

Retention of Phosphorus in Peatland Buffer Zones at Six Forested Catchments in Southern Finland

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Our current knowledge of the P retention efficiency of peatland buffer zone areas used to reduce sediment and nutrient leaching from forestry areas is insufficient. Especially the role of P sorption by soil in buffer zones needs closer examination as there is considerable variation in the efficiency of P retention. Six sites in southern Finland were chosen for the study. The buffer zone areas varied between 0.1–4.9% of the catchment area. A total of 10 kg of solute PO₄-P was added to the inflow of the buffer zone areas and the concentrations of PO₄-P in inflow and outflow were measured for 2–4 years. P retention characteristics of the surface peat were determined with sorption-desorption isotherms before and after PO₄-P addition and the effective buffer zone area over which the added P was spread was determined from soil water samples. P retention in the two largest buffer zone areas was complete (100% retention), and the third largest buffer retained 94%. Retention in the three smallest buffer zones was 24%, 95% and 95% of the added P. As a result of P addition reduction in peat P retention capacity was detected in three out of four cases. The effective buffer zone area varied from 67% to 100% of the total buffer zone area. Factors contributing to efficient P retention were large buffer size and low hydrological load whereas high hydrological load combined with the formation of preferential flow paths, especially during early spring or late autumn was disadvantageous. High P retention capacity in peat contributed to the sustainability of P retention. The study showed that even relatively small buffer zone areas are able to efficiently reduce P load.

Keywords buffer zone area, peatland, phosphorus, retention

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1 Introduction

In most boreal lakes phosphorus (P) along with nitrogen is the growth-limiting nutrient (Pietiläinen and Räike 1999 and the references within). Hydrological losses of P from forested catchments are generally low (Saukkonen and Kortelainen 1998, Mattsson et al. 2003), but can increase especially in peatland-dominated catchments when forests are harvested (e.g. Lundin 1998, Ahtiainen and Huttunen 1999, Cummins and Farrell 2003, Nieminen 2003), drained (Maninen 1998, Åström et al. 2005) or fertilized (Kenttämies 1981, Ahti 1983, Nieminen and Ahti 1993). To prevent this increased P to reach the recipient watercourse, it is recommended to direct the outflow over a buffer zone area (Metsätalouden ympäristöopas 2004), where particulate and soluble P can be reduced.

A primary condition in removal of particulate P and suspended solids is that the transport capacity of the water flow is reduced by the buffer zone. This reduction is achieved by creating sheet flow or subsurface flow instead of channel flow. This sets requirements on the flatness and size of the area. The processes for removing soluble P and other soluble compounds from the inflow are more complex. If the soluble nutrients are to be removed through uptake by vegetation, the biota should be in an active phase during the period of the nutrient transport. Similarly, removal of soluble P by chemical sorption in soil presumes that the soil has capacity to retain P and that the water flows through the soil matrix.

Typically buffer zones used to purify outflow water from forestry or peat mining areas are formed or modified on peatlands (e.g. Ihme 1994, Heikkinen et al. 1995, Kubin et al. 2000, Nieminen et al. 2005a, b). The efficiency of these peatland buffer zones in reducing P load seems to vary considerably from complete 100% retention (Kubin et al. 2000) through partial P removal (Ihme 1994, Sallantausta et al. 1998, Nieminen et al. 2005b, Silvan et al. 2005) to even increased leaching of phosphate (Liljaniemi et al. 2003, Vasander et al. 2003). The varying achievements in reducing P load of these previously studied buffer zone areas raises the question whether the buffer zones recommended in good forestry

practise are functional at all. With the current level of understanding definite conclusions of their efficiency cannot be drawn and therefore, the possibilities of peatland buffer zone areas in retaining P still need further evaluation. The varying conditions of the buffer zone areas studied so far, such as size, vegetation composition, soil type, management history, life and construction method, environmental conditions during the study period, and the length of the study complicates the detection of the common nominators for their P retention performance. This indicates that our current knowledge on the factors effecting on P retention are inadequate to design efficient buffer zone areas.

In most studies the P retention efficiency of the buffer zone area has been evaluated from the differences in P concentration between inflow and outflow water (e.g. Sallantausta et al. 1998, Liljaniemi et al. 2003, Nieminen et al. 2005b) or differences in stream water concentrations between areas with and without a buffer zone (Ahtiainen and Huttunen 1999). However, these studies provide little information on the actual processes controlling P retention or release. The connection between P reduction by buffer zones and P assimilation by biota in boreal conditions has been evaluated recently (Huttunen et al. 1996, Silvan et al. 2003, Silvan et al. 2004) but the corresponding connection between P sorption properties of peat soil in buffer zone areas and total P retention still needs clarification. Chemical P sorption in soil can form a more sustainable sink for P than assimilation in biota because a large part of the assimilated P is released along with mineralization of the vegetation biomass (Richardson and Marshall 1986) and the long-term effect of biological P retention can therefore be low (Huttunen et al. 1996). The sustainability of the retention capacity of the buffer zones is of great importance because the increased P load from managed areas continues for several years after the operation (Ahtiainen and Huttunen 1999), and in fertilized areas, even over a decade (Joensuu et al. 2001). However, the P retention capacity of peat soil is limited (e.g. Kaila 1959, Cuttle 1983, Heikkinen et al. 1995, Nieminen and Jarva 1996), and its possibilities in maintaining P retention capacity under continuing load needs further examination.

Table 1. Background information of the buffer zones.

	Location	Area, ha	Area, % of watershed area	Site description	Site type ¹	Stand volume, m ³ ha ⁻¹
INTENSIVE STUDY AREAS						
Asusuo	60°26'N 23°37'E	0.20	0.23	Pristine mire forest	Tall-sedge spruce swamp	80
Murtsuo	61°01'N 28°19'E	0.16	0.16	Drained peatland	MT	80
Kirvessuo	61°14'N 25°16'E	0.12	0.09	Drained peatland forest	Herb-rich type	100
Kallioneva	62°16'N 23°48'E	1.03	4.9	Pristine mire	Tall-sedge fen	0
EXTENSIVE STUDY AREAS						
Hirsikankaansuo	64°04'N 26°40'E	1.01	1.1	Pristine mire	Low-sedge bog	0
Vannesorvenoja	61°51'N 23°42'E	1.00	2.5	Drained peatland forest	MT, VT and herb-rich type	0

¹ Site types according to Heikurainen and Pakarinen (1982) and Cajander (1926)

The aim of this study was to evaluate the long-term efficiency of peatland buffer zone areas with differing size, site type and vegetation composition, and peat properties in retaining soluble P. P retention capacity of peat soil was determined in order to evaluate the importance of soil P sorption capacity on P retention efficiency and sustainability of a buffer zone area. Based on the results, the characteristics of the buffer zones and the environmental factors that have the strongest effect on P retention efficiency are summarized.

2 Material and Methods

2.1 Site Description

The study was carried out at six watershed areas in south-central Finland. In each watershed there was an old peatland drainage area and outflow water from the watershed was directed over a buffer zone area. The watershed boundaries, peatland drainage areas and the location of the buffer zone areas are presented in detail in Nieminen et al. (2005a, b) and Sallantausta et al. (1998). The buffer zones were constructed by either restoring and rewetting a section of the drainage area or by conducting the outflow water from the drainage area to an undrained peatland area downstream.

A detailed description of the construction of the Vannesorvenoja buffer zone area is given in Sallantausta et al. (1998) and the construction of the other buffers is presented by Nieminen et al. (2005a, b). Ditching operations were performed in drainage areas of the catchments at Murtsuo (in 1996), Asusuo (in 1997), Kallioneva (in 1998), Kirvessuo (in 1999) and Hirsikankaansuo (in 1999) and the retention of suspended solids by the buffer zone areas was studied by Nieminen et al. (2005a).

According to a careful levelling of the buffer zones and the watershed areas upstream, the sizes of the buffer zones varied from 0.12 to 1.03 hectares, accounting for 0.1%–4.9% of the area of the watershed (Table 1).

The most common plant species in the field and bottom layer of the buffer zone areas are presented in Table 2. The Kallioneva and Hirsikankaansuo buffer zones were pristine, treeless mires. Except for the areas next to the in-filled ditch, the Asusuo buffer zone was also classified as an undrained, pristine mire according to the site type classification of peat soils used in Finland (Heikurainen and Pakarinen 1982). It was covered with a dense <10-m-tall birch stand (*Betula pubescens* Ehrh.). Due to drainage the ground vegetation at the Kirvessuo and Murtsuo buffer zones had transformed from the pristine state and they were classified as *Vaccinium myr-*

Table 2. The most common plant species in the field and bottom layer of the buffer zone areas are expressed as the percentage of average coverage. At Vannesorvenoja, vegetation was inventoried before rewetting and restoration and three years after and the changes in vegetation cover are presented in the text.

