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*Published in:*  
Water

*DOI:*  
[10.3390/w11091783](https://doi.org/10.3390/w11091783)

*Publication date:*  
2019

*Document version*  
Publisher's PDF, also known as Version of record

*Document license:*  
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*Citation for published version (APA):*  
Nisbeth, C. S., Jessen, S., Bennike, O., Kidmose, J., & Reitzel, K. (2019). Role of Groundwater-Borne Geogenic Phosphorus for the Internal P Release in Shallow Lakes. *Water*, 11, [1783]. <https://doi.org/10.3390/w11091783>

Article

# Role of Groundwater-Borne Geogenic Phosphorus for the Internal P Release in Shallow Lakes

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Received: 28 June 2019; Accepted: 18 August 2019; Published: 27 August 2019



**Abstract:** This study explores the under-investigated issue of groundwater-borne geogenic phosphorus (P) as the potential driving factor behind accumulation of P in lake sediment. The annual internally released P load from the sediment of the shallow, hypereutrophic and groundwater-fed lake, Nørresø, Denmark, was quantified based on total P (TP) depth profiles. By comparing this load with previously determined external P loadings entering the lake throughout the year 2016–2017, it was evident that internal P release was the immediate controller of the trophic state of the lake. Nevertheless, by extrapolating back through the Holocene, assuming a groundwater P load corresponding to the one found at present time, the total groundwater P input to the lake was found to be in the same order of magnitude as the total deposit P in the lake sediment. This suggests that groundwater-transported P was the original source of the now internally cycled P. For many lakes, internal P cycling is the immediate controller of their trophic state. Yet, this does not take away the importance of the external and possibly geogenic origin of the P accumulating in lake sediments, and subsequently being released to the water column.

**Keywords:** internal phosphorus release; geogenic phosphorus; groundwater-borne phosphorus; groundwater-surface water interaction; phosphorus cycling

## 1. Introduction

It is well established that eutrophication of freshwater lake ecosystems is controlled by nutrient input, and in particular the availability of phosphorus (P) [1–4]. In many eutrophic lakes, internal P release, derived from P accumulated in the sediment, is the most important component of the annual P cycle [5–9]. Various processes affect the exchange of P between the water column and the sediment. These include chemical (e.g., redox conditions, nitrate and sulphate availability, pH, alkalinity), biological (e.g., biomineralization), and physical processes (e.g., bioturbation, resuspension, discharging groundwater) [10–16].

The redox conditions in the surface sediment strongly affect the sediment's capacity to bind P [10], especially for sediments with a high iron content [15,17–19]. Phosphorus is sorbed to Fe-oxides under oxidized conditions, while under reducing conditions, microbial respiration uses the ferric iron as electron acceptors, subsequently remobilizing some of the sorbed P to the water column [14,17,19]. Accordingly, higher sediment temperatures during summer lead to accelerated biomineralization [20], which is accompanied by an increase in P release due to development of anoxia in the surface sediment [5,6,20]. In winter, lower temperatures inhibit biomineralization and enable a sufficient supply of oxygen to the sediments to establish a high redox potential, which leads to P retention by Fe-oxides. In addition, a downward flux of P bound in organic matter occurs as primary producers sink to the bottom.

Thus, P is particularly re-accumulated in the sediment during winter. This seasonally-dependent process results in higher lake-water P concentrations during the summer than in winter [9,21–23]. Throughout the year, though mainly during the summer, a continuous long-term P mobilization driven by mineralization of slowly biodegradable organic compounds [23] and reducible Fe-oxides buried deeper in the sediment in preceding years, may also occur. It should be emphasized, however, that only a proportion of the Fe-oxides buried in the sediments are re-mobilized and returned to the water column. The rest is permanently buried in the lakes sediments [23].

Phosphorus accumulated in the lake sediment originates from external P sources entering the lake. The magnitude of the P pool accumulated in the sediment is lake-specific, depending on loading history, flushing rate, and chemical characteristics of the sediment [4,5,22,24]. Particulate P (PP) entering the lake most often settles directly by gravity on the lake-bed [25]. In contrast, dissolved P (DP) remains in the water column until incorporated in organic matter, co-precipitated with calcium carbonate or adsorbed by Fe-hydroxides, which all eventually sink to the bottom. When looking for the root cause of the trophic state of a lake, internal P release is therefore only indirectly relevant.

External P loads are generally associated with surficial hydrological pathways [26–29], due to the common assumption that P is retained readily in the vadose zone, during percolation, before it reaches the aquifer [30,31].

Awareness of groundwater-transported P has increased in recent years and been proven as a more important contributor of external P than previously assumed [32–38]. Substantiating evidence for this hypothesis was reported by Kenoyer and Anderson [39], Vanek [40], Shaw et al. [41], Kidmose et al. [36], and Meinikmann et al. [42]. These studies found that groundwater-borne P can account for more than half of the external total P (TP) load to a freshwater eco-system. So far, however, studies of external groundwater-P loading to eutrophic lakes have not considered the importance of internal P release. Moreover, research focusing on internal P release does not, to our knowledge, include cases where groundwater-P loading is the main external contributor of P.

Furthermore, enriched P concentrations in eutrophic freshwater ecosystems are generally considered to originate from anthropogenic surficial-deposited P sources such as agricultural fertilizers, sewer overflows, wastewater treatment plants, and septic tanks [28,43–46]. The impact of long-term loadings by geogenic P, released by natural processes, is only rarely considered and documented, especially in relation to groundwater-transported P to freshwater ecosystems.

