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ECOSYSTEMS

Phosphorus Limitation in Boreal Forests: Effects of Aluminum and Iron Accumulation in the Humus Layer

Reiner Giesler,* Tomas Petersson, and Peter Högberg

Soil Science Section, Department of Forest Ecology, Swedish University of Agricultural Sciences, 901 83 Umeå, Sweden

ABSTRACT

Plant growth in boreal forests is generally considered to be predominantly nitrogen (N) limited, but forested groundwater discharge areas may be exceptions. In this study, we conducted tests to determine whether highly productive forested groundwater discharge areas generally differ from adjacent groundwater recharge areas in terms of humus chemistry and the availability of phosphorus (P) and N to plants. We investigated six forested sites, divided into groundwater discharge and adjacent groundwater recharge areas, in northern Sweden. The humus layers of the forested groundwater discharge areas were clearly distinguished from the adjacent groundwater recharge areas by having higher acid-digestible calcium (Ca) and/or aluminium (Al) and iron (Fe) content and higher organic P and N content. Soil solution inorganic N (NH_4^+ and NO_3^-) and pH were higher in the groundwater discharge areas than in the groundwater recharge areas. The organic P content showed a positive linear relationship to the Al and Fe content in the humus layer, indicating that organic P is associated with Al and Fe compounds in the humus. A plant bioassay using humus substrate from one groundwater discharge area and the adjacent groundwater recharge area found that plants grown in groundwater discharge area humus (with a high P-fixation capacity) increased their biomass upon P fertilization, whereas no growth response was found for N additions. By contrast, plants grown in humus from the groundwater recharge area did not respond to added P unless N was added too. This study suggests that groundwater discharge can affect the nutrient availability of N and P both directly, via increased P fixation due to the redistribution of Al and Fe, and indirectly, via the inflow of groundwater high in Ca and alkalinity, maintaining a high pH in the humus layer that favors *in situ* N turnover processes.

Key words: aluminum; groundwater discharge; iron; phosphorus limitation; phosphate sorption; nitrogen availability.

INTRODUCTION

Plant growth in boreal forest ecosystems is generally considered to be nitrogen (N) limited (Tamm 1991). In contrast, many tropical forests soils are phosphorus (P) limited due to a high P-fixing capacity and low available P contents (compare Vitousek and Sanford 1986). In boreal forest soils, P fixation is generally restricted to the B horizon due to the accumulation of aluminum (Al) and iron (Fe) in this horizon (compare Wood and others 1984; Yuan and Lavkulich 1994; Li and others 1999).

Wood and others (1984) showed a vertical stratification of the relative distribution of biological sinks (fine roots, bacteria and fungi) vs geochemical sinks (surface-reactive Al and Fe sesquioxides), which contribute to P retention in podzols under temperate forests. The geochemical sinks dominated in the mineral B horizon, whereas biological

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Corresponding author; e-mail: Reiner.Giesler@sbek.slu.se

sinks dominated in the surface humus layer. Organically bound P dominates the soil P pool in the humus layer; mineralization of this pool is thus probably the major pathway for the release of plant-available P (Wood and others 1984; Cade-Menun and others 2000).

However, Giesler and others (1998) found large amounts of Al and Fe in the surface humus layer of a spodosol in a forested discharge area in northern Sweden. A re-distribution of Al and Fe into the humus layer generates surface sites that can adsorb P (Bloom 1981; Pare and Bernier 1989; Gerke 1993), creating a geochemical sink to the humus layer. Previous studies on peat soils have shown that accumulation of Al and Fe in these organic soils increases the P-adsorption capacity (Cuttle 1983; Richardson 1985; Nieminen and Jarva 1996). Accumulation of Al and Fe in the humus layer has been reported from forested discharge areas (Mulder and others 1991; Norrström 1993, 1995), but it has been documented in only one case in the context of P adsorption and P availability (Giesler and others 1998). The presence of a geochemical sink in the humus layer differs from previous findings on the vertical stratification in spodosols and suggests that forested discharge areas might differ in this context.

In a landscape perspective, groundwater discharge areas are found in toe slope areas; hence, they comprise only a small part of the total area (about 10%) (Rohde 1987). In Fennoscandian boreal forests, these sites often have higher forest productivity, and have field layer vegetation dominated by tall herbaceous plants rather than dwarf shrubs and "short" herbs. Regional surveys have demonstrated that the total N content in the humus layer is higher in the sites dominated by tall herbaceous plants (Dahl and others 1967; Lahti and Väisänen 1987). Along a local productivity gradient encompassing a large part of the natural landscape variation, Giesler and others (1998) found that inorganic N concentrations in the soil solution of the humus layer increased toward the local groundwater discharge area. They also noted that inorganic N source shifted from NH_4^+ domination in the groundwater recharge area to NO_3^- domination in the groundwater discharge area. In addition, phosphate concentrations were close to zero in the groundwater discharge area, where the P-fixing capacity of the humus soil was high, and plant bioassays indicated a plant P limitation. Read (1991) postulated a relationship between the predominant form of plant-available N, mycorrhizal type, and the most limiting nutrient and suggested that this condition is related to altitude or latitude, climate, and soil. In Read's model, NO_3^- is the predominant N form in P-limited areas, whereas NH_4^+ or organic N is predominant in boreal N-limited forests.

Although regional surveys have demonstrated a linkage between the humus layer N content and forest productivity (Dahl and others 1967; Lahti and Väisänen 1987), there are no data available on an eventual P limitation in groundwater discharge areas other than the single productivity gradient investigated previously. To gain more insight into this question, we investigated five additional sites with features similar to the previous site (Giesler and others 1998). The objectives of this study were (a) to compare humus layers from forested groundwater recharge and groundwater discharge areas with respect to plant P and N availability, soil solution composition, and P-fixation capacity; and (b) to determine if there is a linkage between Al and Fe in the humus and the above variables.

MATERIALS AND METHODS

Study Sites

Six forested sites in northern Sweden were selected for the study (Table 1). Each site was comprised of a groundwater discharge area and the adjacent groundwater recharge area. The separation between the groundwater discharge and groundwater recharge areas was based on topography and field layer vegetation. All sites were situated in toe slope areas except site 3, which was situated in a midslope position. Mean annual temperature and precipitation are 1°C and 570 mm, respectively. Diurnal mean monthly temperatures in June, July, and August are between 11° and 14°C. At site 5, the most northern site, mean annual temperature and precipitation are −1°C and 500 mm, respectively. On average, the sites are snow-covered from late October to early May.

The field layer vegetation in the groundwater recharge areas was dominated by dwarf shrubs (mainly *V. myrtillus* L.) and intermingled with "short-herb" plants such as *Gymnocarpium dryopteris* (L.) Newman and *Majanthemum bifolium* (L.) Schmidt. The groundwater discharge areas were dominated by "tall-herb" species (Table 2) except site 1, where grasses dominated the field layer vegetation. The forest stands were dominated by Norway spruce (*Picea abies* (L.) Karsten) but with individual trees of Scots pine (*Pinus sylvestris* L.) and aspen (*Populus tremula* L.). The forest types, according to Hägglund and Lundmark (1977), were "tall-herb spruce forest" for all groundwater discharge areas except site 1, which was classified as "short-

Table 1. Location and Site Index for the Groundwater Discharge (GDI) and the Adjacent Recharge Areas (GRE) at the Six Sites Studied

Site No.	Site Name	Latitude/Longitude/Altitude	Site Index, GDI/GRE Area $H_{100}{}^{a}$(m)
1	Rusksele	64°50′N, 18°10′E, 230 m a.s.l.	22/18
2	Flakastugan	64°25′N, 19°25′E, 225 m a.s.l.	23/18
3	Vorrberget	64°25′N, 19°30′E, 225 m a.s.l.	23/18
4	Kryddgrovan	64°59′N, 19°35′E, 220 m a.s.l.	23/18
5	Varjisån	66°01′N, 19°52′E, 230 m a.s.l.	21/16
6	Betsele	64°39′N, 18°30′E, 235 m a.s.l.	23/18

