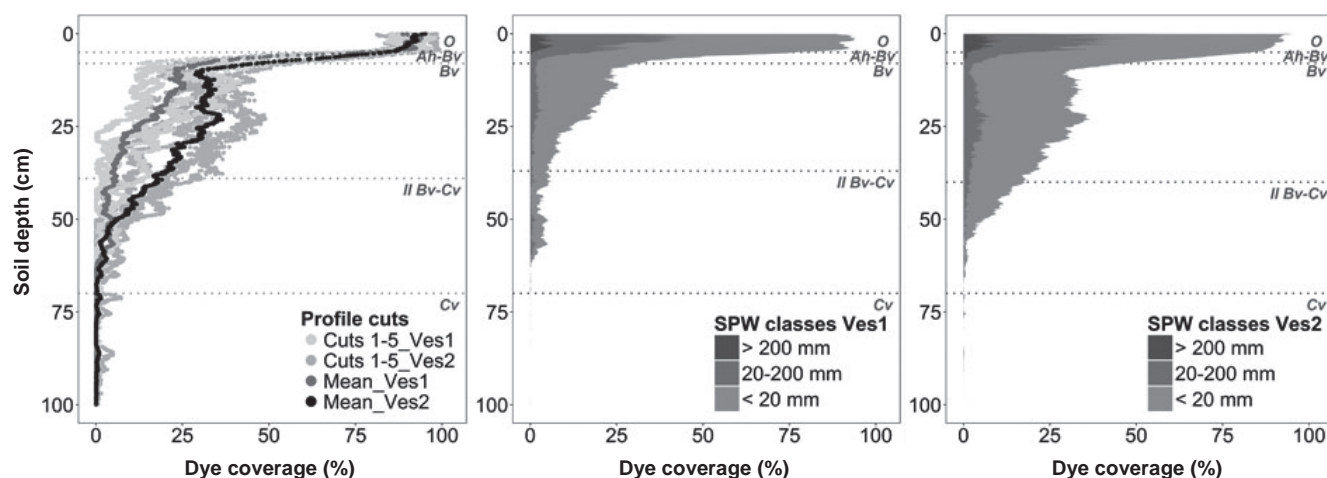


Figure 3: Left: Dye coverage curves of profile cuts (light colors) and mean per plot (dark lines) at the Vessertal study site (Thuringian Forest, Central Germany) with Ves1 = downslope and Ves2 = upslope profile. Middle and right: Stained path width (SPW) classes of detected flow pathways at Ves1 and Ves2 (classified after Weiler and Flühler, 2004). Dotted horizontal lines are boundaries between soil horizons (cf Tab. 1).

alized values of the P fractionation steps in order to determine the recovery rate of the method. The correlation coefficient was 0.89 including all data and 0.95 without the O-layer. The recovery of P in the O-layer during the fractionation procedure was rather low (74%).

The content of labile P forms (resin- P_i + $NaHCO_3$ -P) strongly decreased with soil depth (Fig. 4). The highest contents were detected in the O-layer, with slightly lower values in Ves1 compared to Ves2. In both profiles, the easily soluble resin- P_i accounted for a higher percentage of the labile P pool of the

O-layer, but decreased significantly in the topsoil, and was negligible in the subsoil horizons. $NaHCO_3$ - P_i was highest in the O-layer and strongly decreased with depth in the mineral soil horizons, whereas $NaHCO_3$ - P_o increased from the O-layer to the mineral topsoil and then decreased again in the subsoil horizons. The relation P_i to P_o of the $NaHCO_3$ fraction was almost balanced in the O-layer (50:50 in Ves2, 55:45 in Ves1), but clearly shifted to P_o in all mineral soil horizons. For the labile P fractions, almost no significant differences between P contents of PFP and soil matrix samples were found. The only exception was $NaHCO_3$ - P_o in the IIBv-Cv horizon of