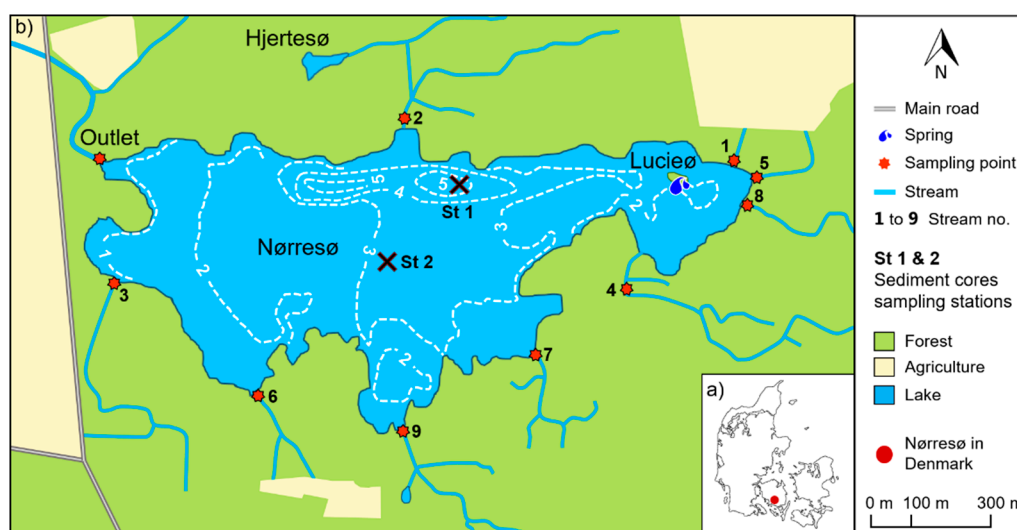
The objectives of this study were therefore to: (1) investigate whether groundwater-borne geogenic P can potentially be the driving factor behind accumulation of P in a lake's sediment, (2) investigate whether this could also apply for lakes where internal P cycling is the immediate controller of the trophic state of a surface freshwater ecosystem, and (3) assess the possibility that the P accumulated in the sediment, where a fraction is being internally cycled, may have entered the lake with groundwater throughout the Holocene.

## 2. Materials and Methods

### 2.1. Study Site

Nørresø is a shallow (mean depth 2.3 m, maximum depth 5.7 m [47]), high alkalinity (water column alkalinity ~3 meq/L), and hypereutrophic (annual mean: 330 µg P/L) lake located in a glacial moraine landscape in southwestern Fyn, Denmark (55°08'50" N, 10°22'40" E) (Figure 1a). The lake has a surface area of 69.3 ha, including three small islands: Lucieø, in the eastern part of the lake, with a prominent perennial spring, and two unnamed islets. Nine small streams discharge into the lake (Figure 1b), numbered 1 to 9 in order of decreasing annual P loading to the lake. This numbering was based on the relative size of the annual dissolved inorganic P (DIP)-flux quantified by Nisbeth et al. [48]. Stream 1 and the spring on Lucieø both represent anoxic groundwater discharging from a regional confined aquifer, with geogenic P and ferrous iron concentrations of ~150 µg P/L and 1700 µg Fe/L, respectively [49]. Stream 2 drains a small lake, Hjertesø, north of Nørresø. The other streams represent

surface water of which just one, stream 3, receives water from drainage pipes connected to a large agricultural field located to the west of Nørresø (Figure 1b). Nørresø has one surface water outlet at the western end of the lake.



**Figure 1.** (a) Location of Nørresø in the southern part of Fyn, Denmark. (b) Locations of the outlet, the nine inlet streams and their respective numbering, and of station 1 and 2 from where sediment were cored in the present study. The small island, Lucieø, hosts a spring. A small lake, Hjerteresø, north of Nørresø, is indicated. Dashed white lines indicate lake bathymetry in meters [47].

Table 1 shows the water balance of Nørresø compiled by Nisbeth et al. [48]. Quantification of the different numbers in the water balance was inferred from a year-long record of the lake's water levels, stream and spring discharges to the lake, and the water output via the outlet. Precipitation and evaporation data were extracted from a database compiled by the Danish National Monitoring Program for Aquatic Environment and Nature [50]. Groundwater was assumed to enter the lake via the spring and stream 1, combined with hot spots in the lake-bed. The latter groundwater contribution was calculated as the residual in the water balance. During the hydrological year from the 6th of June 2016 to the 21st of June 2017, Nørresø received 450,000 m<sup>3</sup> groundwater compared with 110,000 m<sup>3</sup> surface of water. Precipitation and evaporation amounted to 410,000 m<sup>3</sup> and 550,000 m<sup>3</sup> respectively, and the outlet discharge was 480,000 m<sup>3</sup>. The lake's hydraulic retention time is 1.6 years.

**Table 1.** Water balance components of Nørresø (6 June 2016 to 21 June 2017, [48]).

<b>In (m<sup>3</sup>/yr)</b>	
Groundwater input	450,000
Precipitation	410,000
Surface water input	110,000
<b>Out (m<sup>3</sup>/yr)</b>	
Lake evaporation	550,000
Outlet	480,000
<b>Storage change (m<sup>3</sup>/yr)</b>	−60,000
<b>Lake hydraulic retention time (yr)</b>	1.6

The current mean lake-water table is 40.76 m above sea level and the seasonal variation is 0.1 m. The elevation of the water table has varied over millennia. From 13,000 cal. yr BP to about 7500 cal. yr BP, the lake was a closed basin with a low water level. After 7500 cal. yr BP, the lake had an outlet [51].

In the early 1900s, according to historical maps, the lake was somewhat more extensive with a water level of 41.2 m above sea level [48].

Besides water-borne contributions of P to the lake, other potential sources of P include bird droppings from a colony of cormorants (*Phalacrocorax carbo*) found at the margin of Nørresø, and leaf fall. Historically, the area around Nørresø has seen major changes in cultivation. For instance, from 1785 to 1885, half of the area was forest, with the other half used for agriculture. Today, 90% of the catchment is forested. Nonetheless, pollen analyses indicate that the lake was surrounded by forest or at least a rim of forest along its perimeter during the Holocene [52]. Lake stratification was not observed in Nørresø [47,53], most likely due to the shallow depths relative to the surface area, combined with exposure to westerly winds. The lake is therefore assumed to be well-mixed. Paleolimnological studies indicate that Nørresø is, and probably was throughout most of the Holocene, a eutrophic lake [51].