[a] *Site index estimated from site properties (vegetation, soil, moisture, latitude and altitude) according to Hägglund and Lundmark (1977). Site index is the height of dominant trees at a reference age of 100 years and is an index of relative site productivity.*

Table 2. Tall-Herb Plant Species Found in the Groundwater Discharge Areas of the Different Sites Indicating Higher Site Productivity According to Hägglund and Lundmark (1977)

Species	Site No.					
	1	2	3	4	5	6
Aconitum septentrionale Koelle						X
Actaea erythrocarpa Fisher				X		
Actaea spicata L.				X	X	X
Cirsium heterophyllum (L.) Hill		X	X			
Crepis paludosa (L.) Moench		X				
Dryopteris assimilis Walker		X				X
Filipendula ulmaria (L.) Maxim			X	X		
Geranium sylvaticum L.		X	X	X	X	
Lactuca alpina (L.) Grey		X	X			
Matteuccia struthiopteris (L.) Tod				X		
Paris quadrifolia L.	X				X	
Urtica dioica L.				X		

Nomenclature of species follows Tutin and others (1964–80).

herb spruce forest without dwarf shrubs." All groundwater recharge area sites were classified as "short-herb spruce forests with dwarf shrubs."

Soil parent materials at sites 3 and 4 were post-glacial sandy sediments, whereas the other soils were developed in loamy-sandy till. Soils in the groundwater recharge areas were classified as Typic Haplocryods (Soil Survey Staff 1992), whereas soils in the groundwater discharge areas are Aquic or Oxyaquic Haplocryods (Soil Survey Staff 1992) since water saturation within 100 cm from the soil surface most likely occurs during part of the year.

Soil Sampling

The humus layer (O horizon) was sampled in July 1996 at sites 1–5 and in June 1994 at site 6. Five humus layer cores were taken randomly with a soil auger (0.10-m diameter) in the groundwater discharge area, and an additional set of five humus layer cores were taken in the adjacent groundwater recharge area. The distance between the two areas was less than 50 m, and the distance between individual sampling spots was greater than 3 m. Each sample was kept separately in a polyethylene bag and kept in a cooler at approximately 5°C during the transport to the laboratory. Within 24 h of collection, humus samples were sieved in the laboratory through a sieve (5-mm mesh). A subsample of approximately 100 g was taken for immediate extraction of soil solution, and another portion was used for determination of water content (105°C, 24 h). An additional portion was used for the P-partitioning experiment and kept at 4°C until the onset of the experiment within a week after sampling. The rest of the humus, as well as the centrifuged humus, was frozen until further treatment.

In August 1999, centrifuged humus samples were thawed and dried (40°C, 5 days). The dried samples were gently milled by hand in a ground mortar. The milled samples were dried at 70°C 48 h, (in vacuum) before digestion.

Plants

Within 0.5 m of each humus sampling spot (sites 1–5), plant shoots of a small herb, *Majanthemum bifolium (L.)* Schmidt, and a small fern, *Gymnocarpium dryopteris (L.)* Newman, were sampled. The plant species were selected because they were commonly found in both the groundwater discharge and groundwater recharge areas. The sampled plants were kept in a cooler at approximately 5°C during transport to the laboratory, where the shoots were immediately dried (70°C, 48 h) and milled in a ball mill to a fine powder before analyses of N and P (total N between 48 and 49 since some analyses failed).

Soils Solution Extractions

Soil solution was extracted on a portion of the humus samples within 24 h after sampling using a centrifugation drainage technique (Giesler and Lundström 1993). Humus samples were centrifuged for 30 min at 14000 rpm and filtered through a 0.45-μm filter (Syrfil-M; Costar Corporation, Cambridge, MA, USA). Soil solution pH was determined immediately after centrifugation on a subsample of the soil solution. The remaining soil solution was kept at 4°C until further analyses.

Acid-digestible and Acid-extractable Pools of Al, Fe, Ca, and P in the Humus

Acid-digestible Al, Fe, calcium (Ca), and P in air-dried humus were determined using about 0.2 g of humus. The samples were digested in a mixture of nitric and perchloric acids (10 and 1 ml, respectively) in 50 ml Teflon tubes at 110°–130°C until less than 1 ml of the acid remained (but not continued to dryness). After digestion, de-ionized water was added to a total volume of 10 ml and the solution kept for further analyses. In addition, pyrophosphate-extractable Al and Fe were determined on humus samples from the groundwater discharge areas of sites 1–5 following the procedure of Buurman and others (1996) and using 2 g dry weight (dw) of humus and 50 ml sodium pyrophosphate. Sodium pyrophosphate is assumed to extract mainly organically bound Al and Fe.

The acid-extractable amount of P (P_{HCl}) was determined using 1.0 M HCl. Air-dried humus samples were shaken (16 h; humus:solution ratio, 1:30) and filtered (Munktell 00H filter paper; Stora AB, Grycksbo, Sweden). The filtrate was kept at 4°C until further analyses. The difference between the acid-digestible P and 1.0 M HCl extractable P is assumed to be mainly organically bound P and is hereby denoted P_o, whereas the HCl-extractable fraction mainly constitutes inorganic P associated with Al, Fe, or Ca.

Partitioning of Phosphate

The phosphate adsorption capacity of the humus was determined following the procedure of Nodvin and others (1986). The ability to remove or release PO_4 can be described by the relationship between the amount removed or released from the soil solution (*RE*: in mmoles per kilogram) and the initial amount of PO_4 added (X_i: in millimoles per kilogram); it is defined by the linear isotherm $RE = mX_i - b$, where the slope (m) is defined as the partitioning coefficient of the initial mass isotherm (Nodvin and others 1986)—that is, the fraction of total reactive substance in a soil/water system that is retained by the soil. A value of 1.0 thus indicates total adsorption, whereas a value of 0 indicates no adsorption.

We equilibrated 25 ml of either 0 or 1 mmol of KH_2PO_4 with about 1 g dw of humus on a shaker (16 h, 20°C) using three replicates from the groundwater discharge and recharge areas of sites 1–5. After the equilibration period, the humus suspension was filtered (Munktell 00H filter paper; Stora AB) and the filtrate collected for further analyses.

Plant Bioassay

A plant bioassay to test plant response to N, P, and NP treatments was conducted using humus layer soils with different P-fixing capacities. Humus from the groundwater discharge and the adjacent groundwater recharge area at site 6 were used for the plant bioassay (previously described in Giesler and others 1998; groundwater discharge area humus equals 90 m position, and groundwater recharge area humus equals 80 m position in the described productivity gradient). Due to the accumulation of Al and Fe, the humus from the groundwater discharge area has a high P-adsorption capacity in contrast to the humus from the adjacent groundwater recharge area, which has a low P-adsorption capacity (Giesler and others 1998).

Acid-washed (0.01 M HCl) silica sand (Silversand 90; Ahlsell Mineral, Sweden) was mixed with humus so that a loss on ignition (LOI) of approximately 4% was achieved. The mixed soil was used as substrate, and 420 g of the substrate was used for each 0.3-L pot.