	Asusuo	Kirvessuo	Average coverage, %		
			Murtsuo	Kallioneva	Hirsikankaansuo
FIELD LAYER					
<i>Andromeda polifolia</i>					2.1
<i>Calamagrostis canescens</i>		13.8			
<i>Calamagrostis purpurea</i>	3.5	8.3	1.0		
<i>Carex globularis</i>		9.2			
<i>C. lasiocarpa</i>				2.7	
<i>C. magellanica</i>				2.3	
<i>C. pauciflora</i>					3.6
<i>C. rostrata</i>	8.6			19.2	2.8
<i>Dryopteris carthusiana</i>		4.7	0.7		
<i>Epilobium angustifolium</i>			0.2		
<i>Equisetum sylvaticum</i>	1.1				
<i>Menyanthes trifoliata</i>					1.4
<i>Potentilla palustris</i>	1.4			1.0	
<i>Trientalis europaea</i>	0.7				
<i>Vaccinium myrtillus</i>		6.7			
<i>V. oxycoccus</i>				3.7	1.5
<i>V. vitis-idaea</i>			1.4		
<i>Viola palustris</i>			0.2		
BOTTOM LAYER					
<i>Brachythecium</i> sp.		3.9	1.6		
<i>Plagiothecium</i> sp.			0.1		
<i>Pleurozium schreberi</i>	0.7	5.4	0.1		
<i>Polytrichum commune</i>	18.3	1.1	1.0	7.6	
<i>Sanionia uncinata</i>			0.1		
<i>Sphagnum angustifolium</i>	28.3			17.4	
<i>S. girgensohnii</i>	0.6	10.4			
<i>S. papillosum</i>					29.4
<i>S. russowii</i>		2.8			
<i>S. fallax</i>				49.9	9.5
<i>S. majus</i>					3.4
<i>S. pulchrum</i>				5.3	
<i>S. riparium</i>	21.4			9.6	
<i>Straminergon stramineum</i>					0.3

tillus type and Herb-rich type drained peatland forests, respectively (Heikurainen and Pakarinen 1982). Kirvessuo buffer was characterized by a mixed spruce (*Picea abies* Karst.), pine (*Pinus sylvestris* L.) and birch (*B. pubescens*) stand and a relatively open area in the middle. The Murtsuo buffer zone was dominated by a dense birch (*B. pubescens*) stand.

The Vannesorvenoja buffer zone was a drained peatland forest that had been restored by harvesting the *Picea abies* tree stand in 1996 and rewetting the site in 1997. Before restoration,

Vaccinium vitis-idaea type, *Vaccinium myrtillus* type and herb-rich type drained peatland forests were dominant. Three years after restoration, the increase in light, nutrient availability and moisture had resulted in a drastic change in the composition of the vegetation. *Carex globularis*, which dominated the field layer before restoration declined in coverage from 44 to 25% while there was an increase in *Calamagrostis purpurea* (from 40 to 60%), *Eriophorum vaginatum* (from 3 to 28%) and *Betula pubescens* (from 1 to 15%). In the bottom layer, the overall coverage

Table 3. Soil properties of the Asusuo, Kirvessuo, Murtsuo, Kallioneva and Hirsikankaansuo buffer zone areas.

	BD ^a g dm ⁻³	Al _{ox} ^b g kg ⁻¹	Fe _{ox} ^b g kg ⁻¹	CEC ^c mmol kg ⁻¹	Carbon ^d %	Nitrogen ^d %	pH ^e
INTENSIVE STUDY AREAS							
Asusuo peat	161 ± 118	3.21 ± 0.56	3.49 ± 1.55	155 ± 52	20 ± 7	0.9 ± 0.3	4.1 ± 0.1
Asusuo mineral soil	1047 ± 198	1.62 ± 0.17	0.90 ± 0.24	27 ± 12	2 ± 1	0.1 ± 0.0	4.3 ± 0.1
Kirvessuo	141 ± 30	1.27 ± 0.24	8.73 ± 0.57	422 ± 46	48 ± 2	1.8 ± 0.0	4.0 ± 0.1
Murtsuo	188 ± 64	3.97 ± 0.69	3.24 ± 0.49	390 ± 69	34 ± 9	1.7 ± 0.4	4.3 ± 0.2
Kallioneva	49 ± 24	2.64 ± 0.34	4.27 ± 1.05	247 ± 68	36 ± 10	1.1 ± 0.2	4.0 ± 0.2
EXTENSIVE STUDY AREAS							
Hirsikankaansuo	75 ± 21	2.20 ± 0.15	7.54 ± 1.39	202 ± 23	40 ± 7	1.7 ± 0.6	4.0 ± 0.1

^a Bulk density is expressed as oven-dried (105 °C 24 h) mass per volume.

^b Oxalate extractable iron and aluminium were extracted with acid ammonium oxalate (0.2 M, 1:50 w/v) (Wang, 1981); elements measured with inductively coupled plasma mass spectrometer (ICP-MS ELAN 6000).

^c Cation exchange capacity was measured with KCl extraction (1 M, 1:50 w/v for peat and 1:10 w/v for mineral soil); elements measured with inductively coupled plasma mass spectrometer (ICP-MS ELAN 6000).

^d Carbon and nitrogen was measured with the combustion method (Leco CNS 1000).

^e Measurement was done from an aliquot of KCl extraction.

of bryophyta had increased. After the restoration the most common species were *Polytrichum commune*, *Sphagnum angustifolium*, *S. russowii* and *Pleurozium schreberi*.

Most of the water flow at all six buffer zones occurred as overland flow across the relatively flat buffer area. At the Asusuo, Murtsuo and Kirvessuo buffer zones the channel flow was considerable, but while almost no channel flow occurred at the largest, the Kallioneva, buffer zone.

Before the beginning of the present study, i.e. 1995–2001 at Asusuo and Murtsuo, 1996–2001 at Kirvessuo and 1998–2001 at Kallioneva and Hirsikankaansuo, water samples were collected from the catchment areas. The results of the water analyses of these five buffer zone areas indicate that they were typical peatland dominated catchments where the average total P in water flow was 0.014–0.031 mg l⁻¹, total Al 0.1–0.7 mg l⁻¹ and total Fe 0.5–1.9 mg l⁻¹, respectively (Nieminen et al. 2005a, b). The inflow and outflow from the Vanneskorvenoja buffer was sampled before restoration in 1993 and after that in 1997–1999. PO₄-P outflow increased significantly and was high (0.050–0.300 mg l⁻¹) for about 3 months after restoration (Vasander et al. 2003).

At all buffer zones, the average depth of the peat layer was over 1 meter. In the Asusuo buffer, the peat profile also contained mineral soil layers of varying thickness. The probable source of these mineral soil layers was that they were formed of the soil material that was eroded from the ditches

of the peatlands upstream during and after their initial drainage in 1967. Bulk density and basic chemical characteristics of the peat deposits of the buffer zone areas and of the mineral soil layers in Asusuo are presented in Table 3.

2.2 Field Experiment and Sampling

2.2.1 Intensive Study Areas: Asusuo, Murtsuo, Kirvessuo and Kallioneva

Four of the areas, i.e. Asusuo, Murtsuo, Kirvessuo and Kallioneva were selected for an intensive study. During five consecutive days in summer 2003 phosphate phosphorus was added to the water flowing to these buffer zones (for the location of PO₄-P input, see Figs. 1–4). The experiment was conducted at Asusuo in May, at Murtsuo in June and at Kirvessuo and Kallioneva buffer zone areas in July. Each day, two kilograms of PO₄-P (KH₂PO₄) was dissolved in local runoff water in a 200 l PVC tank; the solution was then allowed to trickle into the runoff water at a constant rate for 24 h. During the five-day addition period each buffer zone received a total of 10 kg of PO₄-P. Addition of phosphate in kg P per hectare of buffer area was 50, 63, 80 and 10 kg ha⁻¹ for the Asusuo, Murtsuo, Kirvessuo and Kallioneva buffer zone areas, respectively.

At each buffer zone, sampling of the outflow waters started on the same day with the PO₄-P

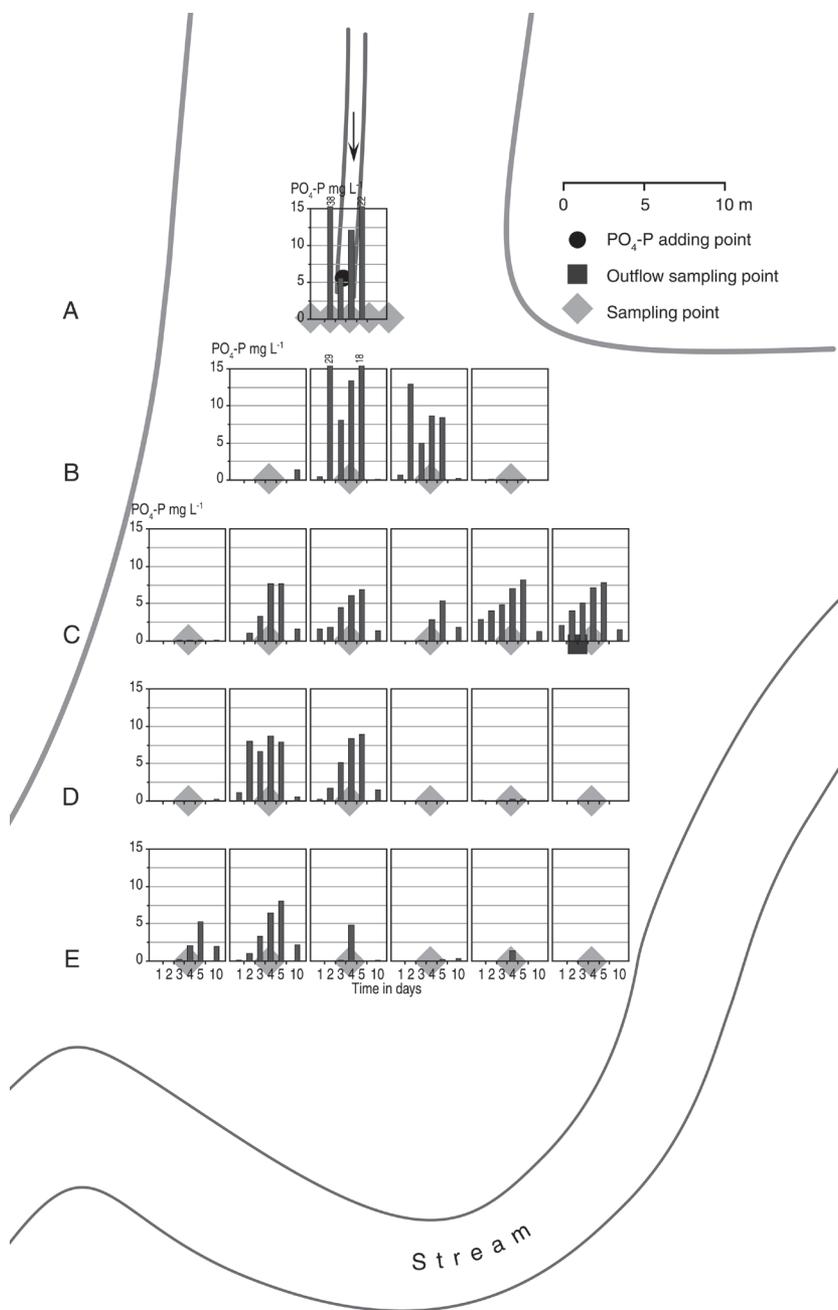


Fig. 1. Asusuo buffer zone area (0.20 ha) receives its inflow water from a 87 ha catchment area. The buffer was constructed by filling in the main outlet ditch from the drainage area upstream as shown in Nieminen et al. (2005a,b). Sampling lines A–E with sampling points for the collection of soil and surface water samples. Concentration of $PO_4\text{-P}$ in soil water at days 1–5 and 10 after the start of the P addition are shown as bar charts.