## 2.2. Data Collection

In order to meet the objectives of the current study, the overall research approach was to: (i) Establish the P contribution to the lake via discharging groundwater, on the basis of previously determined external P loads entering the lake throughout the year 2016–2017 [48]. (ii) Use Vollenweiders P mass loading model [54] to estimate the amount of accumulated total dissolved P (TDP) in the lake-water column driven by external P loadings. (iii) Estimate the annual internal-P release contribution to the lake-water column based on the summer vs. winter-deficit in the total P content in the lake-bed sediments. (iv) Evaluate the possible role of geogenic groundwater-borne P as a controlling factor for P accumulated during the Holocene. The evaluation was based on an estimate of the total amount of P accumulated in the sediment, which was compared with an estimate of the total groundwater P input to the lake, from the beginning of the sediment-P accumulation and until present.

### 2.2.1. External Phosphorus (P) Loadings

Investigation of the different external waterborne sources of P entering Nørresø was conducted by Nisbeth et al. [48] during 2016 to 2017. Their quantification of the external P loadings was based on the water balance of the lake (cf. Table 1) and the associated measured P concentrations of the different water components. The groundwater contribution was assumed to come from the Lucieø spring and stream 1, combined with a calculated residual groundwater input, based on the water balance.

Observed TDP concentrations for the lake, the outlet, as well as streams 1, 2, and 3, were similar in values (within ~10%) to TP monitoring concentrations published by the Danish Ministry of Environment and Food [55]. It is therefore assumed that TP mainly consists of TDP and thus the measured TDP concentrations are representative of the P balance at Nørresø (i.e., particulate P is of secondary importance).

### 2.2.2. Water Sampling and Dissolved P Analysis

Water sampling from the spring, the nine inlet streams, and the outlet were conducted, on average, once every month from June 2016 to December 2017 (see Figure 1 for sampling points). The samples were vacuum filtered in the field with 0.22 µm Minisart Sartorius cellulose acetate membrane filters, directly into polyethylene vials, and then preserved with 2 vol% 2 M H<sub>2</sub>SO<sub>4</sub>. See Nisbeth et al. [48] for a more detailed sampling description. Dissolved inorganic P concentrations in the samples were determined spectrophotometrically by the molybdenum-reactive P method [56]. TDP was measured as DIP after wet oxidation by potassium peroxydisulphate. Dissolved organic P (DOP) was calculated as the difference between total TDP and DIP. Due to the fully mixed conditions in Nørresø, TDP, and DIP concentrations for the outlet are assumed to be representative of the entire lake.

### 2.2.3. Mass-Loading Model of lake Water Column P

It is possible to evaluate whether the accumulated TP concentration in a lake water column is predominantly controlled by external P loadings, by using the P mass loading model of Vollenweider [54], usually expressed as:

$$TP_{lake} = \frac{TP_{in}}{1 + \sigma\tau_w} \quad (1)$$

where,  $TP_{lake}$  is the TP concentration in the lake ( $\text{mg}/\text{m}^3$  or  $\mu\text{g}/\text{L}$ ),  $TP_{in}$  is the flow-weighted TP input concentration ( $\text{mg}/\text{m}^3$  or  $\mu\text{g}/\text{L}$ ),  $\tau_w$  is the lake hydraulic retention time (yr), and  $\sigma$  is a first-order rate constant ( $\text{yr}^{-1}$ ) for P loss.

Two important assumptions apply in the derivation of Equation (1). (i) The lake is well mixed and at a steady state, thus the TP concentration in the outlet represents the TP concentration in the fully mixed lake. (ii) The TP can be removed from the water column by either advection (i.e., via the outlet) or by one or more first-order processes occurring within the lake. The latter is assumed to represent net loss due to sedimentation, since this is the dominant internal process driving TP concentration in the water column [57]. Note that the model does not consider P input from internal P release, hence it expresses an estimation of the accumulated TP in the water column if external loads are the only input of P.

Brett and Benjamin [58] conducted a statistical assessment of various mathematical expressions for  $\sigma$ . They found that  $\sigma$  was the best predictor of  $TP_{lake}$  when expressed as the inverse function of the lake's hydraulic retention time:

$$\sigma = k\tau_w^x \quad (2)$$

where,  $k = 1.12 \pm 0.08 \text{ yr}^{-0.47}$  and  $x = 0.53 \pm 0.03$  are constants. By combining Equation (1) and Equation (2), we obtain:

$$TP_{lake} = \frac{TP_{in}}{1 + k\tau_w^x \times \tau_w} \quad (3)$$

Equation (3) was applied to the data from Nørresø assuming well-mixed conditions and that TDP corresponds to TP concentrations.

### 2.2.4. Estimation of the Internal P Release Load

In the present study, the internal P release load, which is released to the water column during a year, is assumed to be constituted by: (i) A rapid seasonal mobilized P pool ( $P_{\text{seasonal\_released}}$ ) released from the upper sediment, combined with (ii) a slowly long-term mobilized P pool ( $P_{\text{longterm\_released}}$ ), mobilized by mineralization of slowly biodegradable organic compounds and Fe-oxides under low redox potential.

Phosphorus in freshly settled material, containing easily degradable organic matter and redox-sensitive P, accumulated during the winter, is rapidly mobilized and released during the summer. The depth of the sediment layer in which the rapid mobilization of P occurs is hence reflected by a seasonal variation in the sediment TP depth profile. This layer is referred to as the active mobilization layer. In Nørresø the lower boundary of the active mobilization were found at 7 cm depth.

The  $P_{\text{seasonal\_released}}$  pool was estimated as the difference in TP content (in  $\text{mg P}/\text{g DW}/\text{cm}$ ) between the winter and summer cores in the active mobilization layer (i.e., upper 7 cm), multiplied by the depth-specific dry-weight density ( $\text{g DW}/\text{cm}^3$ ). This quantity difference was then multiplied by the lake surface area, to obtain the total amount of  $P_{\text{seasonal\_released}}$  in the lake.