Six different treatments, control (C), N, P1, P2 (that is, two levels of P addition), NP1, and NP2 and one plant species (the herb *Solidago virgaurea* L., found in both groundwater recharge and discharge areas) were used in the plant bioassay. Each treatment was replicated four times ($n = 4$ replicates × 6 treatments × 2 soils) and only one plant was growing in each pot. Before the start of the assay, P (treatments P1, P2, NP1, and NP2) was added as a single addition to the groundwater discharge area substrate with a high P-adsorption capacity to achieve an equilibrium concentration of 300 (P1) and 600 (P2) μM PO_4 based on a P-adsorption isotherm for the humus (Petersson 1998). Equilibrium concentrations were selected so that 300 μM was approximately equal to the soil solution concentration found in the humus layer of the adjacent groundwater recharge area (Giesler and others 1998).

Each pot was treated with de-ionized water (every day) and N and/or P (every 2nd day) during the experiment. The total amount of added solution was always the same for all treatments. Phosphate was added in two concentrations (P1, 0.4 mM; P2, 0.8 mM, respectively) as NaH_2PO_4 and nitrogen as NH_4NO_3 (N, NP1, and NP2; concentration, 1.6 mM). The control treatment (C) received equal amounts of solution (de-ionized water) as the N and P treatments. All additions were made with a dispenser (100-ml dispenser; Socorex, Switzerland), and the volume added was noted at each addition to enable calculation of the total amount of fertilizer added. The total additions of N and P for each treatment were 150 and 300 mg P kg^{-1} dw organic matter (P1 and P2, respectively) and 600 mg N kg^{-1} dw organic matter. The single initial additions to the groundwater discharge area substrate were 780 and 1470 mg P kg^{-1} dw (P1 and P2, respectively). The total additions correspond to approximately 60 kg^{-1} N ha^{-1}, 15 and 30 kg^{-1} P ha^{-1} (groundwater recharge area), and 90 and 180 kg^{-1} P ha^{-1} (groundwater discharge area), assuming a bulk density of 0.1 kg dm^{-3} and a humus layer thickness of 0.1 m.

A climate chamber (Weiss, Germany) was used for the study, and day length was set to 16 h (full illumination). Temperature was 20°C at daytime until day 11 and thereafter 15°C to avoid substrate drying. Night temperature was 15°C. The relative air humidity was set to 75% throughout the assay. Pots were moved systematically during the experiment.

The plants were harvested after 2 months and shoot and root biomasses were determined. The plants were dried (70°C, 24 h) and milled (roots and shoots together), and P and N concentrations were determined for the plants.

Analyses

Plant and humus digests were analyzed for Ca, Al, and Fe using inductively coupled plasma-mass spectrometry (ICP-MS; Perkin-Elmer SCIEX, Norwalk, CT, USA) and P colorimetrically on a flow injection analyzer (5020 Analyzer; Tecator, Höganäs, Sweden).

Total N in plants sampled in the field was analyzed on an elemental analyzer coupled to an isotope ratio mass spectrometer (ANCA-NT solid/liquids preparation module coupled to a model 20-20 IRMS; Europa Scientific Limited, Crewe, England). Total N in plants from the bioassay and humus was analyzed on a C and N element analyzer (2400 CHN Element Analyzer; Perkin-Elmer SCIEX).

Soil solution PO_4, NO_3^-, and NH_4^+ concentrations were determined colorimetrically on a flow injection analyzer as above. Acid-extractable PO_4 (P_{HCl}) was analyzed as above. Soil solution pH was determined on an ATI Orion pH meter model 370 and sure flow electrode model 9272 (ATI Orion, Boston, MA, USA).

Statistics

For statistical comparison between groundwater discharge and groundwater recharge areas, two-way analysis of variance (ANOVA) was used with site and area (groundwater discharge or recharge areas) as fixed factors. Only bulked samples were available for analyses for site 6 and were thus excluded from the statistical analyses (except for soil solution data, where replicates were available). Treatment effects in the plant bioassay were analyzed statistically using one-way ANOVA for each substrate used (substrates considered independent). Multiple comparisons in variance analyses were performed with Tukey's test. Because no difference was found between the two P-addition levels (P1, P2, NP1, and NP2), these are treated as one treatment (P and NP) in the statistical analyses. Significant differences refer to the $P < 0.05$ level unless stated otherwise.

RESULTS

Acid-digestible Pools of Al, Fe, Ca, and P

The groundwater discharge areas had significantly higher acid-digestible Al, Fe, and Ca concentrations in the humus layer than the groundwater recharge

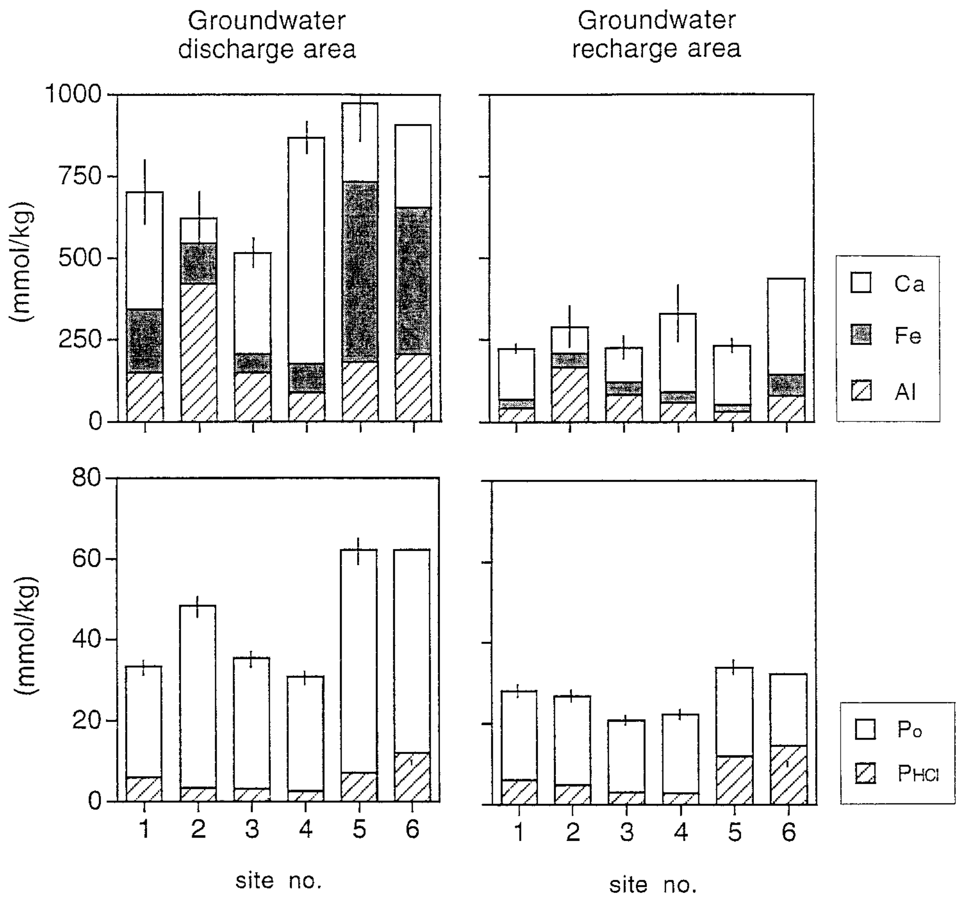

Figure 1. Comparison of acid-digestible Ca, Al, Fe, and P concentrations (mean values) in the humus layer of groundwater discharge and the adjacent recharge areas (standard error for sum of elements, except for site 6, where bulked samples were used). Organic P (P_o) is defined as the difference between the 1.0 M HCl-extractable PO_4 and the acid-digestible P content. Sites as in Table 1.

areas. (Figure 1). At sites 1, 3, and 4, Ca concentrations were significantly higher in the groundwater discharge areas than in the adjacent groundwater recharge areas, whereas Al and Fe were significantly higher in the groundwater discharge areas in sites 1, 2, 5, and 6. Site 1 was the only site where both A_l and Fe and Ca concentrations were higher at the groundwater discharge area than in the adjacent groundwater recharge area. The relative distribution of Fe and Al differed between the sites. At sites 5 and 6, Fe comprised about 75% of the total amount of Al + Fe, whereas Al dominated in site 2 (about 77%).

