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## Review Article

# Dissolved and colloidal phosphorus fluxes in forest ecosystems—an almost blind spot in ecosystem research<sup>#</sup>

Roland Bol<sup>1</sup>, Dorit Julich<sup>2</sup>, Dominik Brödlin<sup>3</sup>, Jan Siemens<sup>4</sup>, Klaus Kaiser<sup>5</sup>, Michaela Anna Dippold<sup>6</sup>, Sandra Spielvogel<sup>7</sup>, Thomas Zilla<sup>8</sup>, Daniela Mewes<sup>9</sup>, Friedhelm von Blanckenburg<sup>10,11</sup>, Heike Puhlmann<sup>12</sup>, Stefan Holzmann<sup>12</sup>, Markus Weiler<sup>13</sup>, Wulf Amelung<sup>1,14</sup>, Friederike Lang<sup>16</sup>, Yakov Kuzyakov<sup>15</sup>, Karl-Heinz Feger<sup>2</sup>, Nina Gottselig<sup>1</sup>, Erwin Klumpp<sup>1</sup>, Anna Missong<sup>1</sup>, Carola Winkelmann<sup>9</sup>, David Uhlig<sup>10</sup>, Jakob Sohr<sup>13</sup>, Klaus von Wilpert<sup>12</sup>, Bei Wu<sup>1\*</sup>, and Frank Hagedorn<sup>3</sup>

<sup>1</sup> Institute of Bio- and Geosciences, Agrosphere (IBG–3), Research Centre Jülich, Wilhelm Johnen Str., 52425 Jülich, Germany

<sup>2</sup> Institute of Soil Science and Site Ecology, Faculty of Environmental Sciences, TU Dresden, Piener Str. 19, 01737 Tharandt, Germany

<sup>3</sup> Biogeochemistry Group, Swiss Federal Institute for Forest, Snow and Landscape Research WSL, Zürcherstrasse 111, 8903 Birmensdorf, Switzerland

<sup>4</sup> Institute of Soil Science and Soil Conservation, Justus-Liebig University Giessen, Heinrich-Buff-Ring 26-32, 35392 Gießen, Germany

<sup>5</sup> Soil Sciences, Martin Luther University Halle-Wittenberg, von-Seckendorff-Platz 3, 06120 Halle (Saale), Germany

<sup>6</sup> Agricultural pedology, Georg-August-University Göttingen, Büsngenweg 2, 37077 Göttingen, Germany

<sup>7</sup> Geographical Institute, University Bern, Hallerstrasse 12, 3012 Bern, Switzerland

<sup>8</sup> Ecopedology of temperate zones, Georg-August-University Göttingen, Büsngenweg 2, 37077 Göttingen, Germany

<sup>9</sup> Applied Stream Ecology, Institute of Integrated Natural Sciences, University of Koblenz-Landau, Universitätsstrasse 1, 56070 Koblenz, Germany

<sup>10</sup> Earth Surface Geochemistry, Helmholtz Centre Potsdam GFZ German Research Centre for Geosciences, Telegrafenberg, 14473 Potsdam, Germany

<sup>11</sup> Institute of Geological Sciences, Freie Universität Berlin, Malteserstr. 74–100, 12249 Berlin, Germany

<sup>12</sup> Boden und Umwelt, Forest Research Institute Baden-Württemberg, Wonnhaldestr. 4, 79100 Freiburg i.Br., Germany

<sup>13</sup> Chair of Hydrology, Faculty of Environment and Natural Resources, University of Freiburg, Freiburg, Germany

<sup>14</sup> Soil Science and Soil Ecology, Institute of Crop Science and Resource Conservation, University of Bonn, Nussallee 13, 53115 Bonn, Germany

<sup>15</sup> Department of Soil Science of Temperate Ecosystems, Department of Agricultural Soil Science, Georg-August-University Göttingen, Büsngenweg 2, 37077 Göttingen, Germany

<sup>16</sup> Chair of Soil Ecology, Albert-Ludwigs-Universität Freiburg, Bertoldstraße 17, 79098 Freiburg i. Br., Germany

## Abstract

Understanding and quantification of phosphorus (P) fluxes are key requirements for predictions of future forest ecosystems changes as well as for transferring lessons learned from natural ecosystems to croplands and plantations. This review summarizes and evaluates the recent knowledge on mechanisms, magnitude, and relevance by which dissolved and colloidal inorganic and organic P forms can be translocated within or exported from forest ecosystems. Attention is paid to hydrological pathways of P losses at the soil profile and landscape scales, and the subsequent influence of P on aquatic ecosystems. New (unpublished) data from the German Priority Program 1685 “*Ecosystem Nutrition: Forest Strategies for limited Phosphorus Resources*” were added to provide up-to-date flux-based information.

Nitrogen (N) additions increase the release of water-transportable P forms. Most P found in percolates and pore waters belongs to the so-called dissolved organic P (DOP) fractions, rich in orthophosphate-monoesters and also containing some orthophosphate-diester. Total solution P concentrations range from ca. 1 to 400  $\mu\text{g P L}^{-1}$ , with large variations among forest stands. Recent sophisticated analyses revealed that large portions of the DOP in forest stream water can comprise natural nanoparticles and fine colloids which under extreme conditions may account for 40–100% of the P losses. Their translocation within preferential flow passes may be rapid, mediated by storm events. The potential total P loss through leaching into subsoils and with streams was found to be less than 50  $\text{mg P m}^{-2} \text{a}^{-1}$ , suggesting effects on ecosystems at centennial to millennium scale. All current data are based on selected snapshots only. Quantitative measurements of P fluxes in temperate forest systems are nearly absent in the literature, probably due to main research focus on the C and N cycles. Therefore, we lack complete ecosystem-based assessments of dissolved and colloidal P fluxes within and from temperate forest systems.

**Key words:** forest ecosystem / phosphorus / fluxes / soil / processes / hydrology

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\* Correspondence: B. Wu; e-mail: b.wu@fz-juelich.de

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## 1 Forest phosphorus cycle during ecosystem development

Forests are complex biogeochemical systems in which nutrient cycles readily change and become re-adjusted upon interactions with biotic and abiotic controls over diurnal, annual, decadal, centennial, and longer timescales (Hedin et al., 2003). Phosphorus (P) is an essential element for all living organisms. Modern agriculture avoids P limitation of primary production by continuous application of fertilizers, while forest ecosystems have developed efficient strategies for adapting to low P supply (Eiser et al., 2007; Ilg et al., 2009; Rennenberg and Schmidt, 2010; Hinsinger et al., 2011). Increasing production of forests biomass in response to high atmospheric nitrogen (N) input and climate change likely will increase imbalances in P nutrition of forest ecosystems. Thus, P availability in forest ecosystems gained increasing scientific interest (Medlyn et al., 2011; Peñuelas et al., 2012). Yet, processes and factors ruling P (re)cycling and P nutrition strategies of forests have only received limited research attention (Lambers et al., 2008; Bünemann et al., 2010; Rennenberg and Herschbach, 2013), probably due to the focus on the carbon (C) and N cycles during the last decades (Aber et al., 1989; Luo et al., 2004).