Assuming that the TP content in the sediment during summer represents the P remaining in the sediment after the release of the easily mobilized P, a decrease in the summer TP content with increasing depth in the active mobilization, may reflect the mobilization of the long-term mobilizable P pool.

The annual released P from the  $P_{\text{longterm\_released}}$  pool was hence calculated as the difference in TP (in  $\text{mg P}/\text{g DW}/\text{cm}$ ) between the upper sediment sample and the TP content at 7 cm depth, multiplied

by the mean sediment dry-weight density ( $0.071 \text{ g DW/cm}^3$ ) and subsequently divided by the age of the sediment at 7 cm. According to a previously established age-depth model for Nørresø, the upper 7 cm of the sediment represents 50 years of deposition [51]. The  $P_{\text{longterm\_released}}$  pool is further based on assumptions of constant P-sedimentation rates during this 50-year period.

The mineralization rate presumably decreases with increasing depth once these easily degradable compounds are gone. Hence, the TP content decreases exponentially, reaching a steady state at the lower boundary of the active mobilization layer. Accordingly, a significant decline in the TP content beneath the active mobilization is believed more likely to reflect a change in the sedimentation rate than an additional mobilization of P.

### 2.2.5. Total P Sediment Depth Profiles

Lake sediment cores ( $n = 12$ ) were collected on two dates, on 24 July 2017 (summer) and on 9 April 2018 (winter). The winter coring was conducted relatively late due to an unusually cold and long winter period, during which the lake was covered by ice [59]. The sampling was conducted with a Kajak gravity corer [60] using a 40 cm long core with an inner diameter of 5.2 cm. At each of the dates, three cores were collected at each of the two sampling stations (i.e.,  $n = 2 \text{ stations} \times 3 \text{ cores} \times 2 \text{ dates} = 12 \text{ cores}$  in total). Station 1 (Figure 1b), represented the deepest part of the lake (water depth  $\sim 5 \text{ m}$ ), and station 2, represented the mean water depth of 2.3 m.

In the laboratory, each sediment core was sectioned in 1 cm intervals from 0 to 10 cm depth. Thereafter, three additional 1 cm samples were collected at 15, 20, and 25 cm.

The total P content of the individual sediment samples was determined after drying the sediment for 24 h at  $105 \text{ }^\circ\text{C}$  followed by combustion at  $520 \text{ }^\circ\text{C}$  for 8 h. The combusted sample was boiled for one hour in  $120 \text{ }^\circ\text{C}$  1 M HCl. Total P was then measured as DIP in the extract by the molybdenum-reactive P method [56]. Each sediment sample was analyzed individually, after which mean values for each sectioned depth of the summer and winter cores respectively, were calculated by combining the six sediment samples from the two stations ( $n = 6$  for each depth interval).

The dry weight (DW) content of the sediment was determined gravimetrically, before and after drying the samples at  $105 \text{ }^\circ\text{C}$ .

### 2.2.6. Sediment-P Composition

A general idea of the P composition of the sediment was obtained by determining the depth profiles of eight different P fractions in the sediment. In accordance with the P sequential extraction technique presented by Paludan and Jensen [61], quantification was conducted by extracting: (i) Loosely sorbed water-soluble P ( $P_{\text{Water}}$ ), (ii) redox-sensitive bicarbonate-dithionite (BD;  $0.11 \text{ M NaHCO}_3 + 0.11 \text{ M Na}_2\text{S}_2\text{O}_4$ ) extractable P ( $P_{\text{BD}}$ ), (iii)  $0.1 \text{ M NaOH}$  extractable P ( $P_{\text{NaOH}}$ ), (iv)  $0.5 \text{ M}$  extractable HCl-soluble P ( $P_{\text{HCl}}$ ), and finally, (v) residual P not extracted ( $P_{\text{Res}}$ ).

The humic-bound organic P fraction ( $OP_{\text{Humic}}$ ) was determined by acidification of the NaOH extractant to pH  $\sim 1$  with  $1.5 \text{ mL } 2 \text{ M H}_2\text{SO}_4$ , which led to the flocculation of humic acids after two days [61]. The humic acids was separated by filtration with Whatman GF/C filters, combusted ( $520 \text{ }^\circ\text{C}$ , 8 h), and extracted by  $1 \text{ M } 120 \text{ }^\circ\text{C}$  warm HCl for 1 h before analysis as DIP. Non-reactive P (nrP), which is assumed to represent organic labile P compounds [62,63], was calculated as the sum of the differences between TDP and DIP in the  $P_{\text{Water}}$ ,  $P_{\text{BD}}$ , and  $P_{\text{NaOH}}$  fractions.  $P_{\text{Res}}$  was determined on the remaining sediment after the sequential extraction technique. The sediment was dried and combusted at  $520 \text{ }^\circ\text{C}$  for 8 h, followed by one hour in  $120 \text{ }^\circ\text{C}$  1 M HCl, and  $P_{\text{Res}}$  was then measured as DIP in the extract.

Inorganic P in the different extracts (DIP) was determined by the molybdenum-reactive P method [56], and TP in the extracts (TDP) was detected by inductively coupled plasma-optical emission spectrometry (ICP-OES; detection limit  $4 \text{ } \mu\text{g/L}$ ), with the exception of  $P_{\text{HCl}}$ , since this fraction only represents inorganic P. In the result section the different P fractions are named according to the form in which they occurred in the sediment (e.g., as either inorganic P (IP) or organic P (OP)).

As for the TP depth profiles, mean values for each sectioned depth of the summer and winter cores were calculated respectively, by combining the six sediment samples from the two stations.

### 3. Results

#### 3.1. External Waterborne Dissolved P Loadings

The total annual external dissolved P load to Nørresø amounted to 97 kg P/yr (Table 2). The external TDP load included the supply of P via groundwater (84 kg P/yr), surface water (9 kg P/yr), and dry and wet deposition (4 kg P/yr), see Table 2. Applying the P mass loading model of Vollenweider [54] (Equation (3)), and assuming a lake hydraulic retention time of 1.6 year (Table 1), the external P load entering Nørresø would result in an accumulation of 40 kg P in the water column.