Pyrophosphate-extractable Al ranged from 15% to 84% of the acid-digestible Al pool (mean values). The lowest values were found at site 1 and seemed to differ from the other sites. The amount of pyrophosphate-extractable Al was negatively linearly related to pH ($r^2 = 0.18$, $P = 0.04$), and the relationship improved excluding site 1 ($r^2 = 0.80$, $P < 0.001$). Pyrophosphate-extractable Fe ranged from 22% to 69% of the acid-digestible Al pool (mean values) and was negatively linearly related to pH ($r^2 = 0.51$, $P < 0.001$).

Acid-digestible P concentrations were higher in the humus layer in the groundwater discharge areas of sites 2, 5, and 6 compared to those in the adjacent groundwater recharge areas (Figure 1). However, there was no difference in the concentration of P_{HCl} between the groundwater discharge and the groundwater recharge areas (Figure 1). The increase in total P concentrations in the humus was due to an increase in P_o (Figure 2). Concentrations of P_o were linearly related to the acid-digestible concentrations of Al+Fe (Figure 2A, $r^2 = 0.65$, $P < 0.001$). Similarly, P_o was also linearly related to the pyrophosphate-extractable Al + Fe ($r^2 = 0.53$, $P < 0.001$) but not to the difference between the acid-digestible and pyrophosphate-extractable pool ($r^2 = 0.14$, $P = 0.08$), assumed to be mainly amorphous and crystalline Al and Fe. Only a weak linear relationship was found between P_{HCl} and Al+Fe (Figure 2B, $r^2 = 0.16$, $P = 0.03$, only groundwater discharge area samples included).

Total N concentrations were significantly higher in the groundwater discharge areas than in the groundwater recharge areas, whereas C:N and C:P, and C:P_o ratios were significantly lower in the

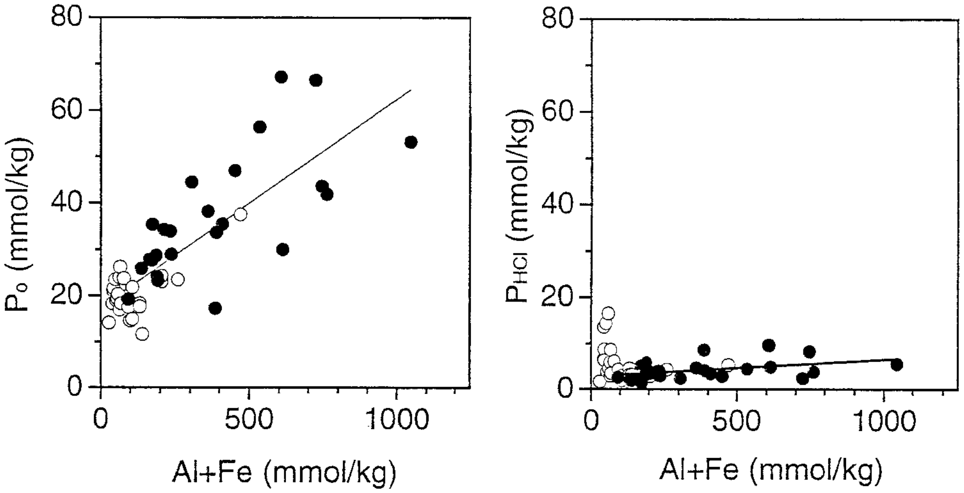

Figure 2. The relationship between organic P (P_o) and 1.0 M HCl–extractable PO_4 (P_{HCl}) vs the total content of Al + Fe in the humus layer (sites 1–5). Filled circles, groundwater discharge area; open circles, groundwater recharge area.

Table 3. Results from Two-way ANOVA Showing *P* Values

Variable	*n*	Type	Site	Type × Site
Acid-digestible Ca	50	$P < 0.001$	$P < 0.001$	$P < 0.001$
Acid-digestible Al	50	$P < 0.001$	$P < 0.001$	$P = 0.051$
Acid-digestible Fe	50	$P < 0.001$	$P < 0.001$	$P < 0.001$
Acid-digestible P	50	$P < 0.001$	$P < 0.001$	$P = 0.020$
N%	50	$P < 0.001$	$P = 0.001$	$P = 0.144$
C%	50	$p = 0.002$	$P = 0.435$	$P = 0.071$
C/N	50	$P < 0.001$	$P = 0.007$	$P = 0.269$
C/P	50	$P < 0.001$	$P = 0.001$	$P = 0.935$
C/P_o	50	$P < 0.001$	$P = 0.008$	$P = 0.617$
Soil solution PO_4	59	$P < 0.001$	$P < 0.001$	$P < 0.001$
Soil solution NO_3^-	59	$P < 0.001$	$P = 0.002$	$P = 0.015$
Soil solution NH_4^+	59	$P < 0.001$	$P < 0.001$	$P < 0.001$
Soil solution pH	59	$P < 0.001$	$P < 0.001$	$P < 0.001$
Plant P/N (*M. bifolium*)	48	$P < 0.001$	$P < 0.001$	$P < 0.001$
Plant P/N (*G. dryopteris*)	48	$P < 0.001$	$P < 0.001$	$P < 0.001$
Plant N% (*M. bifolium*)	49	$P < 0.001$	$P < 0.001$	$P = 0.002$
Plant N% (*G. dryopteris*)	48	$P < 0.001$	$P = 0.004$	$P < 0.001$
Plant P% (*M. bifolium*)	48	$P < 0.001$	$P < 0.001$	$P = 0.002$
Plant P% (*G. dryopteris*)	49	$P < 0.001$	$P < 0.001$	$P < 0.001$

"Type" represents the groundwater discharge and groundwater recharge areas (df = 1); "site" represents the different sites studied (sites 1–5 included in analyses, except for soil solution data, where site 6 is also included in the analyses).
Type × Site is the interaction term; n = 4–5.

groundwater discharge areas than in the groundwater recharge areas (Table 3 and 4).

Soil Solution Composition

Average soil solution pH values were always higher in the humus layer of the groundwater discharge areas than in the adjacent groundwater recharge areas (Figure 3). The soil solution pH in the humus layer encompassed almost four pH units, ranging from 3.57 to 7.56. Average soil solution pH values in the groundwater recharge areas of sites 1–5 were all below 4.5, whereas the average pH value at site 6 was 5.31—that is, higher than some of the groundwater discharge areas at the other sites (Figure 3). Soil solution pH was positively related to acid-digestible Ca and Al + Fe contents (mmol kg^{-1}) in the humus layer ($r^2 = 0.83$, $P < 0.001$; $pH = 3.58 + 0.97 \times 10^{-3}\ Al{+}Fe + 4.8 \times 10^{-3}\ Ca$). Including Al + Fe contents improved the linear relationship ($r^2 = 0.83$) compared to just using the

Table 4. Mean Values and Standard Error for C and N Content and C:N, C:P, and C:P_o Ratios in Humus Layer from Groundwater Discharge Areas (GDI) and Adjacent Groundwater Recharge Areas (GRE)