Forests growing on juvenile substrates rely on the acquisition of mineral P from rock sources (Walker and Syers, 1976; Vitousek et al., 2010). With progressing development, ecosystems and soils become increasingly depleted in primary minerals as direct sources of P for plants. Atmospheric deposition of dust is an important source of P during initial and probably also during later stages of ecosystem development, when an ecosystem can become P-limited (Redfield, 2002; Wardle et al., 2004). Little is yet known on the rates of P depletion in ecosystems, because hardly anything is known on the downward P fluxes that result in P losses from a forest ecosystem.

With mineral nutrients becoming incorporated into biomass and with organic matter accumulating during soil formation, an increasing portion of nutrients, including P, is organically bound (Walker and Syers, 1976; Anderson, 1988; Egli et al., 2012), partially accumulating in organic layers lying atop the mineral soil (Brandtberg et al., 2010). Water percolating through this layer becomes P-enriched in soluble and colloidal forms which then enter the mineral soil, provided there is no surface runoff. Such interflow has been observed in tropical mountain forests (Boy et al., 2008); but they have hardly been monitored in temperate forests.

Chemical weathering of rocks, partly biologically driven (Wallerander, 2000), does not only result in the release of simple hydrated ions available as nutrients, but also in the formation of reactive secondary minerals (Anderson, 1988; Egli et al., 2007). These minerals interact with organic compounds and thus contribute to the stabilization and accumulation of organic matter (Mikutta et al., 2009; Dümig et al., 2011) and also strongly bind or incorporate inorganic forms of P (Walker and Syers, 1976). With most weatherable primary rock sources becoming scarcer during ecosystem development and progressing soil formation, acquisition of mineral P becomes increasingly difficult (Turner et al., 2007). Consequently, mature

ecosystems depend largely on the mobilization of P from the organic stocks. Plants can acquire P from organic compounds through a variety of mechanisms (Neumann and Römheld, 1999), which in some cases can be almost as efficient as the conventional uptake in the form of mineral-derived inorganic P (Adams and Pate, 1992; Turner, 2008). However, they have to invest extra energy and C to access these organic P sources. These investments include the synthesis and release of extracellular phosphatase enzymes (Spohn and Kuzyakov, 2013a, 2013b), the secretion of organic anions, and symbiotic associations with mycorrhizal fungi (Antibus et al., 1992; Richardson et al., 2005). As plants and microorganisms can allocate excess N to phosphatase production, P limitation can be delayed by anthropogenic N depositions (Marklein and Houlton, 2012). Although there is no irrefutable evidence yet, there are suggestions that plants may take up dissolved organic P forms either by plant roots or associated mycorrhizae fungi (Smith and Read, 2008; Rennenberg and Herschbach, 2013), which could contribute to minimize the leaching losses. The latter, however, has not been quantified yet.

In summary, native forest ecosystems and likewise other natural ecosystems might slowly turn from P acquiring systems (wherein primary minerals serve as principal P sources) into P recycling systems (which use predominantly organic, thus, secondary P sources; for details see Lang et al., 2016). We define P recycling efficiency in this context as “the fraction of litter-derived P inputs that is re-taken up by microbes and plants”. Overall, the total recycled P (fraction or amount) should equal the mobilization of P stocks from litter minus ecosystem P losses minus P fixed in forms that are not accessible for plants and soil microorganisms. This is different from the definition used in some geochemical studies, in which the recycling efficiency is perceived to be the total P uptake by the trees relative to the release rate of P from primary minerals (which at steady state is equal to the loss rate into streams; Bouchez et al., 2013). In the geochemical approach, the recycling rate can be more readily quantified by measurable geochemical properties. In the context of our definition, however, the efficiency of P recycling will depend largely on the degree of P losses.

The long-term level of P recycling in forest ecosystems is generally limited by the amounts and dissolution rates of P-carrying primary and secondary minerals, and the losses of inorganic P ( $P_i$ ) and organic P ( $P_o$ ). Losses itself are controlled by runoff and interflow, with the preferential flow and hillslope peak flows being driven by soil types, catchment topography, and climate conditions. Little, however, is known on the magnitude and relevance of some of these constituent fluxes in temperate forest ecosystems, although they are the basis for the long-term modeling and prediction of the P cycle (Davies et al., 2016). The main objective of this review is, thus, to compile available literature on dissolved and colloidal P transport within and from forest ecosystems and add to this our own most recent or as yet unpublished data obtained by the DFG Priority Program SPP1685. The specific focus is on data obtained from temperate forest ecosystems on acidic soils.

## 2 Phosphorus forms and transport fluxes in soils

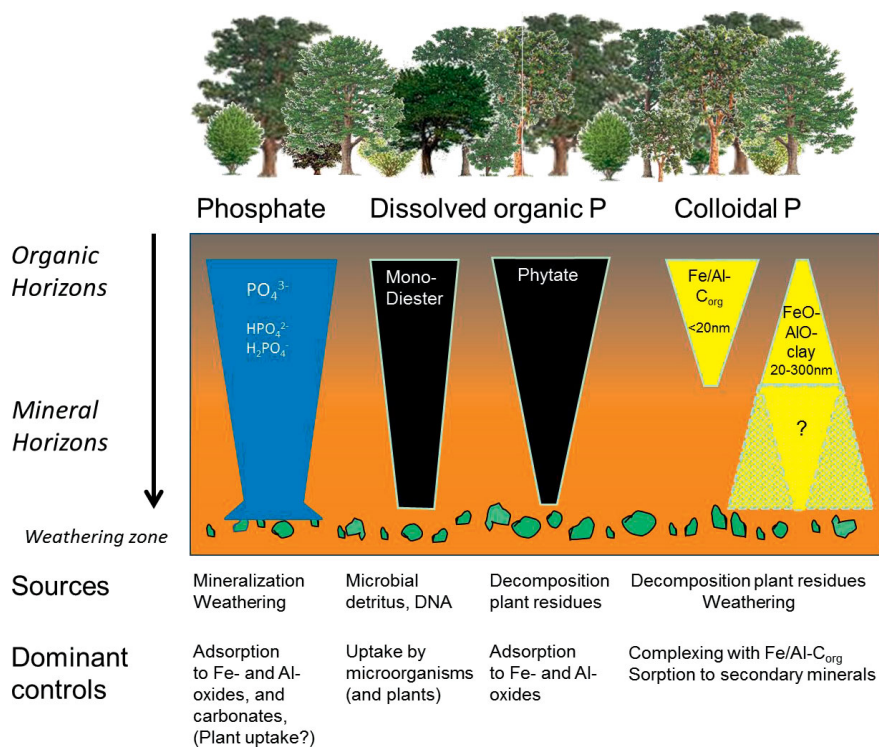
Forest soils contain a wide variety of inorganic and organic P forms, and their availability, sources and dominant controls differ not only between but also within soils (Fig. 1). Inorganic P is bound in various mineral forms (McDowell et al., 2001). Soil solutions in forests have very low concentrations of inorganic P as the mineral-bound P forms are hardly soluble and plants therefore rely more strongly on P released from organic matter. Concentrations of P in soil solution are frequently below the detection limit of many laboratories of 0.05 mg P L<sup>-1</sup>, which may partly explain the little quantitative information on P fluxes in literature. Assumed sources of soil solution P, commonly referred to the labile soil P pool, includes adsorbed P, sparingly soluble P compounds, inorganic P in plant residues, and some organic P forms (McDowell et al., 2001). The inorganic P in soil solution generally decreases with soil depth, probably due to the higher P addition through the surface-litter inputs and relative increase in adsorption to mineral Al and Fe oxides (in acidic soils) or carbonates, and precipitation with Ca (in more alkaline soils) (Cross and Schlesinger, 1995).