The annual quantity of TDP leaving the lake via the one outlet amounted to 126 kg P/yr.

**Table 2.** Annual P loading to and from Lake Nørresø during 2016 to 2017.

	kg P/yr
<b>External TDP loads</b>	
Groundwater <sup>a</sup>	84
Surface water <sup>a</sup>	9
Atmospheric deposition <sup>b</sup>	4
Total external TDP load	97
<b>Internal P release load</b>	
P <sub>seasonal_released</sub> <sup>c</sup>	680
P <sub>longterm_released</sub> <sup>d</sup>	40
Total internal P load	720
<b>TDP Output</b>	126
<b>Net P increase in the water column during summer</b>	650

<sup>a</sup> Ref. [48]. <sup>b</sup> Estimate based on national average of total wet and dry deposition of organic and inorganic P (both 0.02–0.04 kg P/ha) [64]. <sup>c</sup> Rapid seasonal mobilized P pool, release from the upper 7 cm of the sediment.

<sup>d</sup> The annual released P from the long-term mobilized P pool, driven by mineralization of slowly biodegradable organic compounds and slowly reducible Fe-oxides buried in the sediment.

#### 3.2. Internal P Release Load

A higher TP content was measured in the winter sediment, relative to the summer sediment, in the upper 7 cm of the lake-bed (Figure 2). The TP content in both profiles decreased exponentially with increasing depth, going from 2.7 and 2.3 mg P/g DW in the uppermost sediment respectively, reaching a steady state with similar winter and summer concentrations at a depth of 7 cm (~1.7 mg P/g DW). From 7 to 10 cm depth the TP content in both profiles were almost constant at 1.6 mg P/g DW.

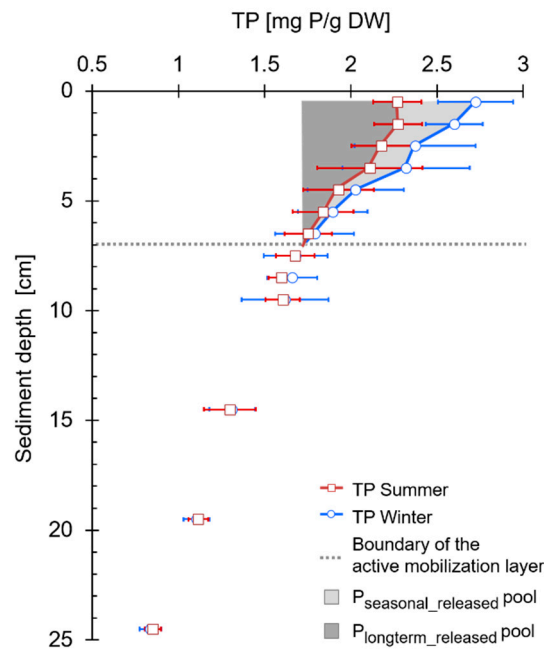
This indicates that the lower boundary of the active mobilization layer is located at a depth of 7 cm (Figure 2). Below 10 cm depth (i.e., beneath the active mobilization layer) the winter and summer TP sediment content remained similar, though with a significant decline in the TP content. This suggest that a change in the sedimentation condition has occurred.

Assuming a lake-bed area of 69.3 ha, an active mobilization layer of 7 cm, and that the sediment cores are representative for the whole lake, the P<sub>seasonal\_released</sub> pool mobilized rapidly during the summer amounted to 680 kg P (i.e., the difference between TP content during winter and summer).

By further assuming that the summer TP depth profile in Figure 2 represents the P sediment content after the release of the easily mobilized P, the total P<sub>longterm\_released</sub> pool which can be mobilized over many years amounted to 1828 kg P. Assuming that the mineralization rate of the slowly biodegradable organic compounds and reducible Fe-oxides have remained constant over the last 50 years, the P<sub>longterm\_released</sub> pool mobilized per year amounted to 40 kg P/yr.

The total internal P release load is, hence, estimated to be 720 kg P/yr (Table 2).

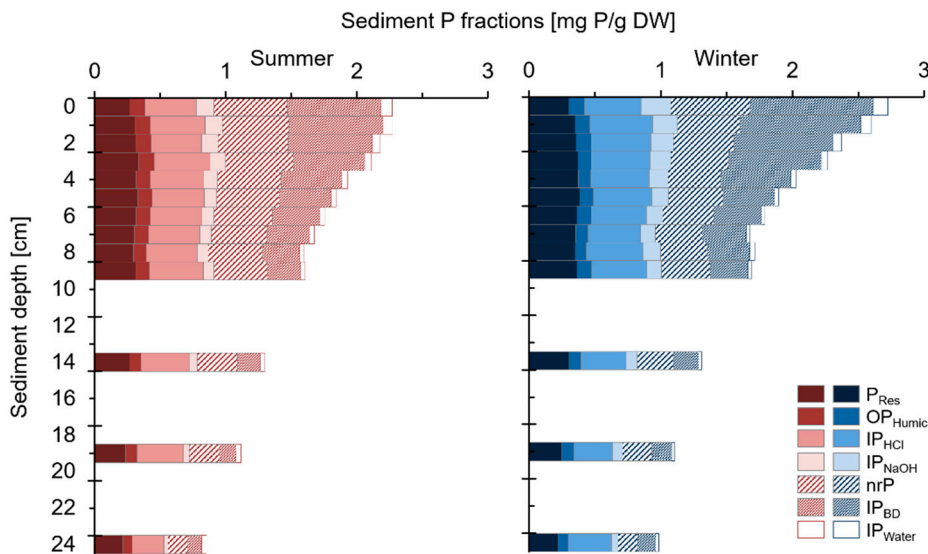




**Figure 2.** Total phosphorus (TP) content in the sediment in the summer (June 2017) and winter (April 2018). Data presented are mean concentrations of the sediment samples of the six cores collected in each season, the error bars shows the standard deviation. The two pools that make up the internal released P are highlighted in gray. For location of the sediment core sampling stations, see Figure 1.