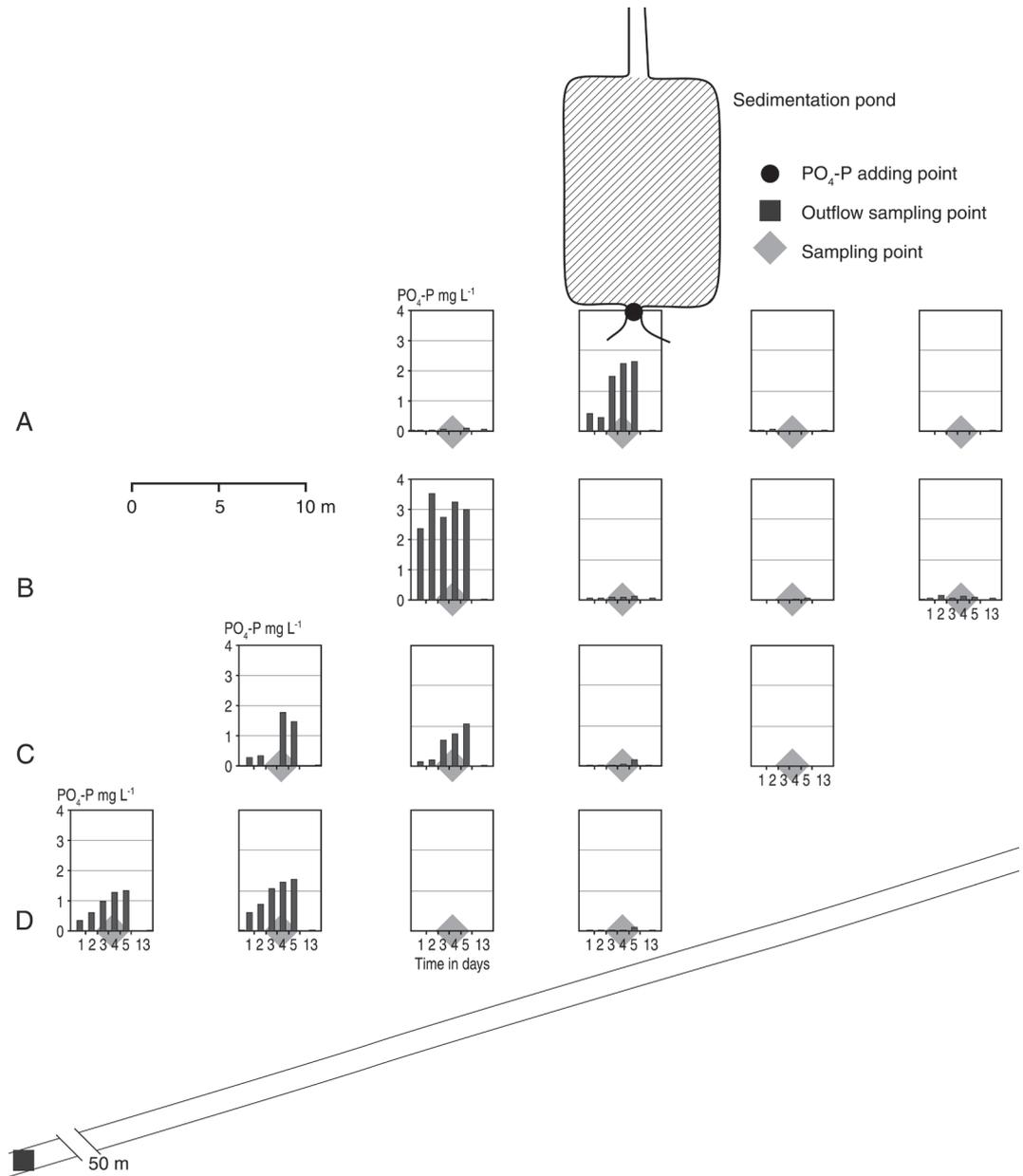


Fig. 2. Kirvessuo buffer zone area (0.12 ha) receives its inflow water from a 133 ha catchment area. First, the inflow waters discharge to a sedimentation pond before spreading over the buffer zone area. The buffer was constructed by filling in the main outlet ditch from the drainage area upstream as shown in Nieminen et al. (2005a,b). Sampling lines A–D with sampling points for the collection of soil and surface water samples. Concentrations of PO₄-P in soil water at days 1–5 and 13 after the start of the P addition are shown as bar charts.

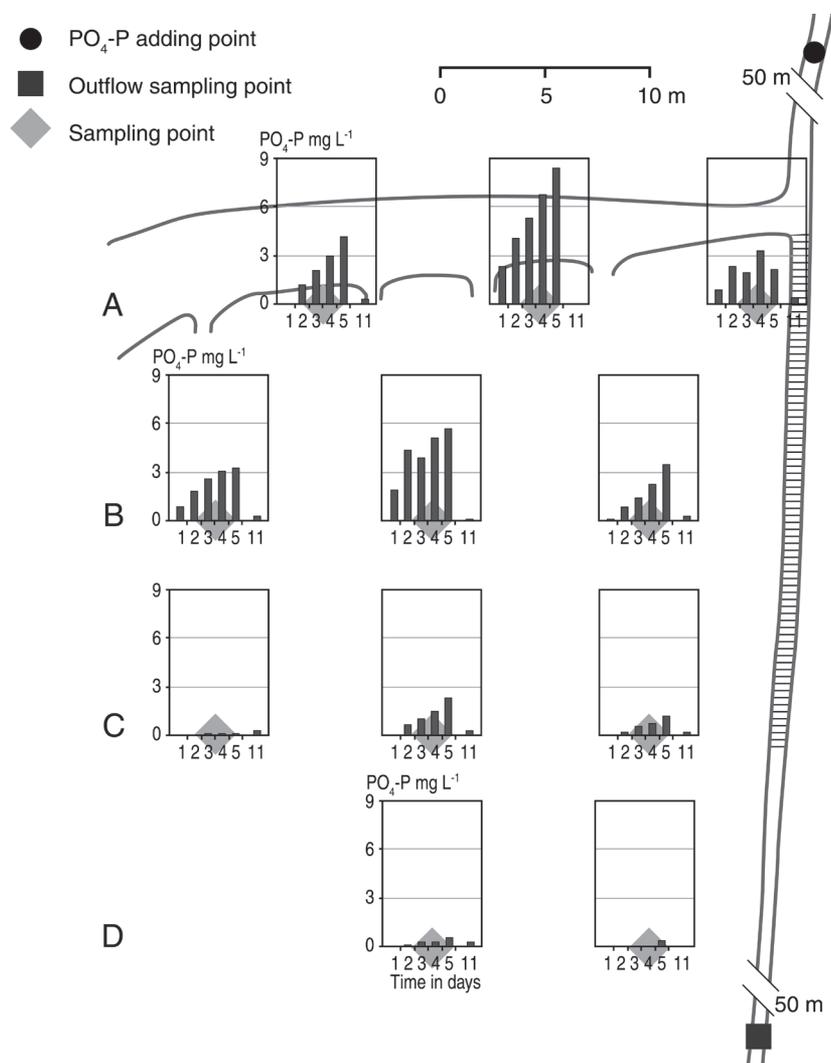
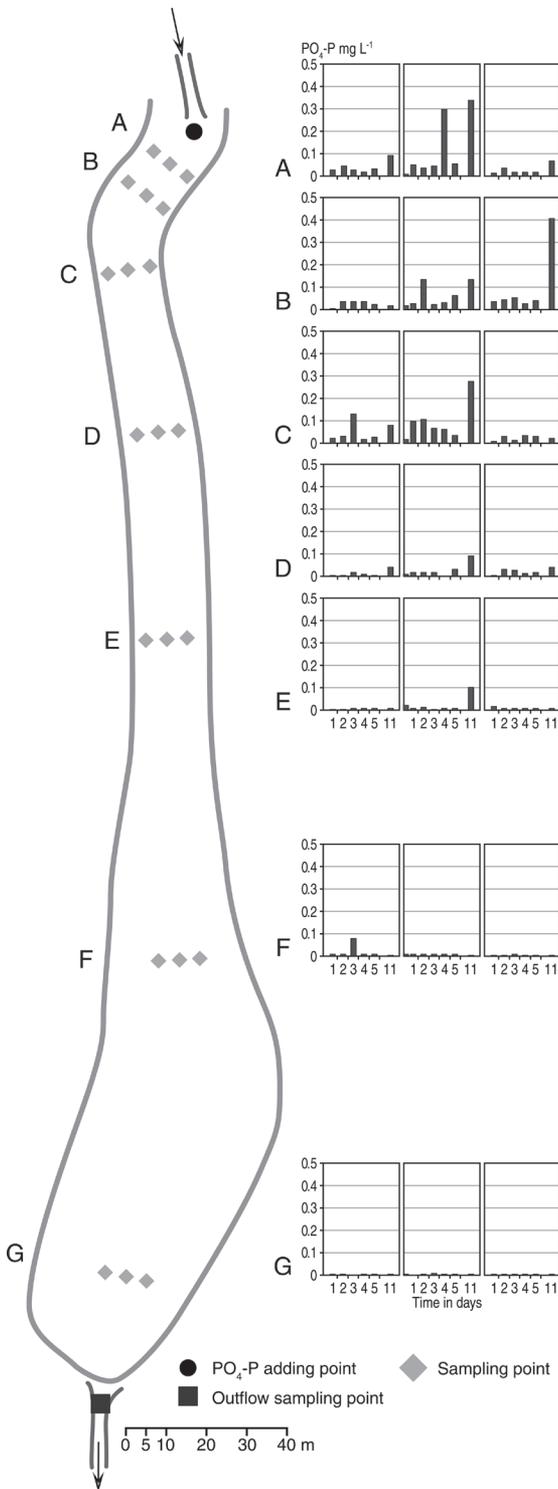