In geochemical and geomorphological studies, P availability predominantly depends on three factors: (1) rock type (Porder and Ramachandran, 2013), (2) soil development or weathering intensity (Hedin et al., 2003), and (3) erosion, which rejuvenates substrate by bringing unleached material closer to the surface (Porder and Hilley, 2011). The classical soil view on P availability highlights the fact that P concentration in soil solution is mainly controlled by the solubility of Ca and Al/Fe phosphates. This implies that ecosystem P losses should be

highest for soils with pH values between 5.5 and 6.0 (irrespective of the stage of vegetation succession). Such soils are free of carbonates but are above the pH at which Al becomes a prevailing ion in solution. The presence and formation of secondary minerals, particularly iron- (Fe-) and aluminum- (Al-) (hydr)oxides, in combination with acidification during soil development from Regosols via Cambisols to Podzols, counteracts the vertical losses of ortho-phosphate P and organic P from the “P recycling zone” in topsoils and organic layers. This continued formation of these secondary minerals leads to a more effective subsoil P retention by sorption (Kaiser et al., 2001). However, a part of the organically bound P and also colloidal P may still pass this mineral soil barrier and escape to greater soil depths. Therefore, an increasing efficiency of plants and microorganisms to acquire organically-bound P or ortho-phosphate P, released into soil water from either organic or colloidal compounds, may prevent the vertical P loss and, thus, enhance the P recycling efficiency. It has been estimated that up to 35% of the total P supply to pine was from litter recycling (Switzer and Neson, 1972). However, there is still little further evidence to fully corroborate this.

Previous results have suggested that maximum P mobilization and plant uptake in forest occurs from early spring to early summer (Jonasson and Chapin, 1991; Huang and Schoenau, 1998), whereas microorganisms show their highest P uptake and incorporation activity during the summer months (Zilla, pers. comm.). A similar annual change of N uptake by plants and microorganisms is known to be an efficient strategy to avoid N losses and increase recycling at ecosystem level (Kuzuyakov and Xu, 2013). Thus, increasing P storage during the summer months within the microbial biomass may be an efficient mechanism of forest ecosystems to reduce P losses in this period. This is important as in ecosystems with low total P the microbial P can be an important pool with respect to P availability and flux. Analyses of <sup>33</sup>P phospholipid fatty acids did demonstrate that shifts in microbial community structure over the course of the year may support the temporal storage of P within microbial biomass. The seasonal shift towards microorganisms is best adapted to the respective C input, i.e., Gram Negatives in spring versus Gram Positives in autumn (Dippold, pers. comm.).

Anthropogenic impacts (e.g., N emissions, modifications of soil acidity and alkalinity, plantations) influence the P mobility, P-pool sizes and composition and, thus, the overall forest P cycle (Gundersen, 1998; Marklein and Houlton, 2012; Liu et al., 2014). Acidification may decrease plant P status (normally observed in the foliage samples) because of elevated Al concentrations, which either reduce plant P uptake due to toxic effects on root growth or limit the P availability due to the formation of



**Figure 1:** Trends of P content in various forms with soil depth, including P sources and the dominant controls.



insoluble Al-P forms. In turn, acidification may increase soil inorganic P sorption, reduce organic P mineralization, overall P solubility as well as fine roots and mycorrhizal associations (Van Breemen et al., 1983; Paré and Bernier, 1989; Talkner, 2009). Overall it remains unclear to what extent the P leaching may change upon acidification. Salih and Andersson (1999) noted that *Picea abies* stands of SW Sweden were growth-limited by N and P, and applications of N induced P deficiency. Liming (increasing soil pH) may enhance organic matter decomposition and increase the root biomass (Persson et al., 1990; Bakker, 1999; Huber et al., 2006), leading to a mobilization of orthophosphate-P and increased root exudates for improving P acquisition and P-uptake intensity. In the SPP1685 research program, results of a mesocosm study with beech forest soils sampled along a soil P gradient and planted with beech seedlings did show that total P leaching at 20 cm depth was rapidly increased by 28–99% by the enhanced addition of N ( $10 \text{ g N m}^{-2} \text{ a}^{-1}$ ; applied as  $\text{NH}_4\text{NO}_3$ ), while liming ( $0.03 \text{ g dolomite m}^{-2} \text{ a}^{-1}$ ) and ambient rain (control treatment) had no significant effects. The N addition effect on P leaching at Bad Brückenau, Vessertal and Luess sites was inversely related to total soil P stocks. The relative contribution of molybdate-reactive P to total P (molybdate-reactive P after digestion with persulfate) in the leachates was 12% higher in mesocosms receiving N (generally  $50\text{--}75 \mu\text{g P L}^{-1}$  depending on the forest location), i.e., 47% against only 35% in the other two treatments (forest liming and ambient rain; Holzmann et al., 2016).

Organically bound P forms include orthophosphate monoesters (inositols, mononucleotides, sugar phosphates), orthophosphate diesters (phospholipids, teichoic acids, nucleic acids, and their degradation products), and phosphonates (Newman and Tate, 1980). Dissolved organic phosphorus (DOP) is the mobile form of organic P. DOP is operationally defined to be smaller than  $0.45 \mu\text{m}$ . However, this fraction encompasses not only truly dissolved compounds but also colloidal and nanosized particulates. As a part of dissolved organic matter (DOM), DOP principally derives from leaching of plant litter and microbial metabolites, exudation by roots, and solubilization of soil organic matter during degradation, but the relative contribution of each of these sources is still unclear and differs among ecosystems, soil types and depths (Kaiser et al., 2003; Hagedorn et al., 2004; Uselman et al., 2009). There are only a few field studies quantifying the fluxes of different P forms in forest soils, but they all indicated DOP to dominate in soil waters, with the contribution of DOP in total dissolved P (TDP) increasing with soil depth (Table 1; Qualls et al., 1991, 2000; Kaiser et al., 2000, 2003).