### 3.3. Sediment-P Composition

The seasonal variation in the TP content in the upper 7 cm of the lake-bed can mainly be attributed to a seasonal difference in the redox-sensitive  $IP_{BD}$  fraction (Figure 3). The exponential decrease in the sediment’s TP content down through the upper 7 cm was also primarily due to a decrease in the  $IP_{BD}$ , together with a minor decrease in the nrP (i.e., organic labile P) and the  $IP_{Water}$  fraction. At 7 to 10 cm depth, both  $IP_{BD}$ , nrP and the  $IP_{Water}$  fraction had reached a steady state.



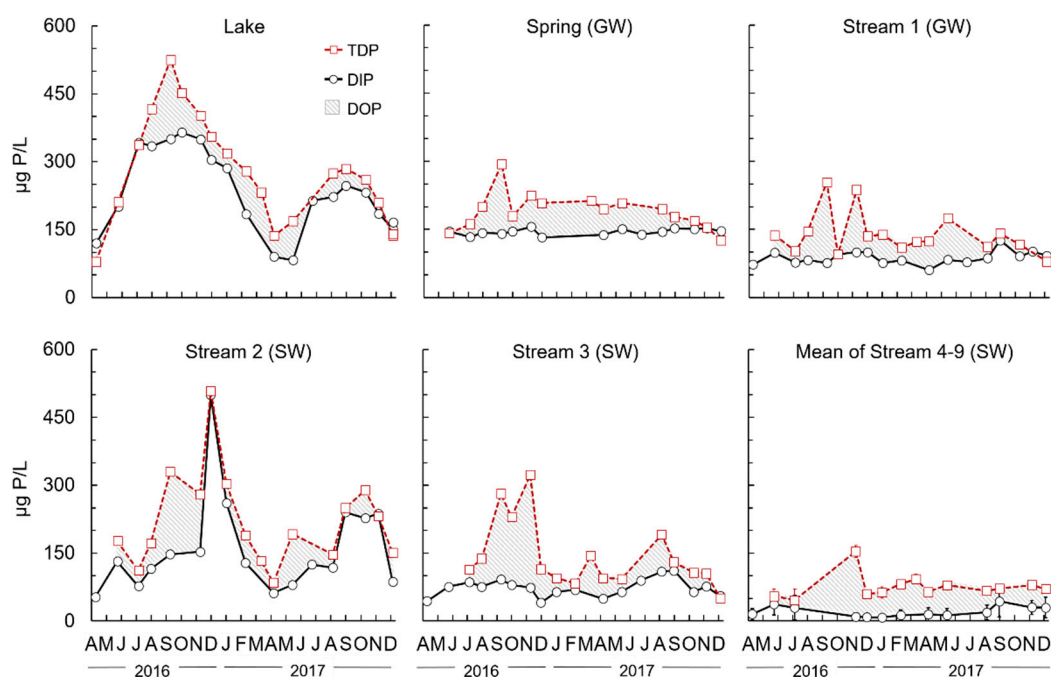
**Figure 3.** Sediment-P fractions from Nørresø in summer (June 2017; left) and winter (April 2018; right). Data presented are mean concentrations of the sediment samples of the six cores collected in each season. For location of the sediment core sampling stations, see Figure 1.

The four fractions  $P_{Res}$ ,  $OP_{Humic}$ ,  $IP_{HCl}$ , and  $IP_{NaOH}$  were relatively constant with depth and displayed similar concentrations in summer and winter in the upper 10 cm of the lake-bed, indicating steady state conditions during the accumulation of the upper 10 cm.

At 15, 20, and 25 cm sediment depth, the amounts of the otherwise stable  $P_{Res}$ ,  $OP_{Humic}$ ,  $IP_{HCl}$ , and  $IP_{NaOH}$  fractions had decreased relative to the upper 10 cm. A decrease in the  $IP_{BD}$ ,  $nrP$ , and the  $IP_{Water}$  fractions could also be observed at 15, 20, and 25 cm sediment depth even though these fractions were at a steady state at 7 to 10 cm.

### 3.4. Dissolved P Concentrations in the Lake, Spring, and Streams

In the lake water column, DIP accounted for the largest share of TDP throughout the year (Figure 4). TDP and DIP concentrations followed the same annual pattern, peaking in August and September, and reaching a minimum concentration in April. If both 2016 and 2017 are taken into account, the mean concentration of TDP and DIP during the peak corresponds to 507 and 336  $\mu\text{g P/L}$ , respectively). During the period with minimum concentrations in April, the mean TDP and DIP concentrations were 98 and 96  $\mu\text{g P/L}$ , respectively. Accordingly, DOP was detected mainly from the end of July to the beginning of November.



**Figure 4.** Concentrations of total dissolved phosphorus (TDP), dissolved inorganic phosphorus (DIP), and dissolved organic phosphorus (DOP) in the lake, spring and streams 1–9 at Nørresø during 2016–2017. Lower left panel shows the mean of streams 4–9 the error bars shows the standard deviation. Spring and stream 1 represent groundwater (GW), and streams 2–9 represent surface water (SW).

The TDP increase in the water column during summer relatively to the lake's background TDP concentration before the onset of internal P loading, as represented by the winter lake-water concentrations [4,65,66] amounted to 650 kg P (Table 2), assuming a lake water volume of 1.6 mill.  $\text{m}^3$  ( $2.3 \text{ m} \times 69.3 \text{ ha}$ ).

Figure 4 shows the TDP and DIP concentrations, for the four main sources of external P loading from measured inflows. The spring and stream 1 represented groundwater and had fairly stable DIP concentrations throughout the year (142  $\mu\text{g P/L}$  and 84  $\mu\text{g P/L}$ , respectively) whereas the DOP concentration varied. DIP and DOP in stream 2 had a pronounced seasonality, both peaking (500  $\mu\text{g P/L}$ ) in December. Stream 2, which represents the main contributor of surface water P, discharges water from a small lake/wetland area called Hjertesø. Thus, the annual internal P cycling occurring

in Hjertesø propagates to the annual DIP variation in stream 2. Stream 3 had a relatively high DOP concentration from August to November whereas the DIP concentration was relatively stable at 70 µg P/L. The rest of the streams (numbers 4 to 9) all had low DIP and DOP concentrations.