Site No.	C		C%		N%		C:N		C:P		C:P_o	
	GDI	GRE	GDI	GRE	GDI	GRE	GDI	GRE	GDI	GRE	GDI	GRE
	(g C/m² × 10³)		(%dw)		(%OM)							
1	1.64	2.24	33 ± 3	45 ± 2	2.5 ± 0.1	1.8 ± 0.1	23 ± 0	31 ± 1	316 ± 25	528 ± 38	397 ± 35	668 ± 44
2	2.88	2.80	36 ± 3	35 ± 6	1.8 ± 0.1	1.6 ± 0.2	28 ± 1	33 ± 2	247 ± 27	445 ± 71	270 ± 33	556 ± 101
3	3.70	2.96	37 ± 1	37 ± 3	2.4 ± 0.1	1.8 ± 0.1	21 ± 1	29 ± 2	342 ± 19	573 ± 30	378 ± 22	678 ± 40
4	5.40	4.50	36 ± 1	45 ± 3	2.3 ± 0.1	1.6 ± 0.1	22 ± 1	34 ± 4	410 ± 58	691 ± 111	452 ± 68	793 ± 122
5	2.04	2.64	34 ± 3	44 ± 1	2.8 ± 0.1	1.9 ± 0.0	20 ± 1	30 ± 1	181 ± 22	423 ± 25	203 ± 28	649 ± 10
6	2.32	2.15	29 ± nd	33 ± nd	3.1 ± nd	2.3 ± nd	17 ± nd	22 ± nd	148 ± nd	326 ± nd	184 ± nd	597 ± nd

OM, organic matter; nd, not determined; P_o, organic P fraction
The C content (expressed as g C/m²) is calculated from the mean humus layer thickness and an assumed bulk density of 100 kg m^{-3}.

Ca content ($r^2 = 0.63$). Soil solution pH values in sampling spots with a high Al+Fe content were underestimated in the latter case.

The highest inorganic N ($NH_4^+ + NO_3^-$) concentrations were generally found in the groundwater discharge areas (Figure 3). Ammonium was the dominant inorganic N species, except for site 6 (Figure 3). Soil solution NO_3^- concentrations above 10 μM were found only at pH values above 6.

The lowest PO_4 concentrations were found in groundwater discharge areas at sites. 2, 5, and 6 (PO_4 concentrations <10 μM), whereas higher PO_4 concentrations (>100 μM) were found in the groundwater recharge areas of sites 1, 5, and 6 (Figure 3). Notably, there is a larger variation in soil solution PO_4 concentrations in the groundwater recharge areas than in the groundwater discharge areas (Figure 3).

The three groundwater discharge areas with the lowest PO_4 concentrations (<10 μM, sites 2, 5, and 6) were also those with the highest partitioning coefficients (Figure 4). The partitioning coefficient, *m*, was linearly related to the amount of Al and Fe in the humus (Figure 4, $r^2 = 0.82$, $P < 0.001$; $m = 66.2 \times 10^{-3} + 1.3 \times 10^{-3}$ Al (mmol kg^{-1}) + 0.4 × 10^{-3} Fe (mmol kg^{-1})).

N and P Concentrations in Field Layer Plants

N concentrations were generally higher and P concentrations lower in plants sampled in the groundwater discharge areas compared to the adjacent groundwater recharge areas (Figure 5). Plant P:N ratios were generally lower in plants from the groundwater discharge areas (mean values, 0.10 and 0.09 for *M. bifolium* and *G. dryopteris*, respectively) than in plants from the groundwater recharge areas (mean values, 0.18 and 0.19 for *M. bifolium* and *G. dryopteris*, respectively; $P < 0.001$, two-way ANOVA). Low plant P:N ratios were associated with low plant P concentrations rather than with high plant N concentrations (Figure 5).

Plant N concentrations in the two plant species were correlated ($r = 0.72$, $P < 0.001$). Similarly, P concentrations in the plants from the groundwater discharge areas were strongly correlated ($r = 0.80$, $P < 0.001$), whereas the relationship was weaker for plants sampled in the groundwater recharge area ($r = 0.64$, $P < 0.001$).

Plant P concentrations could be predicted from the soil solution composition (PO_4, pH, and soil solution P:N ratio; $N = NH_4^+ + NO_3^-$) using multiple linear regression, explaining 58% and 82% of the variation for *M. bifolium* and *G. dryopteris*, respectively (Table 5). The predictability for plants from the groundwater discharge area was generally better than for plants from the groundwater recharge area. For plant N contents, the degree of explanation was less (data not shown).

Plant Bioassay

P and NP additions increased plant growth significantly in soils from the groundwater discharge area compared to the untreated control, but no growth response was found for N additions (Figure 6). In contrast, no significant plant growth response was found for P additions in the groundwater recharge area soil (Figure 6), but the plant biomass tended to increase with N or NP additions.

P additions (as P or NP) increased the plant P uptake in plants grown in the groundwater discharge area soil, but only the combination of N and P (NP) increased P uptake in plants grown in the groundwater recharge area soil (Figure 6). The

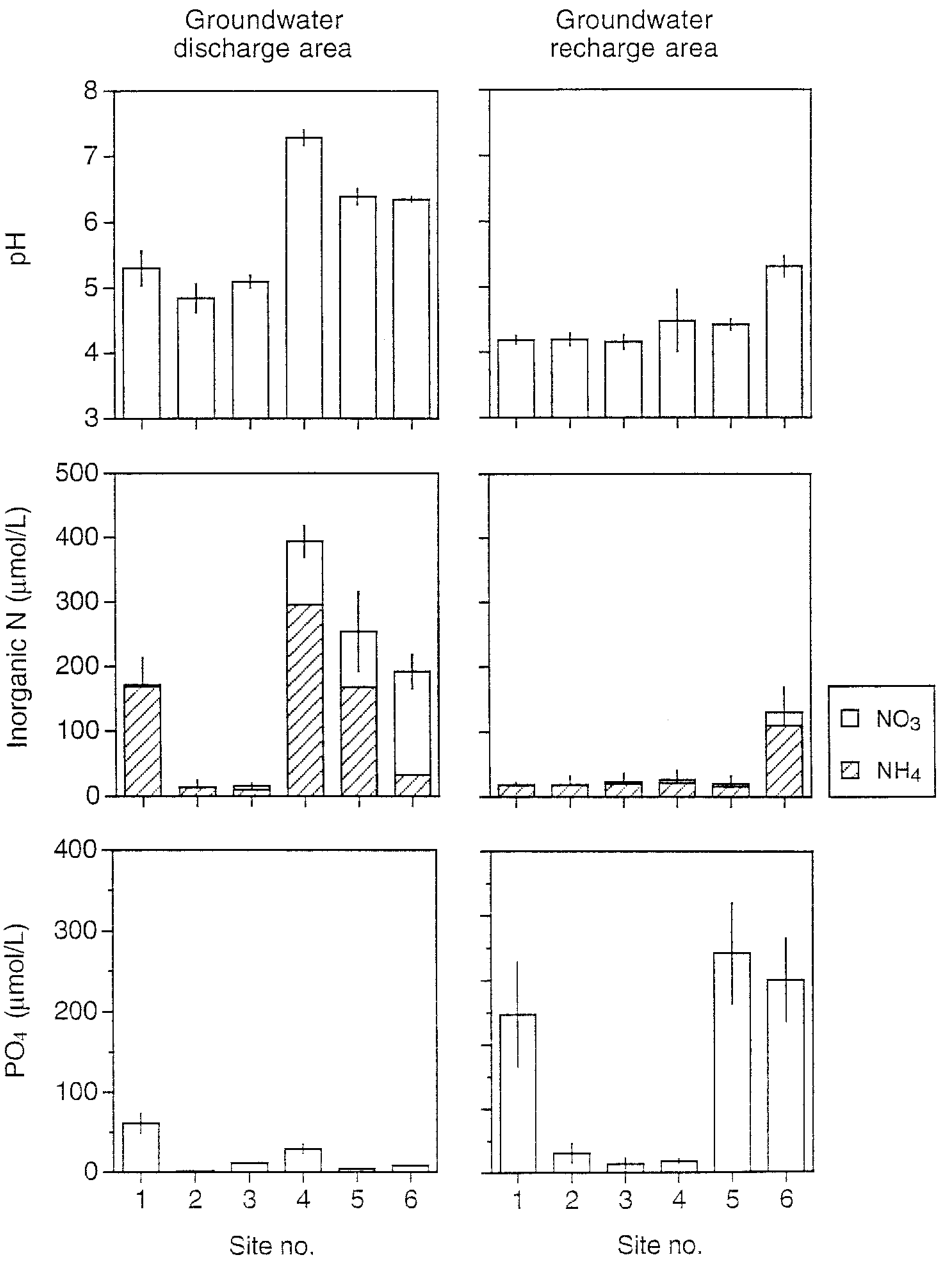

Figure 3. Comparison of soil solution pH, soil solution concentrations of inorganic N (NH_4^+ and NO_3^N), and soil solution PO_4 concentrations in the humus layer of groundwater discharge and the adjacent recharge areas. Mean values and standard error. Sites as in Table 1.