The large contribution of organic forms to nutrient leaching from forest soils has also been recognized before for N (Hedin et al., 1995; Perakis and Hedin, 2001, 2002). The importance of organic forms to drive leaching may be even greater for P than for N (Qualls et al., 1991, 2000). Inorganic P forms may over time bind to or become incorporated into secondary minerals. Thus, despite ongoing mineral weathering and mineralization of organic matter, the concentrations in soil solution of inorganic P forms are therefore usually small (Qualls et al., 1991; Kaiser et al., 2000). Soluble organic compounds containing P are formed during microbial degradation of or-

ganic matter (Uselman et al., 2009). Organic P may also enter the forest soils by stemflow, canopy leaching, or dry deposition. Most organic P forms are retained within soils by mechanisms similar to those for inorganic P forms (Anderson et al., 1974; Celi et al., 2001). Overall, the DOP binding is less strong than that of inorganic P forms (Anderson et al., 1974; Anderson and Magdoff, 2005; Celi et al., 2001; Lilienfein et al., 2004), and the most P-rich fractions of DOM are more mobile than the rest (Qualls and Haines, 1991; Kaiser et al., 2000; Kaiser, 2001). As a result, much of the P in soil solution is organically bound (Qualls et al., 1991, 2000; Kaiser et al., 2000, 2003; Hedin et al., 2003). Therefore, leaching of DOM is likely an important pathway of long-term P losses from soil (Hedin et al., 2003; Alvarez-Cobelas et al., 2009). Losses of DOP from sandy soils developed to quartz-rich substrates can exceed those being richer in clay and reactive mineral phases (Kaiser et al., 2000; Qualls et al., 2000). However, quantitative data on forest DOP losses remain limited and especially DOP losses from subsoil vary by at least a magnitude, e.g., from  $1.7$  to  $38 \text{ mg P m}^{-2} \text{ a}^{-1}$  (Table 1) (Kaiser et al., 2000, 2003; Qualls et al., 2000).

In mineral soils, the remaining mobile fraction of DOM in subsoils is relatively enriched in N and P, thus, it has lower C : N and C : P ratios than total DOM leached from forest floors (Qualls and Haines, 1991; Kaiser et al., 2000, 2003; Hedin et al., 2003). Under identical conditions, the sorption of the so-called hydrophilic fraction (typically rich in P; Qualls and Haines, 1991; Kaiser et al., 2003) of DOM seems weaker than that of other organic fractions (Kaiser, 2001) and of inorganic P forms (Lilienfein et al., 2004). Therefore, the mobility of P-rich organic compounds is linked to structural features. Inositol-derivates (or phytate-like P) binds strongly to mineral soil constituents, while P linked to nucleotides (diester P) seems mobile (Anderson and Magdoff, 2005), thus, potentially becomes more and more prominent in soil solution with increasing depth. In fact, DOP in subsoils is dominated by orthophosphate monoesters and diesters, indicating that they are potentially mobile (Kaiser et al., 2003). The composition of DOP in freshwaters and seawater (Nanny and Minear, 1997; Clark et al., 1999; Kolowith et al., 2001; Young and Inggall, 2010) resembles that of DOP in subsoils, probably linking them either to input from terrestrial settings or suggesting similar microbial processing. The composition of forest-derived DOP, thus, differs from that of water extracts of grasslands, for example, where the largest fractions are orthophosphate diesters and hydrolyzable inositol, with only a small fraction of orthophosphate monoesters (Turner et al., 2002). The extraction of P along preferential flow paths in a sandy podzol suggested that P might have been leached as phosphate and labile monoesters and diesters from upper horizons, and as phosphate in the deeper horizon (Backnäs et al., 2012). Also, Huang and Schoenau (1998) determined that inorganic P comprised 75% of total water-extractable P in a sandy loam soil under forest. Consequently, the extraction procedures of dissolved P give completely different results on the involved P species from those by the analysis of soil solutions sampled *in situ*. The likely reason is that the sources and composition of organic matter greatly differ between water-extracts from soils and soil solutions (Hagedorn et al., 2004; Ros et al., 2009). We assume that the finding of a domi-

**Table 1:** Magnitude of P concentrations and fluxes in temperate forest ecosystems.<sup>a</sup>

| Source                         | Concentrations<br>/ $\mu\text{g P L}^{-1}$  | Fluxes<br>/ $\text{mg P m}^{-2} \text{a}^{-1}$   | Source  | Comments   |
|--------------------------------|---|--|---|--|
| Atmospheric input              |   | 7–12<br>33<br>30<br>5–8 (total P)  | Newman (1995)<br>Tipping et al. (2014)<br>Qualls et al. (1991)<br>Möller et al. (unpublished)   | Precipitation (18 sites)<br>Precipitation<br>Throughfall (broadleaf forest)<br>Broadleaf & coniferous forests Thailand   |
| Litter fall                    |   | 440<br>400   | Cole and Rapp (1981)<br>Cole and Rapp (1981)  | Temperate coniferous (13 sites)<br>Temperate deciduous (14 sites)  |
| Weathering                     |   | 5–10   | Newman (1995)   | global data set  |
| Total P organic layer          | 18–22   | n.a.   | Möller et al. (unpublished)   | Broadleaf & coniferous forests Thailand  |
| Inorganic P organic layer      | 30–1000<br>(mean = 380)<br>15–18<br>10–20   | 15<br>4<br>11  | Sohrt (unpublished)<br>Qualls et al. (1991, 2000)<br>Kaiser et al. (2000)<br>Kaiser et al. (2000, 2003)   | Deciduous forest (oak)<br>Coniferous forest (pine)<br>Deciduous forest (beech)   |
| Inorganic P subsoil            | 0–700<br>(mean = 70)<br>1.5<br>1  | 3<br>0.5–1<br>0.6  | Sohrt (unpublished, preliminary data)<br>Kaiser et al. (2000)<br>Kaiser et al. (2000, 2003)<br>Qualls et al. (2000)   | Coniferous forest (pine)<br>Deciduous forest (beech)<br>Deciduous forest (oak)   |
| DOP organic layer              | 50–60<br>110<br>25  | 15<br>45–62<br>30  | Kaiser et al. (2000)<br>Kaiser et al. (2000, 2003)<br>Qualls et al. (1991, 2002)  | Coniferous forest (pine)<br>Deciduous forest (beech)<br>Deciduous forest (oak)   |
| Total P subsoil                | 10–18   | n.a.   | Möller et al. (unpublished)   | Broadleaf & coniferous forests Thailand  |
| DOP subsoil                    | 1–4<br>50<br>70–130   | 1.7<br>9<br>38   | Qualls et al. (2000)<br>Kaiser et al. (2000)<br>Kaiser et al. (2000, 2003)  | Deciduous forest (oak)<br>Coniferous forest (pine)<br>Deciduous forest (beech)   |
| Colloidal P                    | Stream: 0.7–16.4 (mean: 5.5)<br>Soil leachates (20 cm depth) 8–53   | 8–51   | Gottselig et al. (unpublished)<br>Missong et al. (unpublished)  | New method developments (field flow fractionation)<br>Mesocosm experiment  |
| Leachates                      | Leachates (20 cm soil depth) 26–113   | 22–109   | Holtzmann et al. (2016; this issue)   | Mesocosm experiment  |
| Spring discharge               | 0–30 (mean = 14)<br>20–30 (total P)   |  | Sohrt (unpublished)<br>Verheyen et al. (2015)   |  |
| Groundwater                    | 0–20 (mean = 11) (total P)  |  | Sohrt (unpublished)   |  |
| Stream water Forest catchments | 0.5–10 (dissolved P)<br>1–100 (fine particulate P)<br>0–300 (coarse particulate P)<br>3–10, mean 4 (dissolved P)<br>20–310, mean 83<br>0.7–1.9 (DOP)<br>2.4 (inorganic P)<br>9–16 (total P) | 1–60<br>1300 (total P)<br>(242, 807, 252)<br>3–32<br>5 ( $\text{PO}_4$ ), 25 (total P)<br>10 ( $\text{PO}_4$ ), 40 (total P)<br>1.1 (DOP)<br>1.3 (inorganic P)<br>4.5–28<br>10 (total P) | Cole and Rapp (1981)<br>Meyer and Likens (1979)<br>Meyer and Likens (1979)<br>Benning et al. (2012)<br>Mengistu et al. (2014)<br>Verheyen et al. (2015)<br>Palviainen et al. (2014)<br>Benning et al. (2012)<br>Qualls and Haines (1991),<br>Qualls et al. (2002)<br>Qualls et al. (2002)<br>Kunimatsu et al. (2001)<br>Möller et al. (unpublished) | 3 forested catchments<br>Bear Brook<br>Exported as dissolved, fine and coarse particulate P<br>Forested catchment<br>Deciduous forest (oak)<br>Deciduous forest (oak)<br>Broadleaf & coniferous forest Japan<br>Broadleaf & coniferous forest Thailand |