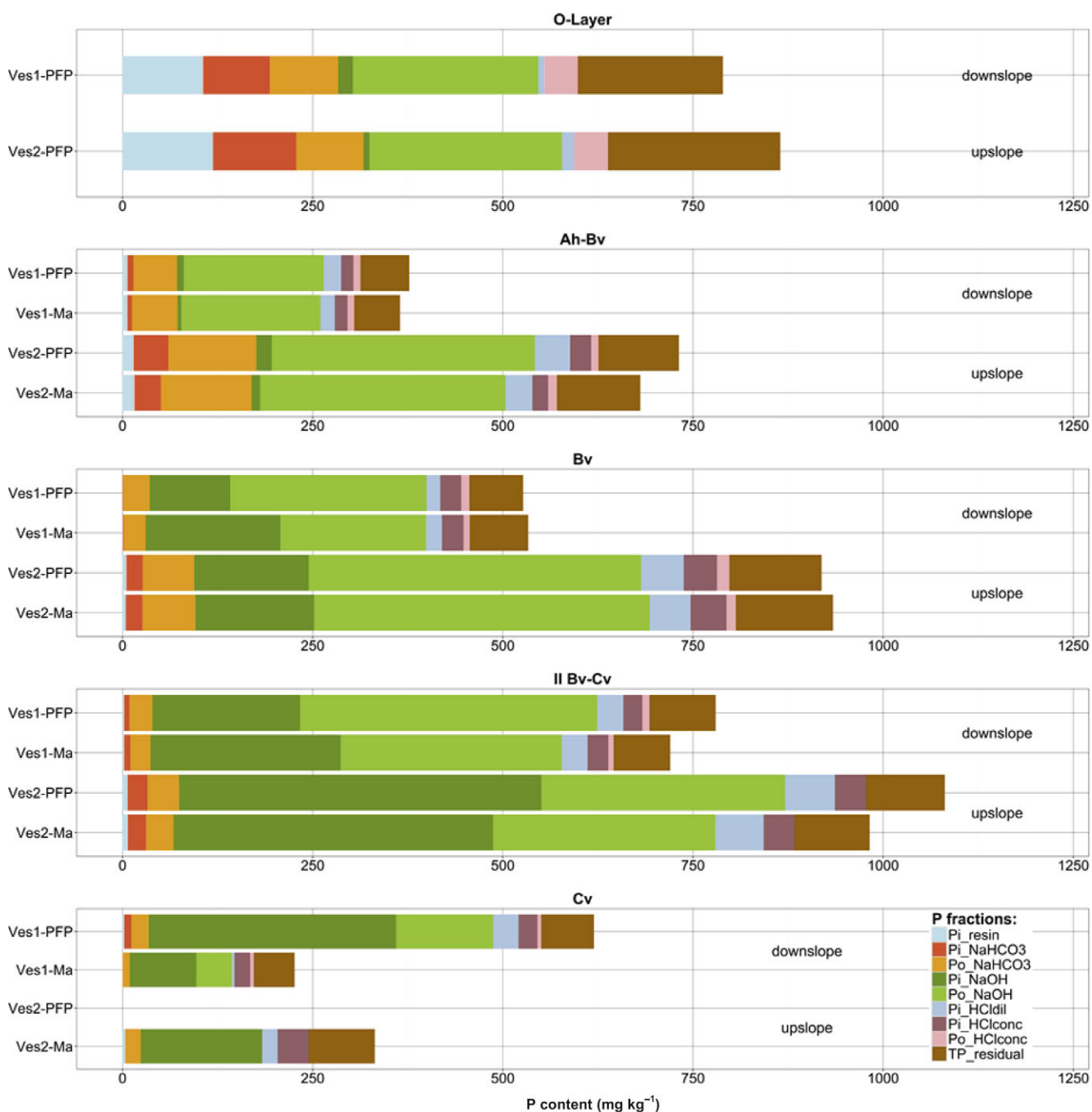


Figure 4: Phosphorus fractions in the downslope (Ves1) and upslope (Ves2) profiles at the Vessertal site (Thuringian Forest, Central Germany) for the horizons: O layer, Ah-Bv, Bv, IIBv-Cv, and Cv; and for PFP (preferential flow pathways) and Ma (soil matrix) samples, respectively.

Ves2, where P_o in PFPs was significantly lower than in the soil matrix. Generally, the contents of labile P in all mineral horizons were clearly higher in the upslope compared to the downslope plot.