Fig. 3. Murtsuo buffer zone area (0.16 ha) receives its inflow water from a 107-ha catchment area. The main outlet ditch from the catchment area upstream was blocked and a new ditch was excavated through which the waters are spread over the buffer zone area (see also Nieminen et al. 2005a,b). Sampling lines A–D with sampling points for the collection of soil and surface water samples. Concentrations of $\text{PO}_4\text{-P}$ in soil water at days 1–5 and 11 after the start of the P addition are shown as bar charts.

addition. Samples were collected daily throughout the adding period in 2003; after that 6–10 samples were taken until the freezing of the waters in late autumn. In the following year 2004, samples were collected 5–9 times; in 2005 4–6 times and in 2006 2–6 times during the snow-free period. The outflow samples were taken from a natural flow channel (Figs. 1–4). The runoff was measured from Asusuo, Murtsuo and Kirvessuo at a V-notch

weir by measuring the height of the water level from the bottom of the notch. The runoff from Kallioneva was estimated by applying daily runoff data collected at two nearby catchments (Finnish Environment Institute, unpublished data).

For the sampling of soil and surface water, a series of sampling lines were laid out over the buffer zone areas in a perpendicular position to the main direction of water flow (Figs. 1–4).



The sampling lines were located at 10 m intervals at Asusuo, Murtsuo and Kirvessuo. At the Kallioneva buffer zone, which is over 300 m long, the interval between the sampling lines varied from 10 m to 80 m (Fig. 4). Sampling points were located at 5 m intervals along the sampling lines in Asusuo and Kallioneva and at 10 m intervals in Kirvessuo and Murtsuo. Surface water samples were taken by pressing a plastic sieve against the soil surface and collecting the emerging water with a 100-ml syringe. With this method, surface water samples were collected seven times. The first samples, representing the background levels for PO₄-P, were taken just before starting the five-day PO₄-P addition period and five samples were taken daily during the adding period. The last samples were taken 5 (Asusuo), 8 (Kirvessuo) and 6 days (Murtsuo and Kallioneva) after the daily addition period had ended.

During summer 2001, i.e. two years before the P addition experiment, soil samples were taken from the top 15 cm soil layer from the sampling points using a rectangular (6.3*4.0 cm) core sampler. At Asusuo, Kirvessuo and Murtsuo, the samples from each sampling point were combined by lines, and at Kallioneva four composite samples were formed by combining the samples from lines A+B, C, D+E and F+G (Fig. 4). At Asusuo the mineral soil layers and the peat layers of the soil samples were analyzed separately. During the year of P addition in 2003, the soil sampling routines were repeated as above and collected simultaneously with the last soil water samples.

Fig. 4. Kallioneva buffer zone area (1.03 ha) receives its inflow water from a 21 ha catchment area. No active construction operations were needed since Kallioneva is an undrained, pristine mire through which the waters from the upstream catchment area have flown long before the start of the present experiment (see also Nieminen et al. 2005a,b). Sampling lines A–G with sampling points for the collection of soil and surface water samples. Concentrations of PO₄-P in soil water at days 1–5 and 11 after the start of the P addition are shown as bar charts.

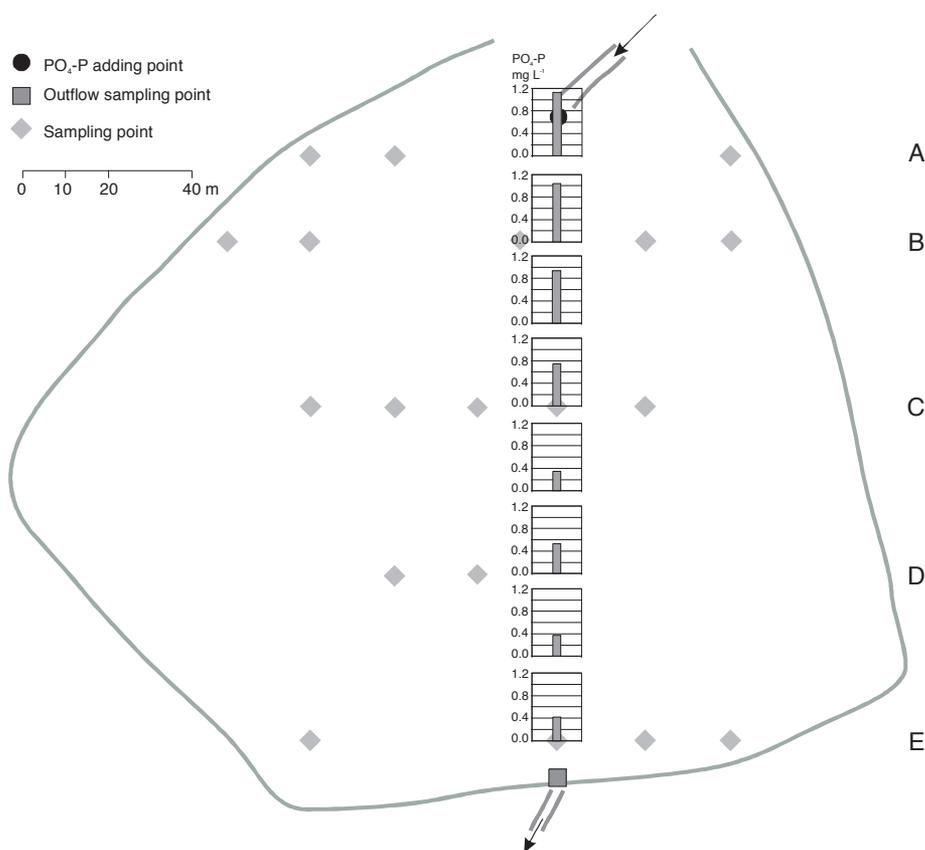


Fig. 5. Hirsikankaansuo buffer zone area (1.01 ha) receives its inflow water from a 90-ha catchment area. The main outlet ditch from the catchment upstream was blocked and a new ditch was excavated through which the waters are spread over an undrained, pristine mire area (see also Nieminen et al. 2005a, b). Sampling lines A–E for the collection of soil water samples. Concentrations of $\text{PO}_4\text{-P}$ in soil water for the last day of the second $\text{PO}_4\text{-P}$ adding period along a transect are shown as bar charts.

2.2.2 Extensive Study Areas: Hirsikankaansuo and Vanneskorvenoja

The buffer zone areas at Hirsikankaansuo and Vanneskorvenoja received the 10-kg $\text{PO}_4\text{-P}$ addition in two four-day periods (for the location of $\text{PO}_4\text{-P}$ input see Figs. 5 and 6). The Hirsikankaansuo buffer received 3 kg P in June 2004 and the remaining 7 kg in September 2005. The corresponding $\text{PO}_4\text{-P}$ additions at the Vanneskorvenoja buffer were 3 kg P in June 2005 and 7 kg in June 2006. The total addition per hectare of buffer area was 10 kg ha^{-1} for both Hirsikankaansuo and Vanneskorvenoja. During the adding periods sampling of inflow and out-

flow water was started simultaneously with the $\text{PO}_4\text{-P}$ addition and continued daily throughout the adding period. After the first adding period at the Hirsikankaansuo buffer, 18 samples from the inflow and outflow waters were taken until the end of 2004 and four samples were collected before and nine after the second adding period in 2005. At the Vanneskorvenoja buffer, 18 samples were taken after the end of the adding period in 2005, and 10 after the end of the adding period in 2006. During the day when the last P dose was added at the Hirsikankaansuo buffer in 2005, a 80-m-long transect was laid across the buffer zone and the progress of the added P was studied by sampling the surface water from 8 sampling points at 10 m

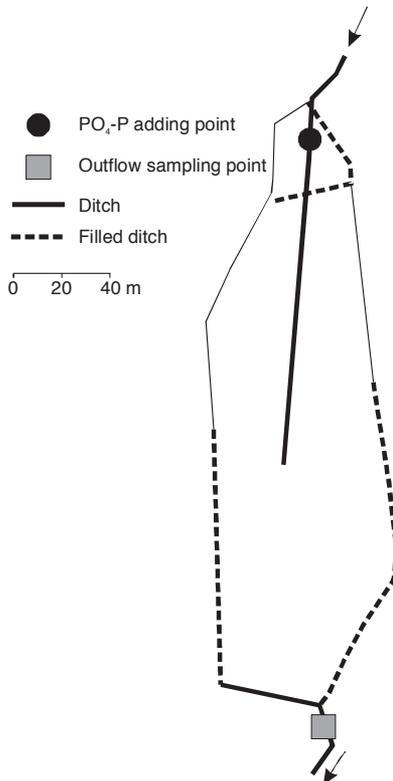


Fig. 6. Vanneskorvenoja buffer zone area (1.0 ha) receives its inflow from a 40 ha catchment area. The buffer was constructed by filling in some of the ditches and by excavating a new ditch through which the waters are directed to the highest elevation of the buffer area (see also Sallantausta et al. 1998).

intervals. The runoff was measured at a V-notch weir at Vanneskorvenoja buffer. The runoff from the Hirsikankaansuo buffer was also measured at a weir in 2004, but in 2005, the runoff was estimated using the daily runoff data collected at two nearby catchments by the Finnish Environment Institute (unpublished data).