nance of DOP in *in situ* leachates (Qualls and Haines, 1991; Kaiser et al., 2003; Table 1) is more relevant for ecosystem fluxes, while extractable P might rather represent a fraction that is available for plant and soil microorganisms.

Few studies addressed dissolved organic P in soil solution by *in situ* sampling and using fairly comparable analytical approaches (Qualls and Haines, 1991; Qualls et al., 1991,

2000; Kaiser et al., 2000, 2003). However, these studies actually cover just five forest stands, thus, cannot be considered truly representative. Concentrations of DOP in the percolates from forest floors ranged from 25 to 110  $\mu\text{g P L}^{-1}$ , while the respective concentration ranges for pore waters from subsoils were 1–130  $\mu\text{g P L}^{-1}$ . The DOC : DOP ratios ranged from 200 to 4200 in forest floor percolation waters. The ratios in pore waters from mineral topsoil were similar and ranged between

185 and 3820, but those in pore waters from deeper subsoils were between 100 and 860. The decrease of the DOC : DOP ratios with depth might be due to the mineralization of organic compounds, release of CO<sub>2</sub>, and uptake and utilization of P from the subsoil. The wide ranges of DOC : DOP ratios suggest differences among soils and vegetation types as well as seasons and climate effects. It is also worth to note that the high DOC : DOP ratios came from the sites with less developed soils, whereas low DOC : DOP ratios came from the sites with more developed soils.

It cannot be taken for granted that all P in the < 0.45 μm fraction is truly dissolved. Significant parts of this P may be colloidal in nature (Gottselig et al., 2014; Jiang et al., 2015a). The composition of larger colloids found in soil water, interflow, or surface runoff commonly reflects the mineralogical composition of the soil clay fraction (Kretzschmar, 2005). Not clays, but especially Fe and Al oxyhydroxides are strong sorbents for P and occur in the colloidal size fraction (1–500 nm), which qualifies them as potential colloidal carriers of P. The nanoparticle fraction, defined as the size fraction ranging from 1 to 100 nm, could serve as a mobile and efficient carrier for P in soil solutions. Natural nanoparticles and colloids are important vectors for P transport in soils (Haygarth et al., 1997; Ilg et al., 2005; Regelin et al., 2013) and can contain high proportions of the P in soil solutions (Hens and Merckx, 2001). However, the factors controlling the distribution, enrichment, and mobilization of colloidal P in soil are rarely investigated. In a field-scale study about 75% of P was transported by small colloids and nanoparticles (< 240 nm; de Jonge et al., 2004). The composition of such leachates, however, may not necessarily reflect the fraction of the particle-bound P finally lost by streams. The percentage of P in the streams bound to the soil nanoparticles and fine colloids is likely smaller. In a study of the Rur catchment, Germany, it ranged from 40 to 100% (Gottselig et al., 2014). Overall, distinguishing between streams receiving large ground water input (dilution) and those receiving much overland flow input (likely containing more colloidal and nano-particulate materials) is required to truly relate the P composition of streams to that of leachates (and surface runoff or interflow).

In experiments by Ilg et al. (2005), concentrations of colloidal P extracted with deionized water or 0.01 M KCl solution from agricultural soils were strongly correlated to colloidal Fe and Al concentrations. The strong hysteresis of the sorption of orthophosphate P or inositol P to these oxides is an important prerequisite for colloid-facilitated transport. However, the point of zero charge of Fe and Al (hydr)oxides of 8.5–9.0 means that these minerals are positively charged under the pH conditions of temperate forests on acid soil, which effectively promotes their deposition on negatively charged clay minerals or moieties of soil organic matter. Yet, the positive surface charge of Fe and Al (hydr)oxides can be turned into negative surface charge as a consequence of the sorption of natural organic matter to these colloids, which strongly increases their mobility in porous media (Kretzschmar et al., 1995; Kretzschmar and Sticher, 1997; Séquaris et al., 2013).

In addition to the effect on the surface charge of Fe and Al (hydr)oxides, natural organic matter molecules sorbed to

these minerals can also impose a steric hindrance to mineral coagulation (Kretzschmar, 2005). This means that mobile organic-loaded Fe and Al (hydr)oxide colloids most likely originate from topsoil horizons rich in organic matter. In experiments of Kaplan et al. (1997), leaching of organic coatings of colloids to greater soil depths in Ultisols suggested that they were mobilized in the A horizon. Chemical characterizations of colloids collected from soil solutions suggest that colloidal P occurs mainly in mixed Fe/Al hydroxide–organic matter–phosphate associations (Hens and Merckx, 2001), underlining the relevance of organic matter for the mobilization of colloidal P.

Recently, P release facilitated by nanoparticles and small colloids (10–200 nm) in mildly acidic agricultural soils has been reported (Rick and Arai, 2011). Desorption experiments revealed that the maximum total colloidal P, which could be desorbed, was 10–20% of the total P. Contrary to previous studies, the release of labile P was not facilitated by soil nanoparticles. Transmission electron microscopy combined with energy dispersive spectroscopy (TEM-EDS) showed that released particles in grassland soils extracts were 200–250 nm nanoaggregates, composed of ~ 50 nm aluminosilicate flakes and Fe clusters (< 10 nm). The latter fine colloidal-sized Fe compounds held onto most the P present in the soil (Henderson et al., 2012). Recent papers (Gottselig et al., 2014; Jiang et al., 2015a, 2015b) did use field flow fractionation (FFF) coupled to different detection methods [e.g., inductively coupled plasma mass spectrometry (ICP-MS), organic carbon detector (OCD), dynamic light scattering (DLS), fluorescence, UVvis] to allow size-resolved characterization and element quantification of the nanoparticles and colloids in soil leachates, water-dispersible materials, and stream waters. Initial results from acidic forest soils showed that P fractions were present both as (1) organic-dominated nanoparticles and (2) mineral-dominated colloids such as Fe/Al/Mn (hydr)oxides and phyllosilicates (Missong, pers. comm.). All fractions had significant amounts of P, with concentrations varying with site characteristics. Initial results of the soil leachate characterization revealed the presence of nanoparticles and colloids, thus, confirming their relevance to transport and leaching of P (Holzmann et al., 2016). The <sup>31</sup>P-NMR spectra indicated that soil nanoparticles and colloids were more enriched in organic than in inorganic P forms than the electrolyte phase, as also shown in other recent studies (Liu et al., 2013; Liu et al., 2014). Overall, P was more enriched in the colloidal fraction than in the bulk soil. The P-diester : P-monoester ratios in the colloidal fraction were 2–3 times higher than those in the bulk soil, indicating diesters to be more prominent in the colloidal fraction. In contrast, relatively large percentages of inorganic P were found in the true solutions (Missong et al., 2016).