plant N uptake increased with NP additions, but it tended to decrease with only N additions in plants grown in the groundwater discharge area soil. Plants grown in the groundwater recharge area soil increased their N uptake with N and NP additions, but P uptake only increased with NP additions. The average seed content of N and P was 0.010 and 0.001 mg/seed, respectively, and plant uptake of N and P exceeded seed contents more than 1000 times.

Plant P:N ratios increased from below 0.1 to about 0.2 for the P and NP additions in the groundwater discharge area (Figure 6). Plant P:N ratios increased only for P additions in the groundwater recharge area.

Relationship Between Soil Solution Inorganic N, pH, and C:N Ratios

Total inorganic N ($NH_4^+ + NO_3^-$) concentrations correlated strongly with soil solution pH ($r = 0.85$, $P < 0.001$, Pearson correlation), indicating that sites with higher pH also had a higher inorganic N soil solution concentration (Figure 7). The increase in soil solution inorganic N also corresponded to a decrease in humus C:N ratios.

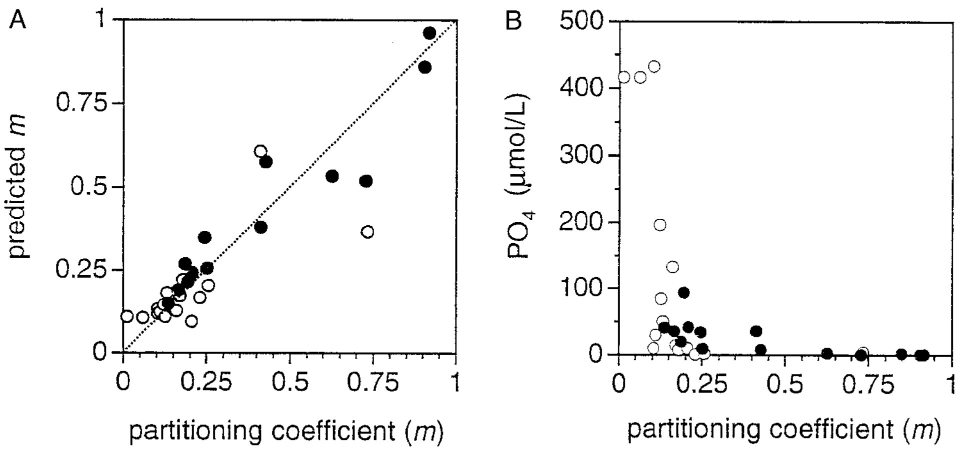

Figure 4. (**A**) Relationship between partitioning coefficient (*m*) and predicted *m* ($m = 66.2 \times 10^{-3} + 1.3 \times$ Al $+ 0.4 \times 10^{-3} \times$ Fe, $r^2 = 0.82$, $P < 0.001$). (**B**) Relationship between the partitioning coefficient (*m*) and the soil solution PO_4 concentrations. Filled circles, groundwater discharge area; open circles, groundwater recharge area.

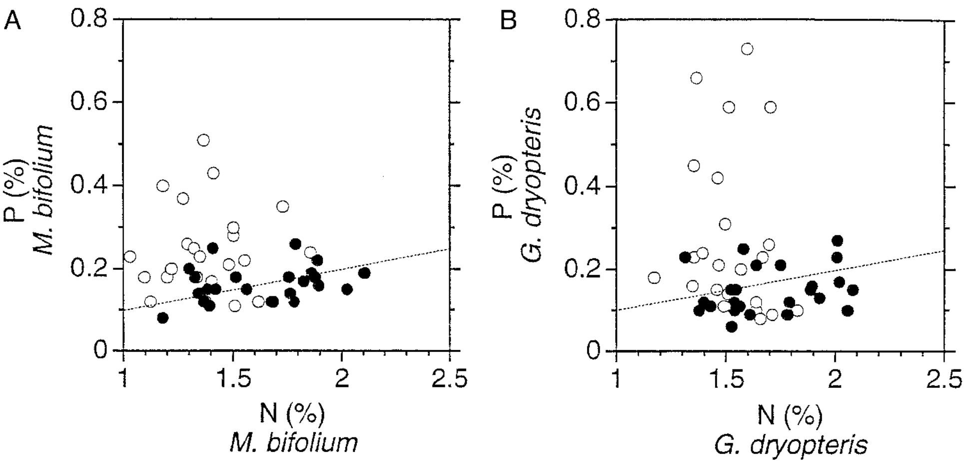

Figure 5. The relationship between plant N and P concentrations in (**A**) *M. bifolium* and (**B**) *G. dryopteris*. The slope of the broken line represents a plant P:N ratio of 0.1; values below 0.1 are considered to indicate a P limitation (Linder 1995).

Table 5. Results from Stepwise Multiple Regression Using Plant Shoot P Concentration as Dependent Variable and Soil Solution Concentrations (pH, NH_4^+, NO_3^-, PO_4 (µmol/L), and Soil Solution P:N Ratio; $N = NH_4^+ + NO_3^-$) as Independent Variables

Species	Dependent Variable	*n*	r^2	*P* value	Model
M. bifolium	P	47	0.56	<0.001	$P = 0.28 + 0.0004 \times PO_4 - 0.02 \times$ pH
G. dryopteris	P	48	0.83	<0.001	$P = 0.26 + 0.0007 \times PO_4 - 0.02 \times$ pH $+ 0.004 \times$ soil solution P:N ratio

One sample omitted as outlier

Discussion

The humus layer in forested groundwater discharge areas is clearly distinguished from the adjacent groundwater recharge areas in terms of C:N and C:P ratios, total N and P content, pH, soil solution inorganic N, and accumulation of total Ca and/or Al and Fe. A high P-fixation capacity, and thus a low soil solution PO_4 concentration, also occurs in cases where the Al and Fe content in the humus are particularly high. We believe that differences in hydrochemistry between groundwater discharge areas and groundwater recharge areas will affect, directly or indirectly, soil biological processes and nutrient availability. In the following sections, we will discuss how these factors may interrelate.