In contrast to labile P, the sum of moderately labile P forms ($\text{NaOH-P} + \text{HCl}_{\text{dil}}\text{-P}$) was lowest in the O-layer and increased in the mineral soil down to the IIBv-Cv horizon. The Cv horizon showed lower values for these P pools in the soil matrix. The NaOH-P content in the Cv of Ves1_PFP was quite high, but cannot be generalized, as the values are based on a single sample in this horizon. Generally, the organic form of NaOH-P dominated in the O-layer, topsoil, and upper subsoil (Bv). In deeper horizons, inorganic NaOH-P was typically more prevalent. $\text{HCl}_{\text{dil}}\text{-P}_i$ values were also elevated in the subsoil, however, they made up only to a small proportion of the moderately labile P pool. This fraction represents the P_i from apatite minerals and Ca-phosphates (Crews and Brookes, 2014). The lack of such primary apatite-like P along with high levels of P associated with secondary pedogenic Fe-minerals (NaOH-P) indicates soils which have been highly weathered (Hashimoto and Watanabe, 2014). The dominance of the Al- and Fe-bound P in the test soils is also in line with other studies for acidic forest soil types (e.g., Prietzel et al., 2016). The differences between PFP and matrix samples were only statistically significant in one pair of values (NaOH-P_i of Bv horizon in the Ves2 soil). In both the labile and moderately labile P forms, all mineral horizons of Ves2 had significantly higher contents compared to Ves1. In the O-layer, the differences between the profiles were less visible and in most cases not statistically significant.

The stable P fractions ($\text{HCl}_{\text{conc}}\text{-P} + \text{residual P}$) showed similar values in all mineral horizons, in sum with higher stable-bound P contents in Ves2 than Ves1 (pair-wise compared). In the O-layer, the organic $\text{HCl}_{\text{conc}}\text{-P}$ and residual P were clearly higher than in the mineral soil, which indicates the presence of P_o associated with very stable organic compounds.

3.3 Preferential vs. matrix flow

As shown in the previous section, no statistically significant differences of P fractions in PFPs and the soil matrix were detected in the analysis of the fractionation data. Previous studies indicated that PFPs in forest soils can be stable for decades, resulting in the hypothesis of biological and chemical gradients between PFPs and soil matrix (Hagedorn and Bundt, 2002). This hypothesis was also suggested by Bogner et al. (2012), particularly when preferential flow along root channels dominates the flow system. Highly stable flow paths may therefore lead to the enrichment of elements, as has been documented for radionuclides, SOC, and N by Bundt et al. (2001) and Hagedorn and Bundt (2002), for different P fractions by Backnäs et al. (2012), and for C, N, Ca, Mg, and Fe by Bogner et al. (2012). However, in addition to P, we also found no significant enrichment of C, N, or oxalate-/dithionite-extractable elements in PFPs, when compared to the soil matrix in the two soil profiles (Tab. 1). This may be due to the high stone contents at the study site which tends to produce flow conditions, where the potential for P sorption is limited due to fast water flow and less sorption interaction with soil

Table 2: Coefficient of variation (%) for phosphorus fractions (A) as analytical variation between three profile cuts per profile (Ves1 and 2) at the Vessertal site (Thuringian Forest, Central Germany), for PFP (preferential flow pathways) and Ma (soil matrix) samples respectively. NA: not available.

Test	resin-P _i	NaHCO ₃ -P _i	NaHCO ₃ -P _o	NaHCO ₃ -P _t	NaOH-P _i	NaOH-P _o	NaOH-P _t	HCl _{dil} -P _i	HCl _{conc} -P _i	HCl _{conc} -P _o	HCl _{conc} -P _t	residual-P	TP	
plot	PFP	Ma	PFP	Ma	PFP	Ma	PFP	Ma	PFP	Ma	PFP	Ma	PFP	Ma
(A) Analytical variation														
Ves1	12.3	18.0	1.3	0.1	NA	NA	3.4	2.2	10.8	6.0	5.8	6.8	NA	NA
Ves2	4.5	7.9	4.4	2.5	NA	NA	2.4	2.3	7.6	8.5	6.8	5.0	NA	NA
(B) Spatial variation														
Ves1	20.6	22.2	2.8	10.9	10.0	22.4	9.0	22.7	34.2	14.3	12.8	33.0	6.9	20.9
Ves2	13.0	10.0	11.5	10.5	5.1	8.1	5.9	5.1	27.9	20.3	19.1	49.5	9.0	8.4