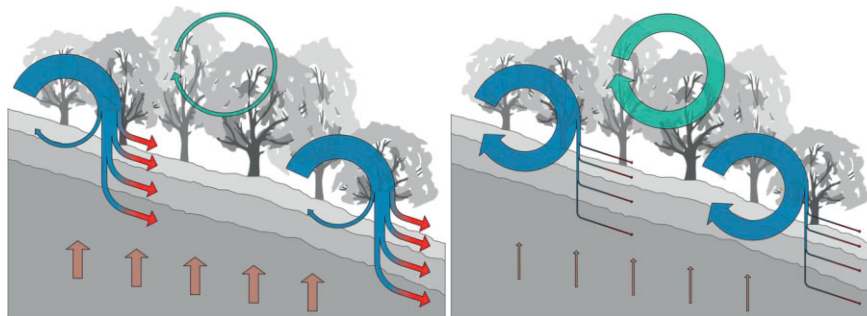
In unsaturated porous media, colloids are effectively retained at water–air interfaces (Wan and Wilson, 1994; Gargiulo et al., 2008), water/air–solid interfaces (Crist et al., 2004), and within thin water films (Wan and Tokunaga, 1997). This means that rapid infiltration of water into dry soil removing those interfaces is an efficient driver of colloid mobilization and partly responsible for the “first-flush” of colloids observed at the onset of irrigation experiments. Rapid infiltration during



rainstorms also triggers water flow through macropores, which promotes the colloid transport in soils (Poulsen et al., 2006; Vendelboe et al., 2011). A large fraction of transported colloids is released from the walls of the macropores (Majdalani et al., 2007; Schelde et al., 2006), also pointing at the role of mechanical shear stress for the mobilization of colloids. An additional factor promoting the mobilization of colloids during rapid infiltration of water in macropores during heavy rainstorms is the rapid decrease of ionic strength (Kretzschmar, 2005). Altogether, this suggests that colloids will most likely be mobilized in organic (O) and A horizons during rainstorms and transported to a large degree through macropores or at the interface between mineral soil and organic layers during high-flow events. Nevertheless, acidic pH values and large concentrations of  $Al^{3+}$  counteract the mobilization of colloids (Kretzschmar, 2005). The initial recovery of forest soils from acidification, a consequence of decreasing past atmospheric inputs of strong acids, can therefore potentially promote release and loss of colloids and colloidal P from the organic forest floor and mineral topsoils.

The general accumulation of (predominantly organically bound) P in topsoils and surface layers with progressing pedogenesis promotes P recycling, but it may also increase the risk of P losses with interflow or runoff (Fig. 1) The experience from agricultural systems shows that P losses from soils not “P-saturated” are often dominated by losses of colloids with surface runoff and interflow (Heathwaite and Dils, 2000; Heathwaite et al., 2005; Turner et al., 2003). Colloids can also be transported vertically in the soil, primarily through macropores during high flow events (Schelde et al., 2006). Since colloidal transport occurs predominantly during short events, re-acquisition of potential bio-available colloid-bound P by plants or microbes is hampered. Loss of more bioavailable organic colloids will limit the recycling of P to a greater extent than loss of P tightly bound to colloidal Fe or Al (hydr)oxides.

Leaching of P, either in dissolved or colloidal form, may not only cause P losses from forest ecosystems. Leaching most likely also drives lateral as well as vertical redistribution of P within forest stands. The lateral transport of P might cause preferential accumulation of P in depressions or riparian zones, while elevated positions become depleted in P. We think that lateral redistribution of P can potentially affect the spatial structuring of forests in denser zones with more vigorous regeneration and more open patches with poorer re-growth. The leaching of P from forest floors or mineral topsoils into subsoils transfers P from a zone of high biological activity and root density into a zone with less roots and higher abundance of freshly formed pedogenic (hydr)oxides that are characterized by strong P sorption, which likely decreases the efficiency of P recycling in forests.



**Figure 2:** Lateral transport and redistribution of P in a forested hillslope underlain below permeable bedrock by overland-flow, subsurface-flow, and deep-flow pathways in a P-acquiring (left) and P-recycling (right) system. The relative thickness of the arrows of the lateral P transport is still unknown and therefore not to scale.

### 3 Hydrological pathways linking P source and P loss

Hydrological pathways form a critical link between the source of mobile P and P export from soils to adjacent headwater streams (Heathwaite and Dils, 2000). It is the combination of source, mobilization, and transport factors that determines the overall P loss to surface waters (Granger et al., 2010; Drewry et al., 2006). It is likely that the (inorganic) P export from hillslopes in acquiring systems (Fig. 2, left) is larger than those in recycling systems (Fig. 2, right) because of perceived larger weathering fluxes in P-acquiring systems. However, in view of the enhanced colloid mobilization which is linked to the leachate organic loading, colloidal P transport and losses could be more important in the recycling systems; yet, decisive studies that confirm or reject either of these assumptions are lacking. In general, studies that differentiate water-bound P fluxes in temperate forest ecosystems in a quantitative manner at a given site are lacking. Furthermore, Heathwaite and Dils (2000) pointed out that it is important to establish thresholds at which the balance shifts from subsurface to near-surface flow pathways, to find out under which conditions matrix vs. macropore flow is initiated and which soil hydrological factors lead to infiltration-excess surface runoff rather than saturation-excess flow. They believed that these factors were the trigger to P transport. Interestingly, transport processes and P fluxes in terrestrial ecosystems have mostly been examined in agricultural systems with focus on P losses from soils and related effects on aquatic ecosystems (Haygarth et al., 1998; Heathwaite and Dils, 2000; McDowell et al., 2001; Jarvis, 2007). For forest soils detailed studies investigating P flow pathways and losses are still extremely rare (Zhang et al., 2008). Heterogeneous water flow paths and solute transport already start in throughfall and hence with the inputs into soils. Levia and Frost (2003) emphasized the influence of stem flow (enriched in nutrients and organic acids) on soil solution chemistry. It was shown that stem flow can concentrate and channel water including P over localized circular areas at the tree base depending on bark surface and precipitation characteristics (Schwärzel et al., 2012; Zhang and Mitchell, 1995). For European beech it was suggested that stem flow and root-induced preferential flow (double funneling effect), which triggered a fast(er) hydrological response to rainstorms (Schwärzel et al., 2012), might promote P losses.