Impact of Groundwater Discharge

The accumulation of Al, Fe, and Ca in the humus layer of the groundwater discharge areas is most likely linked to an upward water flow that redis-

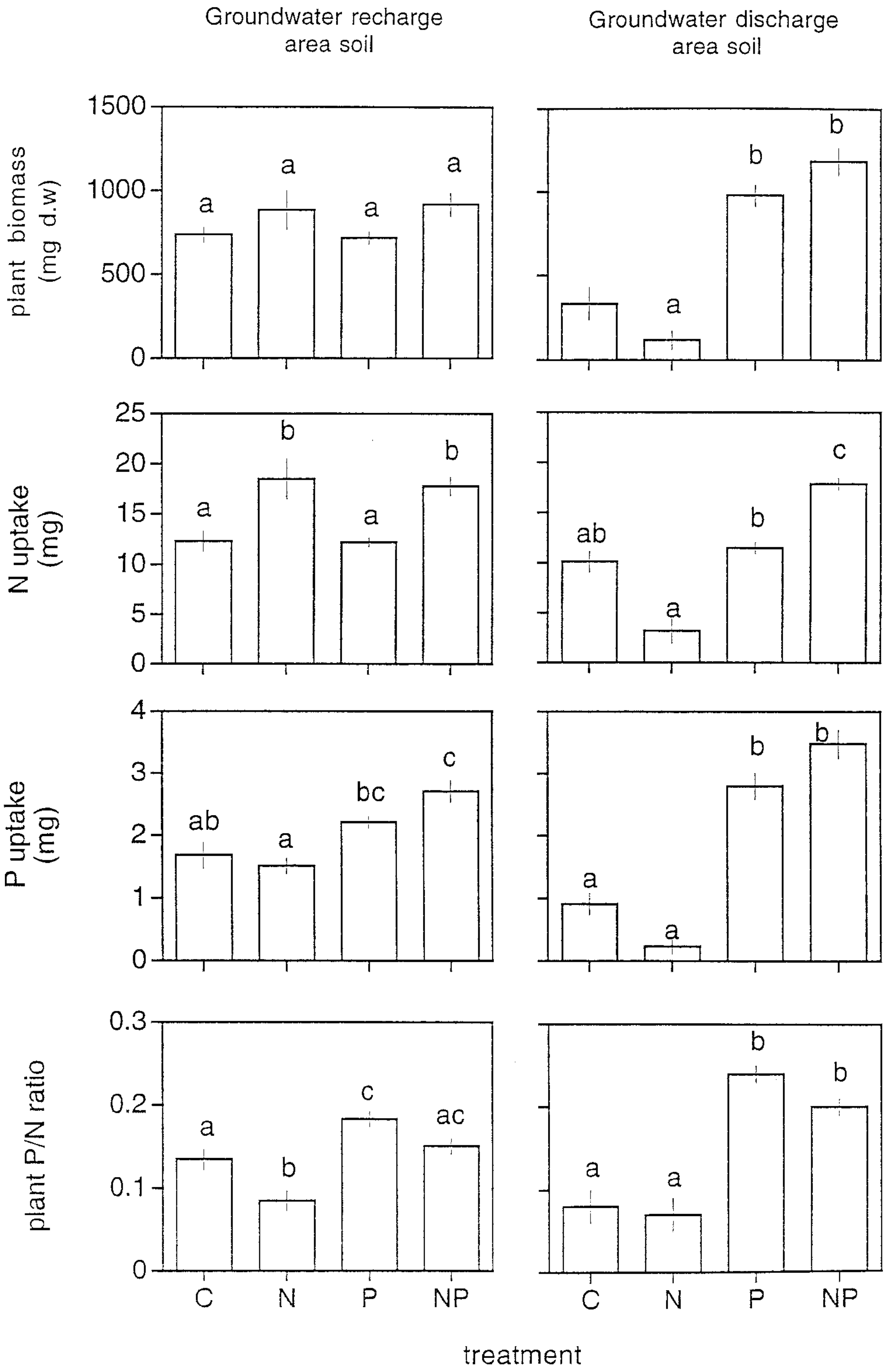

Figure 6. Effects of P, N, and N + P additions in a plant bioassay (mean and standard errors) using humus layer soils from a groundwater recharge area and a groundwater discharge area (site 6, Table 1) with low and high P-fixing capacity, respectively. Different letters denote significant treatment differences.

tributes these elements from the mineral soil into the humus layer. Other mechanisms for redistribution, such as litterfall (compare Vogt and others 1987) or bioturbation due to soil animal activity, seem unlikely explanations for the large differences we found. For instance, at Betsele (site 6), the shift in Al and Fe content appears within some meters between the groundwater recharge and groundwater discharge areas. Large spruce trees (more than 30 m in height) grow on the margin between the two areas; litterfall from these trees will be evenly distributed and unlikely to generate the distinct

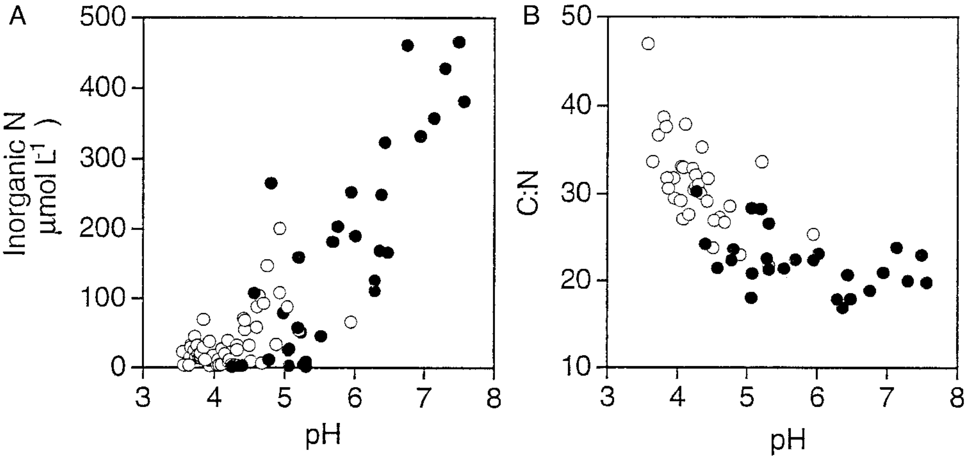

Figure 7. Relationship between (**A**) soil solution pH (centrifugate) and soil solution inorganic N (NH_4^+ + NO_3^-) in the humus layer and (**B**) between soil solution pH (centrifugate) and humus layer C:N ratios. Data from the 90-m productivity gradient at Betsele are included (from Giesler and others 1998). Filled circles, groundwater discharge area; opened circles groundwater recharge area.

shifts that can be seen in the soil. In the Betsele case, when the mineral soil was investigated (Giesler and others 1998), a large increase in Ca saturation in the groundwater discharge area was found in the Bs horizon within the same short distance, supporting the hypothesis that the changes are linked to hydrochemistry rather than aboveground redistribution. Moreover, the amounts of Al and Fe in humus documented in previous studies from forested groundwater recharge areas (Giesler and others 2000; Rustad and Cronan 1995) were much lower than those found in the groundwater discharge areas.

The particular species of Al, Fe, and Ca redistributed in the soil solution might differ due to local conditions. Iron can be transported as Fe^{2+} during reducing conditions—for example, during waterlogged conditions. At least at two sites (sites 5 and 6), rapid changes can be observed (within hours) in the ground water table during rain episodes, sometimes resulting in flooding. A high ground water table that is stagnant for long periods, as is sometimes seen during snowmelt and longer rainfall episodes, would favor reducing conditions. This could promote the dissolution of $Fe(OH)_3$ (s) accumulated in the Bs horizon and the formation of soluble Fe^{2+} and might explain why the humus Fe contents at sites 5 and 6 are higher compared to the other sites. Transport as inorganic Fe (except Fe^{2+}) or Al species is not likely because soil solution pH in the discharge areas is above 5.0 in the humus layer and pH increases with depth (Giesler and others 1998). Alternatively, Al and Fe might be redistributed as organic complexes or as colloidal hydroxide particles. High-molecular-weight organic Al and Fe complexes can be found in the Bs horizon of spodosols (van Hees and others 2000) and may be redistributed with an upward water flow.