#### 4. Discussion

By estimating the external and internal P loadings to a naturally eutrophic, groundwater-fed lake, it became clear that under the current conditions, internally released P was by far the dominant P loading to the lake. Thus, internally released P was the immediate controller of the trophic state of the freshwater ecosystem. The accumulated P in the sediment, and hence the formation of the mobile P pool, was likely conditional upon groundwater-borne geogenic P entering the lake throughout the Holocene, which will be discussed in more detail below. Our findings demonstrate that groundwater-borne geogenic P should be seen as a potential contributor to eutrophication of a freshwater ecosystem.

##### 4.1. Current Lake P Budget

###### 4.1.1. External P Loadings

Groundwater-borne P constituted the primary external P load to the lake, accounting for 88% of the total external P load. The remaining 12% of P was entering the lake via surface water discharging from stream 2 to 9, and atmospheric deposition.

In general, when high P concentrations are observed in discharging groundwater to a lake, it is often shown to be, or expected to be, from an anthropogenic source [32–35,38,42,67]. Nisbeth et al.'s [48] investigation of the external DIP sources indicated, however, that the presence of P in the groundwater discharging into Nørresø was most likely driven by a natural release of geogenic P within a regional artesian, confined aquifer. Hence, causing a natural eutrophication of the lake.

Nisbeth et al. [48] measured a constant groundwater discharge from the spring and stream 1. Thus, the fairly stable and dominant DIP concentration in the spring and stream 1 indicates that groundwater P input, and hence the external P input, remains stable throughout the year. Stream 1 runs under a dirt road via a pipe, which occasionally clogs. This leads to large variations in the water table upstream of the pipe. When clogged, parts of the surrounding wetland are flooded. Phosphorus mobilization processes during flooding may explain the occasionally high DOP concentration.

Under current conditions, the contribution of external P can only explain 8% of the measured accumulated TDP within the lake water column, according to Vollenweider's P mass-loading model. Van der Molen and Boers [9] and Søndergaard et al. [65] emphasize that Vollenweider's model underestimates the TP concentration for lakes in which internal P release was the dominant load. An underestimate of TP (TDP in this study) in Nørresø would substantiate internal P release as playing a dominant role. Nonetheless, the corresponding equilibrium-TDP concentration in the water column, driven merely by the external TDP input (26 µg P/L; based on Equation (3)), would still nearly classify as eutrophic (TP > 30 µg P/L; [4]).

Droppings from the cormorant colony found at Nørresø may contribute an additional external P load to the water column [68]. Previous studies indicate that bird droppings only represent a small fraction [68–70] of the total contribution to TP loads in eutrophic lakes. However, the impact that birds may have on the P budgets of lakes is so far not well documented. Thus, an estimate of the P contribution from the cormorant colony remains uncertain. A preliminary investigation of the DIP concentrations in the lake water column near the colony of cormorants did not indicate elevated DIP concentrations near the colony. This could suggest that the soil has the capacity to retain the P from the bird droppings, and hence indicates a low impact from the cormorant colony [69].

Leaf fall from the forests covering the main part of the area around the lake may also end up in the lake, representing yet another external P load. The leaves probably settle by gravity on the lake-bed, followed by biodegradation, potentially contributing P over time as a part of the internal release.

#### 4.1.2. Internal P Loading

The total annual internally mobilized and released P from the sediment to the water column was estimated to amount to 720 kg P/yr. Comparing this load with the external dissolved P entering the lake during a year (97 kg), it is evident the internal P load is by far the dominant P contributor to the lake under the current conditions. The significant increases in the TPD concentration in the water column during the summer months of August and September can further be seen as an indication of internal, rather than external, P loading dominance [5,9,65,71,72]. Quantitatively, the TDP increase in the water column (650 kg P) more or less equaled the P released from the sediment. The internal P load might even have been much higher than estimated because a strong downward direct P-flux (sedimentation) can be expected in such a productive lake. In parallel, the estimated TDP increase in the water column only represents the net P accumulation, and thus does not directly reflect the gross amount of P released from the sediment.

The net retention of P in the sediment may change over time as the relative ratio of the downward and upward flux of P changes. The stable concentration of the  $P_{Res}$ ,  $OP_{Humic}$ ,  $IP_{HCl}$ , and  $IP_{NaOH}$  fractions within the upper 10 cm of the sediment indicate stable P input within this period, since these fractions are generally considered to be unaffected by diagenesis in the sediment [66].

The significant decline in the TP content and change in the immobile P composition in the sediment at 15 cm depth indicate that the steady state of the lake changed around 50 to 75 years ago. Accordingly, the decline in the TP below the 15 cm is therefore not considered to be an expression of mobilization processes but rather an indication of a lower sedimentation rate. This is supported by findings from another study, where it was shown that the diatom-inferred TP concentrations increased from 30  $\mu\text{g P/L}$  in the mid-1800s to 120  $\mu\text{g P/L}$  at around 1970 [73].

Of the total annual internal P load, consisting of the seasonally and long-term released P, P rapidly released from the sediment during the summer (i.e., the  $P_{seasonal\_released}$  pool) constitutes the majority (95%). The remaining 5% of P originates from the long-term released P pool (i.e., the  $P_{longterm\_released}$  pool).

Based on the sediment-P composition, the  $P_{seasonal\_released}$  pool primarily consists of the  $IP_{BD}$  fraction, i.e., Fe-oxide-bound IP. This strongly suggests that the rapid seasonal P release is mainly controlled by reductive dissolution of the iron oxides in the sediment [6,15,74]. In contrast,  $P_{longterm\_released}$  partly consists of nrP. In general, nrP from the  $P_{NaOH}$  fraction represents by far the largest share of the nrP [61] and consists of organic P such as fulvic acids [75], monoester phosphate and condensed inorganic polyphosphates [76]. The mobilization of P driven by degradation of organic labile P compounds can, however, be estimated to account for just 21% of the total annually released  $P_{seasonal\_released}$  pool. Mobilization of buried Fe-oxide-bound IP (relatively resilient towards reductive dissolution) is, as for the  $P_{seasonal\_released}$  pool, the dominant mobilization process of the  $P_{seasonal\_released}$  pool, accounting for 67%.