Soil samples were taken from the Hirsikankaansuo buffer in 2001 with the same method as described above for the intensive study areas. Five sampling lines (A–E) were laid out along the buffer zone, where the distance between lines A and B was 20 m and between lines B, C, D and E 40 m, respectively (Fig. 5). Along the sampling lines, the distance between the sampling points

varied from 20 to 80 m. The soil samples from each line were pooled to a composite sample, except for the samples from the lines D and E, which were combined. No soil samples were collected from Vanneskorvenoja.

2.3 Laboratory Analyses

The water samples were filtered through 0.46 μm membrane filters. The filtrates of the inflow, outflow and surface water samples were analysed for $\text{PO}_4\text{-P}$ with the molybdenum blue method and for total dissolved P with plasma emission spectrophotometry (ICP-AES).

To illustrate the P sorption properties of the buffer zone soils, desorption-sorption isotherms were determined for the soil samples collected before P addition in 2001 and after it in 2003. Samples of moist soil (equivalent to 1 g dry weight) were added to bottles containing solutions (40 ml) with 0.0, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 or 10 mg l^{-1} of P. The bottles were then shaken on a reciprocating shaker at 180 rpm for 1 hour and were left to equilibrate for 23 hours, after which the suspensions were shaken again for 5 min at 120 rpm. The suspensions were then filtered with glass fibre filters and a 0.2 μm membrane filter and the concentration of the $\text{PO}_4\text{-P}$ remaining in the filtrate was determined with the molybdenum blue method.

2.4 Calculations and Statistical Analyses

A paired value t-test was used to determine if there were statistical differences in $\text{PO}_4\text{-P}$ concentrations between the inflow and outflow water samples. Differences with p values less than 0.05 were considered significant. The outflow of the added P from buffer zones (P_{out} , kg) was calculated as:

$$P_{out} = \sum \frac{(OP_t - BP)}{10^6} \times q_t \quad (1)$$

OP_t is the measured concentration of $\text{PO}_4\text{-P}$ (mg l^{-1}) in outflow water at time t following P addition, BP is the pre-P-addition, background $\text{PO}_4\text{-P}$ concentration (about 0.01 mg l^{-1}) in outflow water and q_t is runoff (l) at time t . If the difference $OP_t - BP$ was negative, the outflow of

the added P was set as 0. The total retention of P by the buffer zones was then calculated as the difference between the added 10 kg of PO₄-P and the total P outflow (P_{out}).

Phosphorus desorption-sorption behaviour was illustrated with adsorption isotherms where the sorbed amount (mg g⁻¹) is plotted as a function of PO₄-P concentration in equilibrium solution (mg l⁻¹). The intersection point on the x-axis, the equilibrium phosphorus concentration (EPC₀) where no net desorption or sorption occurs, was determined graphically. To compare sorption behaviour, EPC₀ was used as a reference value along with two measurements: P₀ which is the desorbed amount of PO₄-P (mg g⁻¹) at the addition level 0 mg PO₄-P l⁻¹ describing instantly labile PO₄-P, and P₁₀ which is P sorbed (mg g⁻¹) at the addition level 10 mg P l⁻¹ and describes the maximum sorption. Variation in reference values between the buffers was tested with one-way ANOVA and Tukey's post-hoc test for pairwise comparisons. Changes in the PO₄-P retention properties before and after PO₄-P addition experiment were tested with Wilcoxon signed rank test. Differences were considered significant with *p* values less than 0.05.

3 Results

3.1 Runoff Load during the P Addition Experiment

During the P adding period the Asusuo buffer received the highest runoff load. In the beginning of the experiment the load was 152 mm d⁻¹, decreasing to 84 mm d⁻¹ by the end of the adding period. In Murtsuo the runoff load increased from 68 to 99 mm d⁻¹ and in Kirvessuo decreased from 81 to 58 mm d⁻¹. In Kallioneva the runoff load remained at 2 mm d⁻¹ throughout the adding period. During the first adding period the runoff load in Hirsikankaansuo was 4 mm d⁻¹, but increased from 60 to 96 mm d⁻¹ during the second adding period. The corresponding values for the first and second adding period at Vannesorvenoja were from 12 to 3 mm d⁻¹ and from 5 to 4 mm d⁻¹, respectively.

3.2 PO₄-P Concentrations in Inflow and Outflow

Before starting the P adding period the background PO₄-P and total P concentrations in the inflow and outflow water were approximately <0.010 mg l⁻¹ and <0.020 mg l⁻¹ at all the six buffer zone areas. During the adding period, the PO₄-P concentration in inflow water raised to very high levels and PO₄-P formed 93±8% of the total P. The outflow concentrations exceeded the background levels at the Asusuo, Kirvessuo, Murtsuo buffers and also at Hirsikankaansuo, but only during the second adding period. The proportion of PO₄-P of the total P in the outflow water was 96±9% during the addition period. The highest outflow concentrations during the adding period were measured from the Asusuo buffer (Fig. 7). At the Kallioneva and Vannesorvenoja buffers, and also at the Hirsikankaansuo buffer during the first adding period, the outflow PO₄-P concentrations remained at the background level throughout the adding period (Fig. 8).

After the adding had ended, PO₄-P in the inflow water generally returned to the background level within a few days and remained at that level until the end of the study (Figs. 7 and 8). However, at the Kallioneva buffer the PO₄-P in the inflow remained significantly higher than the background level after the adding had ended until October 2004, and at the Vannesorvenoja buffer for about one month after the first adding period and five months after the second adding period (Figs. 7 and 8). The outflow concentrations of PO₄-P exceeded the inflow concentrations until the autumn of 2004 at the Asusuo buffer, and until the autumn of 2003 at the Kirvessuo and Murtsuo buffers. At the Kallioneva and Vannesorvenoja buffers the outflow concentrations of PO₄-P remained at background levels throughout the study period.

3.3 Total PO₄-P Retention

At the Asusuo buffer zone, PO₄-P discharge was 4.4 kg of the added 10 kilograms during the five-day adding period and later during 2003 an additional 3.1 kg. In 2004 the PO₄-P outflow was 0.1 kg in 2004; no outflow occurred in 2005 and

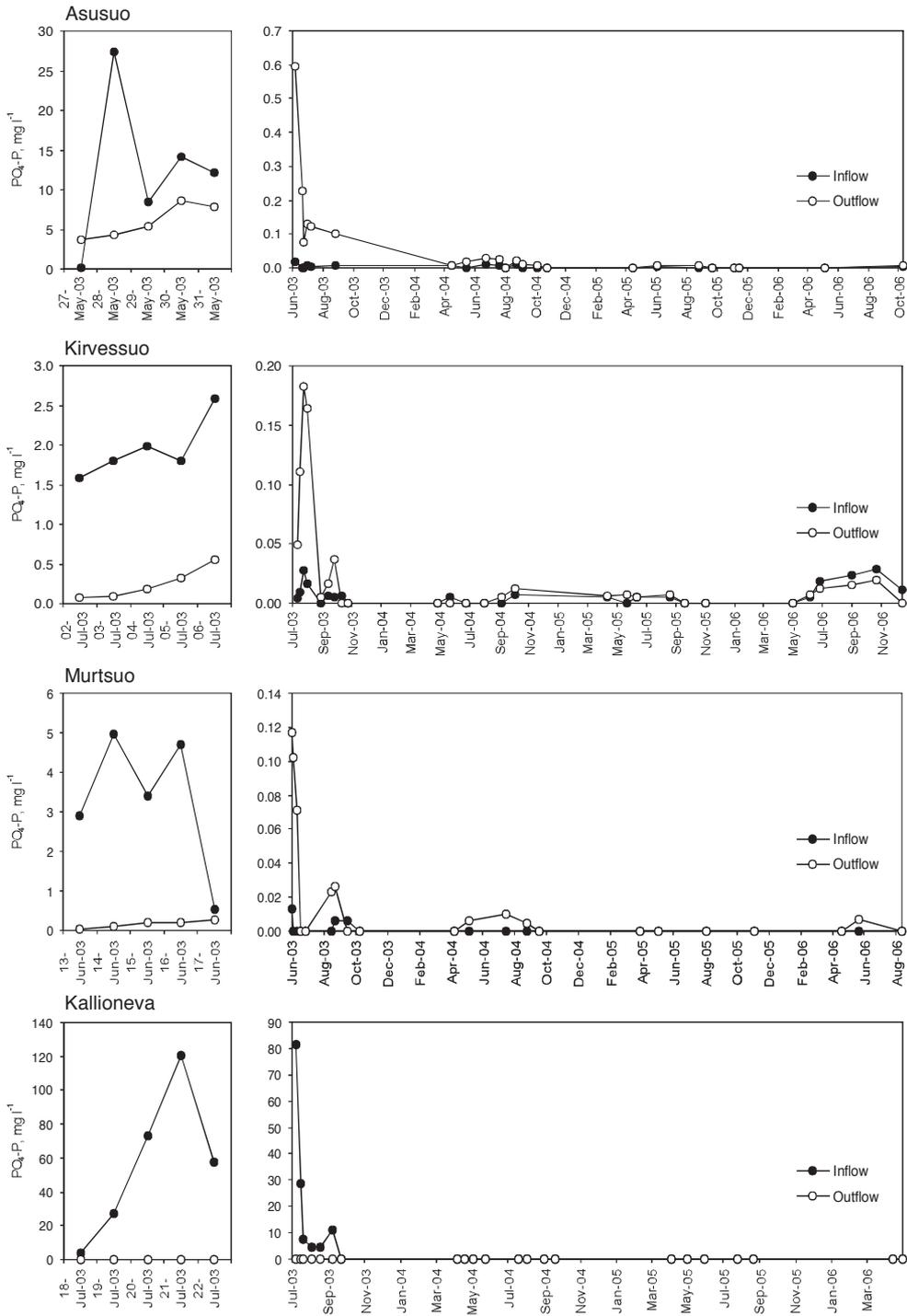


Fig. 7. $PO_4\text{-P}$ inflow and outflow during the adding period in 2003 (left) and after the adding period in 2003–2006 (right) at Asusuo, Kirvessuo, Murtsuo and Kallioneva buffer zone areas.