At the soil profile scale, phosphate mobilization processes are relatively well understood (Haygarth et al., 2005). However, knowledge of P delivery through landscapes and catchments is limited mainly due to the complexities of the transport scales involved and the different P detachment mechanisms that act in runoff and erosion events. These high-magnitude but usually short-timescale events mobilize larger-sized particles and lead to more detachment of soil colloids (Haygarth et al., 2005). Leaching rates of P in forest soils are assumed to be negligible due to strong P-bonding to soil constituents (Achat et al., 2009). Studies on grassland soils showed that, except for losses with surface runoff, P was transported predominantly in preferential-flow pathways (Haygarth et al., 1998; Heathwaite and Dils, 2000; Toor et al., 2005; Jarvis, 2007). Thus, water and P may bypass large parts of the soil matrix, resulting in high P losses during heavy rainfall events when preferential-flow pathways are connected (Beven and Germann, 1982; Djodjic et al., 2004). According to Heathwaite and Dils (2000), the magnitude and composition of the P load transported in individual flow pathways will in reality depend on: (1) land management practices which influence the total amount, spatial heterogeneity and the form of soil P, (2) rainfall characteristics and hillslope hydrology which define the mechanisms and pathways of water flow, and (3) soil type and antecedent moisture status which determine the contact time between “new” water and the soil, and the frequency at which a pathway operates. Transport of P also highly depends on its physical bonding form, *i.e.*, whether P is sorbed to soil particles or to mobile colloids, or it is existent in dissolved form. Sorbed P is mobilized by erosion and is transported with the water flow through larger soil pores; it can be deposited again if flow velocities decrease.

Dissolved P is transported through the soil both by macropore flow and by matrix flow, and is present in the immobile water fraction and is also taken up by roots. Heathwaite and Dils (2000) found that dissolved P in a grassland catchment amounted to over 80% of total P in matrix flow and to 50–60% in surface runoff. The predominance of preferential flow pathways in the transport of nutrients in forest soils was shown by Bundt et al. (2001) and Bogner et al. (2012). However, there is only one known study investigating P transport and P forms involved in preferential-flow pathways in forest soils. From their study on a podzol in Finland, Backnäs et al. (2012) assumed that leaching of P through preferential-flow pathways occurred predominantly on stone surfaces, where P sorption might be limited due to the comparatively small sorptive surface area and the rapid water flow. By contrast, macropores related to coarse grains and roots are smaller and have a larger sorptive surface area, *i.e.*, sorption should be higher and water flow smaller, leading to P accumulation in these pores. Jensen (1998) also suggested higher P saturation in long-term stable preferential-flow pathways, leading to a higher potential for high-P concentration transport and accumulation on aggregate surfaces.

Hillslopes can contribute much to the P export from catchments, because P transport is often connected with fast flow (McGechan et al., 2005) and hillslopes are landscape units where lateral fast flow typically occurs (Bachmair and Weiler, 2012). The first estimates from a monitoring study (April 2014

to September 2015) in the forested catchment of the Vessertal (Thuringian Forest, Germany) measured a mean total P of roughly equivalent to  $0.032 \text{ g m}^{-2} \text{ a}^{-1}$  (Julich, pers. comm.). The main fraction of total P (on average ca. 90%) is likely to be dissolved inorganic P (orthophosphate). In an earlier study in a forested catchment in the Eastern Ore Mountains (Saxony, Germany) by Benning et al. (2012), the annual P export fluxes were found to be much lower ( $0.004 \text{ g m}^{-2} \text{ a}^{-1}$ ), with an orthophosphate share of only 25%. Highly resolved measurements of exports during heavy rainfall events revealed significantly higher losses of orthophosphate P up to  $0.2 \text{ mg m}^{-2}$  and total P up to  $1.6 \text{ mg m}^{-2}$  per rainfall event. The results indicate that a single storm event could account for up to 20% of the total annual orthophosphate P load (40% for total P; Julich, pers. comm.). Therefore, a clear underestimation of P exports occurs when event-based losses are not taken into account.

In summary, it is evident that further studies are required to estimate the magnitude and drivers of the P export fluxes and to identify how they are linked to the site-specific availability of mineral P forms and different nutrition strategies of ecosystems.

#### 4 Stream water P and its influence on the stream biocenosis

The dominant factors controlling P concentrations in headwater streams are the forms and content of P in their bed sediments (van der Perk et al., 2005) and additionally the inputs of colloidal P, especially from soils under agricultural land use (Withers et al., 2001). Both can lead to elevated levels of dissolved P with profound implications for water quality and stream food web structure (Smith, 2003). Transport and delivery of P from soils to headwater streams and headwater sediments in agricultural catchments are, in addition to the extent of erosion intensity, mainly controlled by the contents of P, Al, Fe, organic matter as well as the mineral composition of the soil types present in the catchment (Palmer-Felgate et al., 2009; Rawlins, 2011). However, studies on the relation between soil P status and P concentration of headwater streams in forested catchments with little anthropogenic influence and its consequences for the stream food web structure are scarce (Meyer and Likens, 1979).

It has been shown that P concentrations in streams of forested headwaters follow a pronounced annual cycle with a maximum in summer (Roberts et al., 2007; Bernal et al., 2015; Verheyen et al., 2015; Zelazny and Siwek, 2012). In contrast, no pronounced annual cycle of P concentrations has been observed in soil water and groundwater of such catchments. This implies there must be an additional P source in streams, *e.g.*, in-stream mineralization of organic matter (Verheyen et al., 2015) or a process reducing P concentrations in the stream water during winter and spring such as intensive growth of benthic algae (Hill et al., 2001; Winkelmann et al., 2014). The hyporheic zone and riparian groundwater as well as in-stream release contribute significantly to headwater P concentrations (Mulholland et al., 1997; Bernal et al., 2015), which is consistent with findings that P concentration in headwater streams increases with distance from the spring. How-

ever, it seems questionable whether biological activity alone can account for the increase of P concentrations (Bernal et al., 2015). While P concentrations in streams influenced by agriculture tend to peak during stormflow events, the opposite pattern seems to occur in forested headwaters (Verheyen et al., 2015).

First results from a study of four temperate forest catchments, that represent a sequence of decreasing mineral-bound P contents in the mineral topsoil horizons, did surprisingly not show any correlation between soil P concentration and total P discharge into the surface waters as well as P concentration in headwater streams (Wilpert and Kirstens, pers. comm.). The results obtained between May and December 2014 pointed at significant lower mean phosphate concentrations in the headwater stream ( $8.0 \mu\text{g PO}_4\text{-P L}^{-1}$ ,  $n = 29$ ; Mewes, pers. comm.) in the Bavarian Forest region than in the other German forest experimental sites, i.e., Bad Brückenau, Vessertal, and Conventwald (ranging between 22.7, 12.9, and  $12.1 \mu\text{g PO}_4\text{-P L}^{-1}$ ;  $n = 28, 24, \text{ and } 7$ , respectively; Wilpert and Kirstens, pers. comm.), this despite the former had the second largest soil P stocks of all four sites.