There is no evidence of systematic differences in soil mineralogy between groundwater recharge and groundwater discharge areas. Differences in Ca contents between soils in groundwater recharge and groundwater discharge areas are probably due to the transport of calcium as Ca^{2+}, although organic complexes might not be excluded. Calcium accumulation in the groundwater is probably a result of long-distance transport, generating conditions for a time-dependent accumulation of weathering products and alkalinity. At site 4 (the site with the highest Ca accumulation), pH values in a small brook discharging into the groundwater discharge area were higher than 8.0, suggesting an effect from the more basic rocks in close proximity to the groundwater discharge area.

The groundwater discharge of especially Ca in combination with a high alkalinity would maintain a high base saturation and thus a high pH in the groundwater discharge area soils (Giesler and others 1998), as indicated by the strong positive relationship between the contents of Ca in the humus layer and soil solution pH.

Availability of Phosphate

Both the plant bioassay and plant P:N ratios suggest that the P availability is lower at least for field layer plants in groundwater discharge areas with a high Al and Fe content than in the adjacent groundwater recharge areas. The results support previous findings from the Betsele site, (Giesler and others 1998), where both plant P:N ratios and ^{32}P root bioassays indicated a P limitation in the groundwater discharge area. To what extent low P availability also affects trees is still unclear, especially since large trees might extend their roots beyond areas with low P availability and exploit areas with more easily available P sources.

Low soil solution phosphate concentrations as a result of a high Al and Fe content in the humus layer, and thus a high P-fixation capacity, is likely to be the main cause of the low P availability, although Ca–phosphate precipitation may play a role in sites with a high pH. The presence of a geochemical sink in the humus layer contrasts with the general view of boreal forests with a geochemical sink in the mineral soil, namely, the B horizon (compare Wood and others 1984; Cade-Menun and others 2000). The P-fixation capacity might actually be higher in the humus layer than in the B horizon because the complexation of Al and Fe with organic material inhibits their crystallization (Schwertman and others 1986) and thus generates more adsorption sites per Al and Fe than crystalline forms of Al and Fe.

The accumulation of excess amounts of organic P compared to the adjacent groundwater recharge areas is most likely also related to the presence of Al and Fe in the groundwater discharge areas and the adsorption of organic P compounds to Al and Fe surfaces. Organic P compounds such as inositol phosphates, glucose phosphates, and phosphonates have been shown to adsorb strongly to goethite or Al precipitates (Celi and others 1999; Nowack and Stone 1999; Ognalaga and others 1994; Shang and others 1990, 1992; Anderson and others 1974). It is likely that the adsorption of organic P compounds also occurs on organically complexed Al and Fe as well as other Al and Fe surfaces, as has also been shown for phosphate (Bloom 1981; Gerke 1993). The higher degree of explanation for the relationship between P_o and pyrophosphate-extractable Al+Fe compared to the linear relationship between P_o and the assumed amorphous and crystalline Al and Fe forms supports this assumption. Magid and others (1996) and Stewart and Tiessen (1987) have argued that adsorbed organic P compounds are less susceptible to enzymatic biodegradation, since the organic P compound is bound to the surface via the phosphate group and thus blocked from attack by phosphatase enzymes. This could explain why organic P is accumulating in the forested groundwater discharge areas. The soil C:P ratios in the groundwater discharge areas were comparable to those found in spodic B horizons (Cade-Menun 2000), whereas those in the groundwater recharge area were more comparable to ratios in the organic horizon (Cade-Menun 2000). It has been suggested that high C:P ratios (above 300–500) (Blair 1988; Saggar and others 1998) are indicative of net immobilization of P; thus, net immobilization would be dominating in the humus of the groundwater recharge areas but not in the groundwater discharge areas. The use of C:P ratios is, however, very crude because the ratio does not consider actual C:P ratios for the organic P compounds, but instead uses the total C content. Also, the lower C:P ratios in the groundwater discharge areas may reflect a decreased biodegradation.

Plant P concentration and P:N ratios could be predicted from soil solution pH, PO_4 concentration, and soil solution N:P ratios, especially from the groundwater discharge areas (Table 5). This was surprising because the soil variables represent only a single occasion, whereas plant P and N concentrations can be assumed to represent integrated values over a relatively longer time period. The better predictability for plants growing in the groundwater discharge areas probably reflects more stable P availability conditions in the groundwater discharge areas. Availability of P in the groundwater recharge areas is most likely primarily determined by the mineralization of organic P, and spatial and temporal variability in soil solution PO_4 concentrations may be large. Therefore, plant P concentrations may not correlate with a single soil solution measurement.

Availability of N

The buildup of a readily available pool of inorganic N with increasing pH indicates that there is an excess of N in relation to plant and microbial N demand. The relationship between inorganic N on one hand and pH and humus layer C:N ratios on the other suggests that there is a threshold value around pH 5, above which inorganic N in the soil solution starts to increase (Figure 7). Below pH 5, C:N ratios start to increase from an average of 24 to values above 40. The range in humus layer C:N ratios found in these unpolluted sites is similar to those found in the NITREX project (nitrogen saturation experiments), which encompassed sites from Switzerland to southwestern Sweden (Emmet and others 1998). In fact the single 90-m–long transect at the Betsele site (Giesler and others 1998) shows the same range in C:N ratios as the whole NITREX transect.

High nitrate concentrations in the soil solution (indicative of nitrification) were found at high pH and C:N ratios below 24. This corresponds to earlier findings about autotrophic nitrification (Emmet and others 1998; McNulty and others 1996; Kriebitzsch 1978). A high availability of NH_4^+ in combination with a decreased availability of P may favor autotrophic nitrifiers in their competition for NH_4^+ with plants (Riha and others 1986; Zak and others 1990; Norton and Firestone 1996).

Our results do not provide any evidence to show whether the higher inorganic N supply with increasing pH is due to in situ turnover processes or the result of inflow of N. Leaching losses of inorganic N from unpolluted groundwater recharge areas can, however, be assumed to be small (Johannisson and others 1999; Högberg 2001); thus, they would not favor a larger short-term inflow of N to groundwater discharge areas. Gundersen and others (1998) found that gross and net mineralization rates were highest in the NITREX sites with low C:N ratios (20–22). Prescott and others (2000) found appreciable net N mineralization rates only at C:N ratios lower than 35. These findings suggest that in situ processes are the main cause for the higher short-term N supply and that the high rate of N cycling is faster in N-rich sites.

CONCLUSIONS

Highly productive groundwater discharge areas in boreal forests can be P limited rather than N limited. This condition is most likely linked to the influx of Al and Fe to the humus layer in these sites, decreasing P availability due to P fixation. Sites high in Al and Fe also seem to accumulate organic P, possibly due to specific adsorption of organic P compounds to Al and Fe and a reduced biodegradability due to the adsorption. In this investigation, we focused on forested groundwater discharge areas with high productivity; however, a high P-fixation capacity due to an accumulation of Al and Fe is not necessarily restricted to richer sites, but may also occur in other groundwater discharge areas.

Humus layer solution inorganic N (as well as total N in the humus layer) increased with pH and was highest in the groundwater discharge areas. A high pH may favor in situ N turnover rates; thus, the effect on N availability is indirectly linked to the hydrochemistry due to an inflow of Ca and alkalinity maintaining a high pH in the humus layer (see Högberg 2001 for a detailed discussion). The combination of high N availability and plant P limitation may favor nitrification. Further research may reveal whether nitrifiers have a competitive advantage in highly productive forest sites with plant P limitation.

Our findings show that inherent site-specific conditions are important to the understanding of N and P dynamics, especially in the context of the ongoing discussion on effects of elevated N deposition (compare Binkley and Högberg 1997; Emmet 1999). Site conditions prior to increased N deposition rates probably have a large influence on the response to elevated N inputs and therefore need to be taken into account in any evaluation of the effects of anthropogenic N deposition.

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