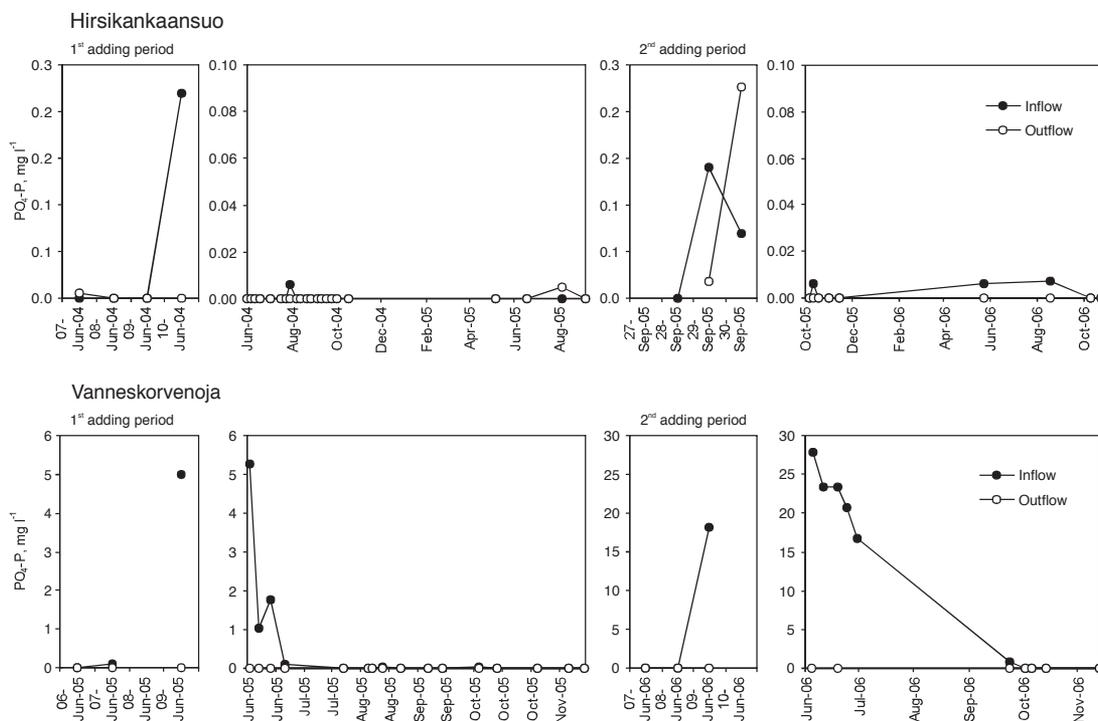


Fig. 8. $\text{PO}_4\text{-P}$ inflow and outflow during and after the first and second adding periods at Hirsikankaansuo and Vannesorvenoja buffer zone areas.

2006. Thus, total retention of the added $\text{PO}_4\text{-P}$ was 2.4 kg. At the Kirvessuo and Murtsuo buffers the outflow of the added $\text{PO}_4\text{-P}$ was 0.1 kg during the adding period and 0.4 kg later in 2003; no outflow occurred in 2004–2006. Thus, the total outflow was 0.5 kg from both areas and the total retention 9.5 kg, respectively. Throughout the study period the concentrations of $\text{PO}_4\text{-P}$ in the outflow water from the Kallioneva and Vannesorvenoja buffers remained at the background level, indicating a complete retention of the added 10 kg $\text{PO}_4\text{-P}$. Similarly, the outflow of $\text{PO}_4\text{-P}$ from the Hirsikankaansuo buffer remained at the background level during and after the first adding period but $\text{PO}_4\text{-P}$ discharge from the buffer zone area was approximately 0.6 kg of the added 7 kg during and after the second adding period.

3.4 $\text{PO}_4\text{-P}$ in Surface Soil Water

Before the P adding period, the average soil water $\text{PO}_4\text{-P}$ concentration at the Asusuo, Kirvessuo, Murtsuo and Kallioneva buffers was 0.04 mg l^{-1} , 0.01 mg l^{-1} , 0.002 mg l^{-1} and 0.01 mg l^{-1} , respectively. During the adding period at the Asusuo buffer, elevated $\text{PO}_4\text{-P}$ concentrations were determined from 82% of the soil water sampling points and from 81%, 100% and 67% of the sampling points in Kirvessuo, Murtsuo and Kallioneva, respectively (Figs. 1–4). At Asusuo, Murtsuo and Kirvessuo the concentrations generally increased towards the end of the adding period, whereas the variation was irregular at Kallioneva. When the last soil water samples were collected 5–8 days after the end of the adding period, elevated $\text{PO}_4\text{-P}$ concentrations in the soil water were still detected. At that event, $\text{PO}_4\text{-P}$ concentrations exceeding the background level were then determined from 56%–100% of the sampling points.

Table 4. Reference values of P_0 , P_{10} and EPC_0 in the soil of the buffer zone areas before (2001) and after (2003) PO_4 -P addition experiment. Values indicate the variation range and average value is given in parentheses.

Sampling year	P_0 $\mu\text{g g}^{-1}$ 2001	P_0 $\mu\text{g g}^{-1}$ 2003	P_{10} $\mu\text{g g}^{-1}$ 2001	P_{10} $\mu\text{g g}^{-1}$ 2003	EPC_0 $\mu\text{g l}^{-1}$ 2001	EPC_0 $\mu\text{g l}^{-1}$ 2003
INTENSIVE STUDY AREAS						
Asusuo	1.2–8.9 (5.3)	1.4–51.3 (18.9)	185–368 (296)	125–262 (186)	33–290 (158)	41–1892 (732)
Kirvessuo	4.8–19.2 (11.5)	3.8–10.4 (7.7)	166–323 (272)	205–234 (224)	161–672 (346)	105–409 (258)
Murtsuo	1.6–7.0 (3.9)	4.1–18.3 (9.9)	246–326 (292)	207–258 (238)	44–278 (140)	142–589 (318)
Kallioneva	0.9–4.0 (2.7)	0.8–1.8 (1.3)	323–397 (372)	340–379 (365)	38–105 (67)	21–54 (34)
EXTENSIVE STUDY AREAS						
Hirsikankaansuo	0.1–0.3 (0.2)	–	267–432 (400)	–	7–12 (8)	–

– No data

The PO_4 -P concentration along the 80-m sampling transect at the Hirsikankaansuo buffer decreased from 1.13 mg l^{-1} to 0.42 mg l^{-1} as the distance from the adding point increased from 10 to 80 m (Fig. 5).

3.5 P Sorption Properties of the Soil

Estimated from the adsorption isotherms, the P retention in peat was less efficient at the Asusuo, Kirvessuo and Murtsuo buffers than at the Kallioneva and Hirsikankaansuo buffers (Figs. 9–13). The reference values (Table 4) indicated that in 2001, i.e. two years before the PO_4 -P adding period, P_0 and EPC_0 at the Kirvessuo buffer were significantly higher than in the Kallioneva and in Hirsikankaansuo buffers. When arranging the sites in order of the highest to the lowest maximum PO_4 -P retention (P_{10}), the buffer zone areas were Hirsikankaansuo > Kallioneva > Asusuo > Murtsuo > Kirvessuo; between the Hirsikankaansuo and Kirvessuo buffers there was a statistically significant difference.

After the PO_4 -P adding period in 2003, the average P_0 and EPC_0 had increased at the Asusuo and Murtsuo and decreased at the Kirvessuo and Kallioneva buffers (Table 4). P_{10} had decreased after the adding period in Asusuo, Kirvessuo, Murtsuo and Kallioneva. The changes in P_0 , EPC_0 and P_{10} were statistically significant at the Asusuo buffer.