The dominant substrate classes of the studied headwater streams at the sites Vessertal (Thuringian Forest), Mitterfels (Bavarian Forest), and Conventwald (Black Forest) were coarse materials, e.g., small to large gravel and boulders. Based on the findings of Lottig and Stanley (2007) it can be expected for these streams that stream water Soluble Reactive Phosphorus (SRP) is greatly influenced by biotic retention rather than abiotic sorption and that sediment buffer capacity is low. Because the sediment of these streams was composed of comparable size classes, the abiotic sorption capacities were assumed to be similar. Therefore, it was expected that changes in P availability primarily affect stream benthic biota. As aquatic primary producers (periphyton) are P-limited below  $15 \mu\text{g PO}_4\text{-P L}^{-1}$  (Bothwell, 1985; Winkelmann et al., 2014), even the observed small differences in the P availability in headwater streams can influence the stream food web structure (Biggs, 2000; Dodds, 2007). Increasing P availability in streams can increase periphyton biomass, benthic invertebrate species richness, and grazer biomass (Godwin et al., 2009). Consequently, transport and delivery of P from soils to the water and sediments of headwater streams can be expected to influence the structure of aquatic food webs. These changes in the structure of the aquatic food web on their part can influence P retention in streams. However, the first results of the study, comparing three temperate forest catchments with stream  $\text{PO}_4\text{-P}$  concentrations between  $8.0$  and  $12.9 \mu\text{g PO}_4\text{-P L}^{-1}$ , indicated no effect of P concentration on periphyton biomass or on the biomass of higher trophic levels (Mewes, pers. comm.). Thus, a larger biotic retention of stream P in terms of larger standing stocks of periphyton or benthic invertebrate biomass at sites with higher P availability were not found. These first results suggest that the effects of and the overall control on P status and concentrations in linked terrestrial and aquatic components of catchments are largely unresolved.

## 5 Magnitude and relevance of P fluxes

The data compilation on P fluxes in and from soils is primarily based on few case studies published between 1991 and 2003, supplemented with new, as yet preliminary and unpublished results from the contributing research groups within the German Priority Program SPP1685 (Table 1).

The explanation for our current limited knowledge on P fluxes is probably the focus of biogeochemical research on N rather than on P during the last decades because of N saturation due to high N deposition in various ecosystems (Aber et al., 1989) and the sensitive response of N cycling to climate change (Luo et al., 2004). Another explanation for the little research on P could be that mature natural boreal and temperate ecosystems are considered to be primarily limited by N but not by P (Vitousek and Howarth, 1991) since P is continuously released during weathering. Also, organic P might be more accessible for microorganisms than organic N since usually ester-bonded, while N is directly C-bonded and, hence, more difficult to mineralize. Another more practical reason for the poor knowledge on P fluxes is the low P concentration of precipitation and surface waters, which are mostly below the detection limits of conventional analytical techniques such as ICP-OES, ion chromatography (IC), and photometry. The low P concentrations of soil solutes require preparative and analytical efforts for accurate flux estimates. Nevertheless, the available flux data clearly indicate that P fluxes in soils are mostly by about one magnitude smaller than P inputs *via* litter fall, thereby indicating a generally effective recycling of P in temperate forest ecosystems with minimal P losses as compared to plant uptake (Cole and Rapp, 1981). Moreover, annual P leaching losses (usually  $< \approx 50 \text{ mg P m}^{-2} \text{ a}^{-1}$ ; Table 1) are also several magnitudes smaller than soil P stocks ( $> 50 \text{ g m}^{-2}$ ; Walther et al., 2004). This implies that P loss rates from soils will affect the P status of forest ecosystems only at centennial to millennial time scales. However, this timescale estimation may be considerably shortened considering the expected increase of rainstorm intensities and frequency in the future by climate change.

The scarcity of data on all types of P transport fluxes (Table 1) currently preclude any conclusive answers on the relationship between P fluxes, P cycling, and the nutrition status of forest ecosystem (i.e., acquiring *versus* recycling; see Lang et al., 2016). Moreover, the distinct lack of P flux data also hinders any quantitative assessment of the extent of anthropogenic and climate impacts (e.g., N deposition, warming) on temperate forest P fluxes and cycles. Table 1 suggests that from a perspective of temperate forest P flux data, the previous 20 years can be considered to have mostly been “lost years” in this research area.

Phosphorus leaching rates in subsoil are higher in weakly developed forest soils (Table 1; Kaiser et al., 2000, 2003) than in more developed soils (Qualls et al., 2000). This might reflect a stronger phosphate and colloidal or truly dissolved organic P retention in weathered subsoils with reactive mineral surfaces (Kaiser et al., 2001). Also, the published data on P fluxes do not show any consistent difference between P inputs *via* precipitation and P losses *via* leaching and stream water,

which prevents any inference on net P accumulation in temperate ecosystem. Earlier studies at the catchment and basin scale, however, revealed a tight balance between P inputs from precipitation, P released by weathering, and the export as dissolved and particulate P (Bear Brook: Meyer and Likens, 1979; Brazil: Gardner, 1990). The importance of the tree scavenging effect on P deposition (Meyer and Likens, 1979), which may lead to higher P deposition rate, has also not been verified for temperate forests.

High P loads in stream water (Table 1), particularly at high flow (Meyer and Likens, 1979), suggest that rapid flow processes, either in the soil by macropore flow or during flood events in streams and rivers, may lead to significant P losses. In the long run, these event-based losses may reduce ecosystem P stocks and limit the ability of forest ecosystems to recycle P. However, so far, there are too few studies encompassing all components of the P cycle to establish a quantitative link of P fluxes with the overall P cycle in forest ecosystems. Nevertheless, P transport or export might serve as sensitive indicators for the P status of forests.

## 6 Conclusions

The literature review shows a surprisingly limited quantitative understanding of P fluxes in temperate forests. Overall, actual P flux measurements seem to have been more or less neglected in the last decades. The scarcity of data on P fluxes in forest ecosystems certainly limits all considerations on aspects of forest P nutrition. Certainly, we need to obtain more transport flux-focused P studies for various forest ecosystems. These studies need to provide data on: (1) inorganic P, DOP, and colloidal P forms and their susceptibility to leaching, (2) P losses at hillslope and catchment scale in forest ecosystems, (3) the share of potentially recyclable P that is exported, and finally, to complete this picture, data on: (4) rates of P release by weathering, (5) atmospheric P inputs into temperate forest systems, (6) spatial heterogeneity of P soil fluxes, as well as (7) the dynamic interactions between plant uptake, mineralization, and leaching. Most of the work presented here refers to acidic forest ecosystems; yet, large forest areas also occur on calcareous soils which are studied to a much lesser extent. Within the whole context, we also need to further improve the sensitivity and selectivity of our analytical methods, because they remain one major obstacle to quantifying the low dissolved (organic) as well as the poorly constrained colloidal P losses. Also, a more complete knowledge and quantification of P fluxes is a key requirement for improving the prediction of future changes in forest ecosystems, and for transferring lessons learned from natural ecosystems to anthropogenic plant-based production systems.

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