matrix (*cf* Backnäs et al., 2012; Jarvis, 2007). Furthermore, the strong laterally directed flow regime in the uppermost soil layers (see section 3.1) triggers water and mass transport laterally along the hillslope and less vertically through the soils via PFPs. Thus, the combination of high stone contents and predominant surface-near lateral flow potentially prevented the build-up of strong gradients in chemical parameters between PFPs and soil matrix.

3.4 Hillslope effect

The P contents in the O-layer of the profiles were similar, with only slightly higher values upslope for resin-P, $\text{NaHCO}_3\text{-P}$, and $\text{HCl}_{\text{dil}}\text{-P}$ fractions. For total P and most analyzed P fractions in the mineral soil, significantly higher P contents in the upslope profile compared to the downslope profile were observed. The accumulation effect in the upper profile was also observed for other elements. Contents of C and N were significantly higher in Ah-Bv and Bv horizons, but similar in the deeper subsoil. Further, amorphous Fe (Fe_{ox}) was significantly higher only in the Bv horizon, and Fe_{di} as well as Mn_{ox} in the whole subsoil of the upper plot. In contrast, the results for Al_{ox} showed significantly higher values in Ah-Bv and IIBv-Cv horizon of the downslope plot. However, high data variability between the three sampled profile cuts per plot often led to non-significant test results (Tab. 2).

The analysis of both the flow patterns and P fractionation data indicated that different microscale conditions (e.g., micro-relief) strongly influenced flow processes. Although the two test plots had a strong lateral flow component which seems to dominate water and mass transport processes, the distribution of flow pathways and elements in the profiles was considerably different (Figs. 2 and 3). The higher vertical infiltration into mineral soil and preferential flow along stones and roots in the upslope profile clearly led to higher contents of P, especially of labile and moderately labile P forms, and to P transport into deeper soil layers when compared to the other profile. However, under the applied test conditions, vertical fluxes into the lower subsoil were clearly reduced due to the occurrence of a dense, stone-rich periglacial basal layer. An accumulation of elements due to downslope translocation of substances with water fluxes was not detected at the tested hillslope section where the two test plots were located. Nevertheless, such an accumulation may occur at a more downslope section where the slope gradient has a greater decrease (*i.e.*, the hillside toe). Conclusion considering the effect of the hillslope position on the distribution of P forms would therefore need test plots located along the entire hillslope and repetitions for the several hillslope positions.

3.5 Factors affecting P fractions

3.5.1 Labile P fractions

In accordance with previous studies (Tiessen et al., 1984; Thomas et al., 1999; Frizano et al., 2002; Prietzel et al., 2016), the labile P fractions (*i.e.*, resin-P + $\text{NaHCO}_3\text{-P}_i$ + $\text{NaHCO}_3\text{-P}_o$) were closely related ($p < 0.01$) to the content of soil organic C and total N (see the correlation matrix Fig. 2). This indicates

that mineralization of organic matter (OM) is an important control on the labile P pool at the site. Strong negative correlations were identified between resin-P and pH, oxalate-extractable Al, Fe, and Mn, dithionite-extractable Al and Mn. Thus, amorphous and crystalline sesquioxides may act as a sink for labile P_i when it is adsorbed onto those surfaces and is precipitated depending on pH (*cf* Tiessen et al., 1984). Renneson et al. (2013) also found negative correlations between available P and Fe_{ox} and Al_{ox} , as well as for TOC, and a positive correlation to pH. However, they applied a different chemical method for the analysis of the labile P pool, and the study was conducted in agricultural soils in Wallonia, Belgium.