4 Discussion

All the six buffer zones had the capacity to retain P, which was reflected in the reduced P concentrations during the adding period in the water flowing through the buffers. The highest total retention of the added P was at the Kallioneva and Vaneskorvenoja buffers, i.e. the two largest buffer zone areas. The size of the buffer, especially in relation to the catchment area has been regarded as one of the critical factors in the functioning of buffer zone areas (Uusi-Kämppe et al. 2000, Koskiaho et al. 2003, Nieminen et al. 2005a, Silvan et al. 2005). However, despite their significantly smaller size, the total retention of P at the Kirvessuo and Murtsuo buffers was only slightly lower than at the two largest buffers. Beside the size of the buffer zone, other factors such as hydraulic load and water residence time strongly affect the P retention efficiency (Ihme 1994, Koskiaho et al. 2003, Syversen 2005). The Asusuo buffer, which is of approximately the same size as the Kirvessuo and Murtsuo buffers, received the highest water load during the PO_4 -P adding period and the area retained much less P than Kirvessuo and Murtsuo buffers (24% vs. $\geq 95\%$). Similarly, the P retention at the Hirsikankaansuo buffer was lower when the hydrological load was higher during the second addition period. A high hydrological load generally leads to the formation of continuous flow channels across the buffer zone area. In such channels, flow velocity is high and water residence time low; both these factors are disadvantageous for an efficient retention of P (Koskiaho et

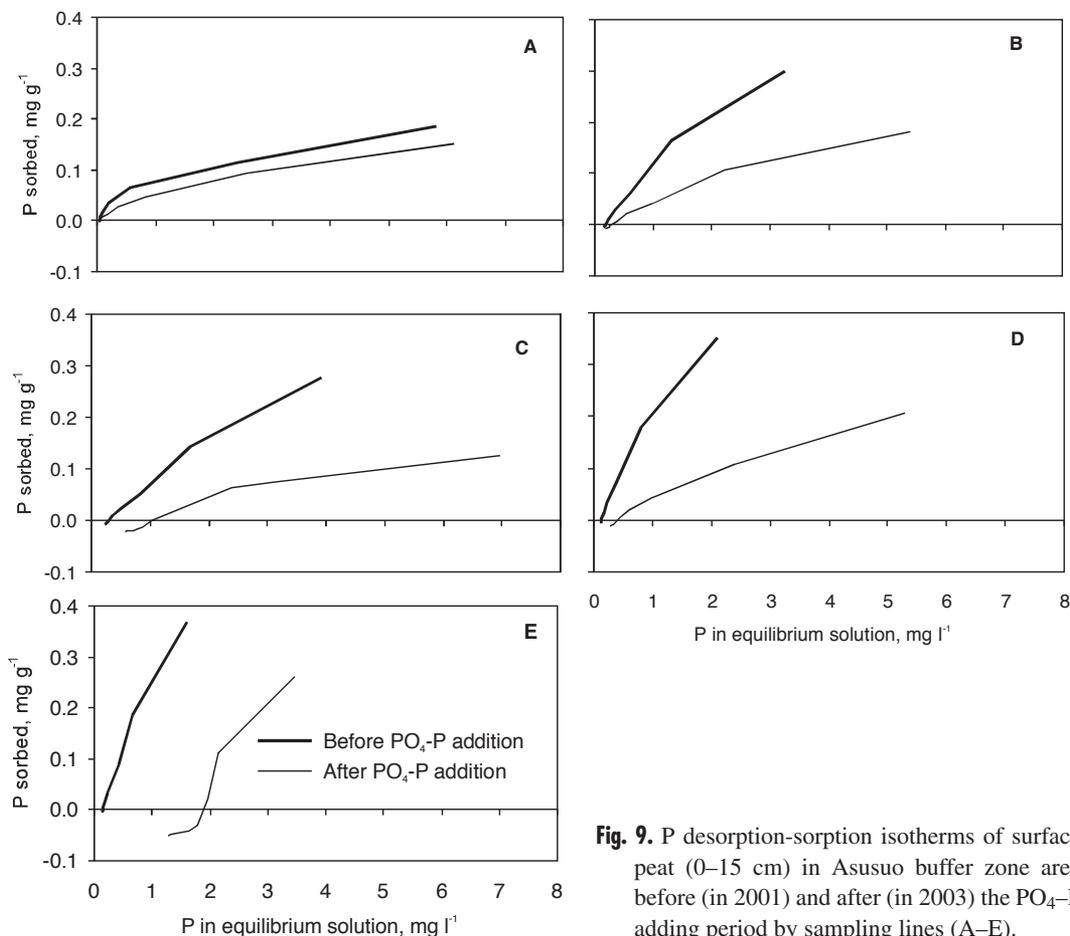


Fig. 9. P desorption-sorption isotherms of surface peat (0–15 cm) in Asusuo buffer zone area before (in 2001) and after (in 2003) the PO₄-P adding period by sampling lines (A–E).

al. 2003). During the time of the P addition at the Asusuo buffer, there was a visible flow channel from the P adding point to the outflow sampling point; the short water residence time was reflected in that elevated PO₄-P concentrations at the outflow point were measured as early as two hours after the onset of the P addition.

Although the size of the buffer and the hydrological load are important in P retention, the results indicate that other factors also may exist. The hydrological load to the two smallest buffer zones (relative to catchment area), Kirvessuo and Murtsuo, was still more than twice as high as the maximum load of 34 mm d⁻¹ recommended by Ihme (1994) for an efficient functioning of buffer zones; however, they retained significantly more P (95%) than Asusuo (24%). The P addition experiment at the Asusuo buffer was conducted

in the beginning of the growing period when the vegetation had not yet fully developed, whereas the Kirvessuo and Murtsuo buffers received their P input in the middle of the growing season. The vegetation has an important role in P retention, not only through P accumulation in the living biomass (Silvan et al. 2004) but also because the living vegetation slows down the water flow in the buffer zones and thereby reduces the formation of preferential flow paths (Braskerud 2001). The lower P retention at the Hirsikankaansuo buffer during the second addition, which occurred late in autumn, may also support the indices that actively growing vegetation is an important contribution to efficient P retention.

Initially, added P in wetlands and peatlands is rapidly allocated into the litter-microbial pool and uptake by vegetation and adsorption in soil

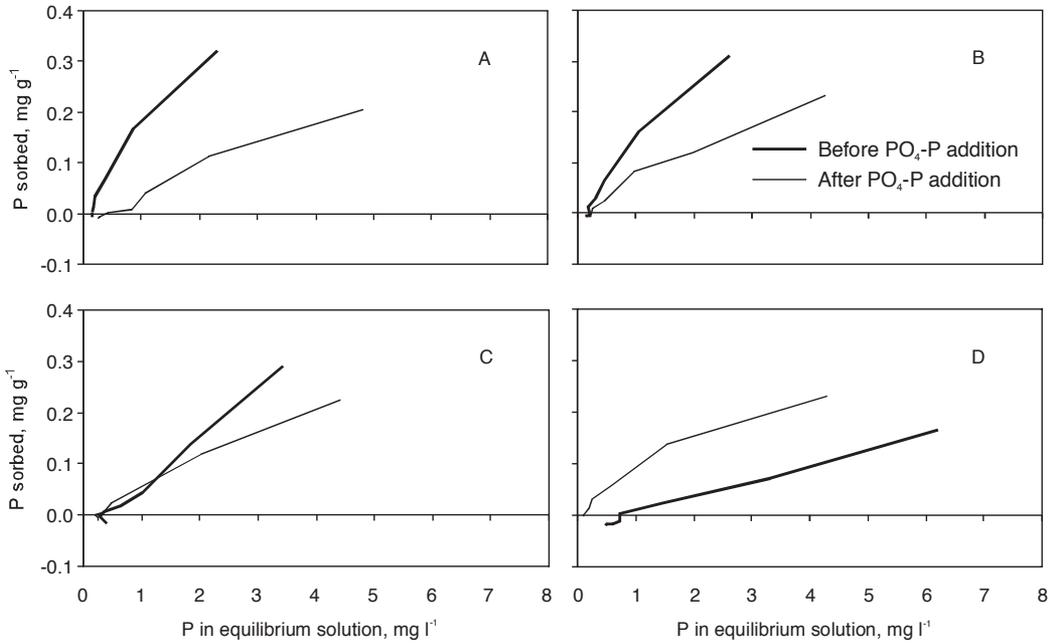


Fig. 10. P desorption-sorption isotherms of surface peat (0–15 cm) in Kirvessuo buffer zone area before (in 2001) and after (in 2003) the PO₄-P adding period by sampling lines (A–D).

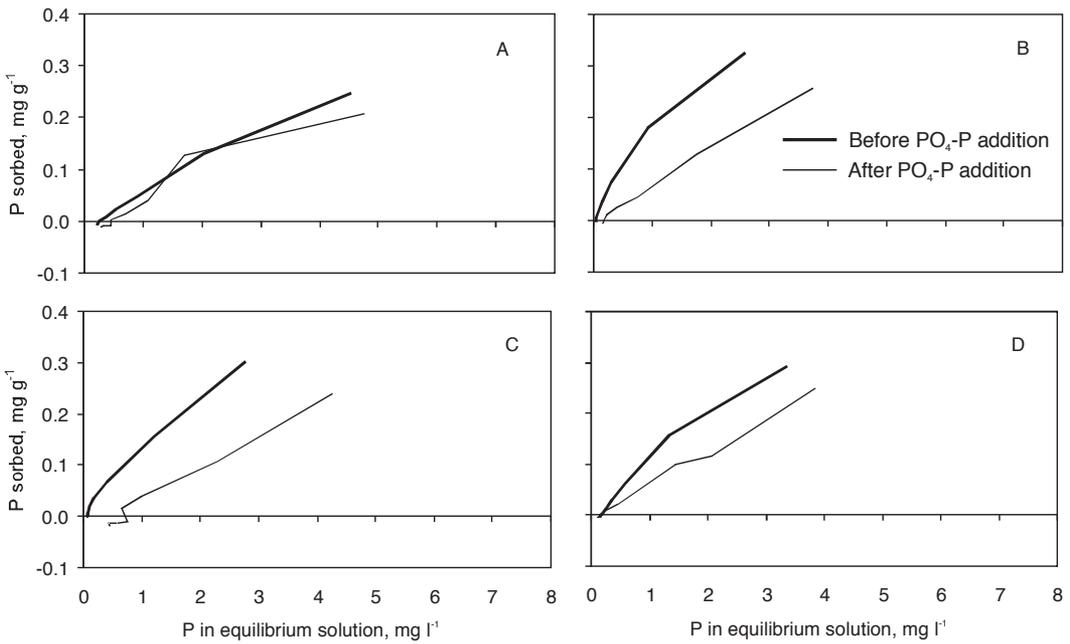


Fig. 11. P desorption-sorption isotherms of surface peat (0–15 cm) in Murtsuo buffer zone area before (in 2001) and after (in 2003) the PO₄-P adding period by sampling lines (A–D).

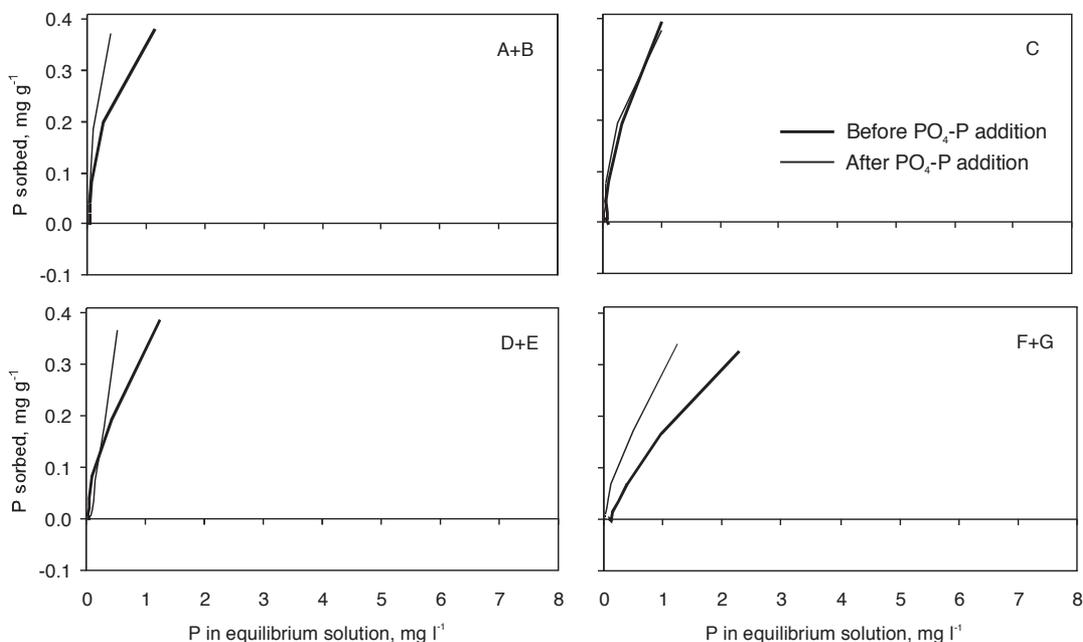


Fig. 12. P desorption-sorption isotherms of surface peat (0–15 cm) in Kallioneva buffer zone area before (in 2001) and after (in 2003) the $\text{PO}_4\text{-P}$ adding period by sampling lines (A+B, C, D+E, F+G).

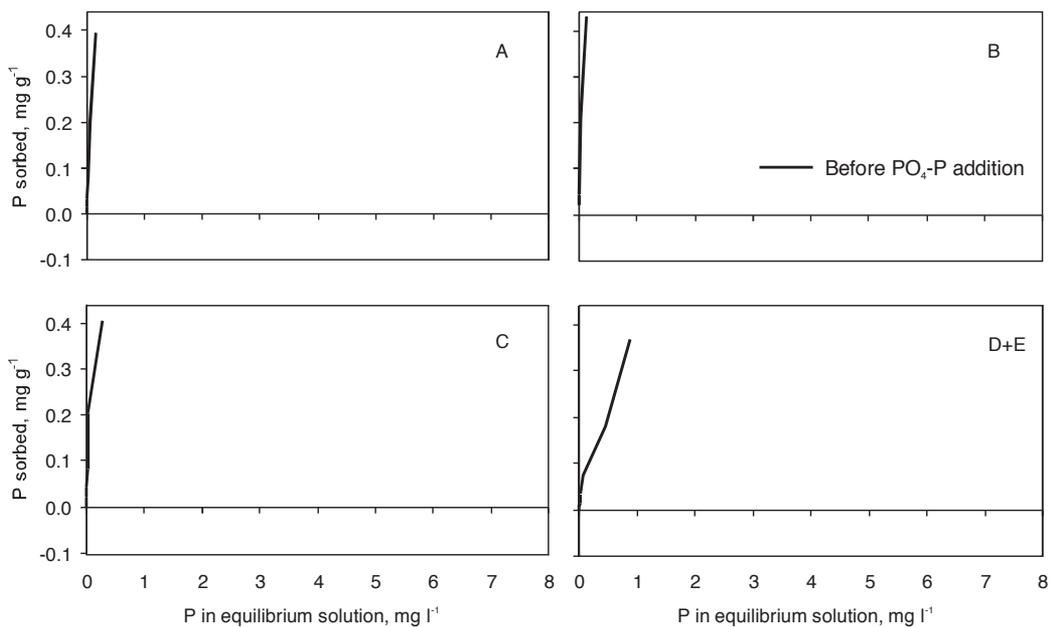


Fig. 13. P desorption-sorption isotherms of surface peat (0–15 cm) in Hirsikankaansuo buffer zone area before (in 2001) the $\text{PO}_4\text{-P}$ adding period by sampling lines (A, B, C, D+E).

will follow within the time scale of several days (Richardson and Marshall 1986, Kellogg and Bridgeham 2003). Increased P outflow during the adding period from the Asusuo, Kirvessuo and Murtsuo buffer zones suggested that the P retention capacity of this litter-microbial pool was exceeded. There are probably several reasons why no outflow of added P occurred during the adding periods from the Kallioneva and Vannesorvenoja buffers or from the Hirsikankaansuo buffer during the first addition in 2004. Their large size itself was a contributing factor for P retention because the litter-microbial sink as well as other P sinks are correspondingly larger, which results in lower relative load and lower probability of saturation of these sinks. In addition, the hydrological load was low and therefore the water residence time was probably long enough for all P-consuming processes (microbial immobilization, soil sorption, vegetative uptake) to be involved in P retention.

The adsorption isotherms measured before the onset of the P addition experiment indicated that the peat soil in all buffer zones had P sorption capacity. Reduction in this capacity after the $\text{PO}_4\text{-P}$ adding at the Asusuo, Kirvessuo and Murtsuo buffers indicated that sorption in peat had contributed to total P retention. The total quantity sorbed by the peat remains uncertain, but a hypothetical calculation was made, where the increase in P_0 after the P addition period was assumed to be the P sorbed in the soil labile P pool and the decrease in P_{10} the P sorbed in the permanent pool. According to these calculations P sorption in the soil would have been 3.3, 2.5 and 1.7 kg at the Asusuo, Kirvessuo and Murtsuo buffers, respectively, of which 86%–92% would have been bound permanently. However, it should be noted that the peat samples for the determination of the P adsorption capacity were collected a few days after the adding period had ended and the P outflow continued after that. A part of that outflow probably originated from the P released from the soil labile P pool and as a result, the total P retention in the soil could have been lower, if it had been determined from the samples that had been collected after the outflow P concentrations had decreased back to pre-addition levels.

No change in P retention properties due to P addition were detected from the peat at the Kallioneva buffer zone area. One reason for this

is probably that the added P remained in the upstream part of the buffer zone and that the downstream sampling points (lines E–G, Fig. 4) were not influenced by P addition. The peat at the Kallioneva buffer also had a higher P sorption capacity than the peat from the other intensive study areas, so its buffering capacity against any measurable changes in P retention properties was probably stronger.

The maximum P retention determined in the laboratory did not correlate with the actual P retention that occurred in the field after P addition. Other factors than the P sorption capacity of peat, such as the hydrological load, as discussed previously, water residence time and the time of the P input may therefore be critical factors for P retention. However, a high P retention capacity of the peat matrix may have contributed to the sustainability of the P retention. At the Kallioneva and Hirsikankaansuo buffers, where the peat had the highest P retention capacity, no P discharged from the areas after the adding had ended and the retention appeared to be permanent. In comparison, part of the initially retained P was released after the P addition had ended from the Asusuo, Murtsuo and Kirvessuo buffers, where the peat had a lower sorption capacity. A likely source for that particular P outflow was the release of P from the soil instantly labile P pool. Thus, the P retention capacity of peat may be one criterion that should be considered when designing efficient buffer zones.

Previous studies have pointed out that the P retention efficiency of buffer zone areas depends on the P concentration in the inflow water and that the P retention is higher with a higher load (Braskerud et al. 2005, Syversen 2005). In our study, the P concentrations during the adding period were raised to significantly higher levels than the P concentrations normally occurring in runoff from forestry land, even though very high concentrations have been detected after P fertilization (Nieminen and Ahti 1993). Before this study started the P concentrations in the inflow and outflow of the buffer zones in this study were monitored. The results show that under a P input level that is more normal for forestry land ($<30\text{--}40\ \mu\text{g P l}^{-1}$) the outflow P concentration was below the inflow concentration at the Kallioneva buffer, but no significant differences occurred at the Asusuo,

Kirvessuo, Murtsuo and Hirsikankaansuo buffers (Nieminen 2005b). The Vannesorvenoja buffer zone area had been formed on drained peatland which probably had been fertilized after its initial drainage, and cutting residues had also been left on the restored area. This had apparently resulted in significantly higher P concentrations in the outflow than the inflow during a period of about three months after the restoration (Sallantausta et al. 1998, Vasander et al. 2003). However, as the Vannesorvenoja buffer zone during this study retained all the added P, it appears that buffer zones that initially release P during and after their construction later can function as significant, sustainable P sinks.

5 Conclusions

Even though large buffer zone areas were the most efficient in retaining P, also small areas had the capacity to decrease a P load to water courses. Factors contributing to efficient P retention were large size of the buffer zone area and low hydrological load whereas large hydraulic load combined with formation of preferential flow paths, especially during early spring or late autumn was harmful. A high P retention efficiency in the peat soil of the buffer zone may contribute to a sustaining P removal from the water discharging from the upstream catchment.

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