Furthermore, resin-P in the plots was strongly positively correlated with $\text{NaHCO}_3\text{-P}_i$ ($\rho = 0.73$) and $\text{NaHCO}_3\text{-P}_o$ ($\rho = 0.81$), indicating the contribution of inorganic as well as organic labile P fractions to the resin- P_i pool. This corresponds with the results of Thomas et al. (1999) from a conifer and broadleaf temperate forest in Chile. Tiessen et al. (1984) also found a close correlation between resin-P and bicarbonate P_o , and suggested that mineralization of P_o supports the resin-P pool. Correlations of labile resin-P with other P_o fractions, as stated by Frizano et al. (2002) for a mountain rain forest soil in Puerto Rico, were not found for our test sites.

3.5.2 Moderately labile P fractions

The inorganic NaOH fraction was strongly positively correlated with pH, oxalate-extractable as well as dithionite-extractable Al and Mn, but negatively correlated with C and N. $\text{HCl}_{\text{dil}}\text{-P}_i$ showed a close relationship to P_{ox} and to Al_{ox} , Fe_{ox} , Al_{di} , and Fe_{di} (Fig. 2). In the organic fractions, a strong positive correlation of NaOH- P_o with Fe_{ox} , P_{ox} , and Fe_{di} was detected. Thus, the inorganic moderately labile P pool in the investigated soils is strongly related to sesquioxides (Al, Fe, Mn), whereas organically bound P in this pool is determined by Fe-oxyhydroxides. This strong contribution of Fe compounds to P_o adsorption, but adsorption of mainly P_i to Al-oxyhydroxides was also suggested by Prietzel et al. (2016) for acidic forest soils.

3.5.3 Stable P fractions and total P status

The $\text{HCl}_{\text{conc}}\text{-P}_i$ fraction was positively correlated with all measured oxalate- and dithionite-extractable elements (Al, Fe, Mn) indicating the important role of sesquioxides for this inorganic fraction. The organic $\text{HCl}_{\text{conc}}\text{-P}$ was strongly correlated to C and N ($\rho = 0.75$ and $\rho = 0.72$), and negatively with pH, Al_{ox} , and Al_{di} . Thus, P_o is mostly associated to stable organic compounds or particulate OM and likely to Al-sesquioxide-stabilized organic compounds like inositols (Turner et al., 2002; Crews and Brookes, 2014). The total residual P had a close relationship to C and N, and interestingly to labile P fractions. Although, previous studies found evidence that the residual pool can be assessed by plants and microorganism by transferring sparingly soluble P into available P forms (*e.g.*, Gahoonia and Nielsen, 1992; Richter et al., 2006), information on the composition and bioavailability of this stable pool are very limited (Velásquez et al., 2016). Prietzel et al.

(2016) investigated factors influencing the soil P status in 10 forest soils throughout the temperate zone in Europe and found strongly positive correlations of both total P and oxalate-extractable P, with the content of oxalate-extractable Al and Fe, and for total P also with the SOM content. For the two test plots, no correlations between total P and oxalate- or dithionite-extractable metals were detected, but the correlation of total P with the C content was confirmed.

4 Conclusion

The analysis of flow patterns and P fractions in two plots along a forested hillslope indicate that local features can lead to very heterogeneous conditions for water and solute flow along a hillslope. The distribution of flow pathways and elements in the profiles was considerably different with higher vertical infiltration into mineral soil and preferential flow along stones and roots in the upslope profile compared to the downslope profile. Following, significantly higher element concentrations (TP and most P fractions, C, N, Fe_{ox}, Fe_{di}, and Mn_{ox}) in the upslope profile were found. An effect of the hillslope position on the distribution of P forms could not be derived because the position of the test plots was rather similar. Furthermore, the gradients of chemical parameters between PFPs and soil matrix were not statistically significant in the two profiles. We hypothesize that the strong lateral flow component at the interface of O-layer and topsoil directed flow mainly laterally (near-surface), and less vertically through the soils via PFPs. Additionally, preferential flow in the mineral soil occurred mainly along stone surfaces which have a lower potential for sorption processes than soil or organic material. Those specific site conditions potentially prevented the accumulation of chemical parameters along PFPs.

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