The accumulation of Fe-bound IP in the sediment can be attributed to a mechanism, often referred to as the 'iron curtain' [77]. In this process, soluble ferrous compounds in anoxic water precipitate as amorphous iron oxides and hydroxides when entering an oxidized environment, which subsequently removes dissolved P from the water column. The same conditions occur at Nørresø. Anoxic groundwater, accounting for 46% of the water input to the lake, continuously transport dissolved ferrous iron and dissolved geogenic P to the oxygenated lake (cf. [48]). Accordingly, Fe-oxide-bound IP continuously precipitates and settles by gravity on the lake-bed where it accumulates over time. Ferrous iron was not detected in the discharging surface water [48], thus indicating that groundwater is the main driving factor of the accumulated  $IP_{BD}$  fraction. Correlation between a pronounced  $IP_{BD}$  fraction and discharging Fe-rich, anoxic groundwater was also found by Chambers and Odum [77] and Pacini and Gächter [78].

#### 4.2. Long-Term Influence of External TDP

Although the internal TDP load supersedes the external load, it is important to emphasize that internal P load is only indirectly relevant for the trophic state of a lake. The accumulated P in the sediment originates from external P sources entering and subsequently sedimented on the lake-bed.

Evidence that these processes have occurred in Nørresø at longer timescales is presented in Nisbeth et al. [48], where a 7.2 m long sediment core, sampled near station 2 (Figure 1), is described. The upper 6 m of the core consists of gyttja which began to accumulate around 7500 cal. yr BP.

Preliminary diatom and pigment analyses indicate that Nørresø has never been P-poor, but rather has been meso- to eutrophic, even in its pristine state. Pigment data further indicates a persistent presence of cyanobacteria and algae blooms during the past 7500 years. High abundances of cyanobacteria have been recorded at other lakes in glacial moraine landscapes, where groundwater P supply dominates [79]. This situation is similar to the present conditions at Nørresø, where groundwater-transported TDP represents the largest contributor of external TDP (88%). This substantiates the assumption that the deposited P is, and probably always has been, conditional on a continuous TDP transport to the lake via groundwater.

Assuming that the data in Figure 3 are representative of the entire lake area, and the TP concentration in the sediment stagnates at 25 cm depth, up to about 1 mg TP/g DW is permanently deposited in the sediment. Assuming a 6 m gyttja layer thickness with a density of 0.10 g DW/cm<sup>3</sup> ( $\rho$  from 25 cm depth) in the lake, the total deposited P in Nørresø would amount to 374 tons. This is likely an overestimate as the thickness of the gyttja probably decreases towards the bank. Nevertheless, if the groundwater P input is of the same order of magnitude as the total deposited P in the sediment, it is likely to be the driving factor behind accumulation of P in the lake. The calculation of total deposited P only accounts for the net-accumulated P in the sediment, and not the total P input to the lake. Since the amount of P leaving the lake via the outlet over the 7500 years is not included, the groundwater input should in fact exceed the total deposited P (i.e., 374 tons).

The P loss recorded in our own short study period is certainly not representative of the conditions occurring through the Holocene, as it would imply that no P was stored in the sediment.

Assuming a continuous groundwater TDP load equal to the current (84 kg P/yr), from the beginning of the gyttja accumulation until the present (~7500 yrs), the total groundwater P input adds up to 630 tons. If the lake had an outlet in its earlier state, the external P load would also have been higher than today in order to generate the accumulated gyttja. It can be argued that the P concentration in the groundwater was probably higher in the past, as the geogenic P pool in the aquifer is slowly being depleted over time, thus leading to a decrease in groundwater-P concentration. A higher surface-water P contribution in the past could, likewise, be the underlying reason for the accumulated P in the sediment. However, there is no reason to expect that past surface water P load was higher than today, since (i) P started to accumulate long before anthropogenic influences, and (ii) the lake has been surrounded by forest, or at least a rim of forest along its perimeter, throughout the Holocene.

Despite the uncertainties in extrapolating back through the Holocene based on limited modern-day data, the estimated amounts of groundwater-borne P and P contained in the lake sediment are of the same magnitude. The groundwater TDP input even exceeds the estimated amount of permanently deposited P in the sediment, suggesting that groundwater-borne geogenic P was the controlling mechanism for the accumulation of P in the sediment during the Holocene.

## 5. Conclusions

This study demonstrates and expands upon how groundwater-borne geogenic P can play an important role in the eutrophic state of a freshwater ecosystem. Our findings demonstrate that even in lakes where internal P cycling is the immediate controller of their trophic state, groundwater-transported geogenic P can potentially be the original source of the internally cycled P.

For naturally eutrophic lakes, this indicates that:

- Geogenic groundwater-borne P can be the dominant cause of P accumulation: the amount of geogenic groundwater-borne P brought to the lake during Holocene is in the same order of magnitude as the total accumulated P in the sediment.
- Even though the seasonal release of internal P controls seasonal fluctuations in water column P, groundwater-borne geogenic P may be the actual eutrophication factor.

When investigating internally released P, one should not ignore the importance of the original, and possibly natural and geogenic, source of this P.

**Author Contributions:** Conceptualization, C.S.N., K.R., J.K. and S.J.; Methodology, C.S.N. and K.R.; Validation, C.S.N. and K.R.; Formal analysis, C.S.N.; Investigation, C.S.N., K.R., O.B., J.K. and S.J.; Resources, C.S.N. and K.R.; Writing—original draft preparation, C.S.N.; Writing—review and editing, C.S.N., K.R., O.B., J.K. and S.J.; Visualization, C.S.N.; Supervision, K.R., J.K. and S.J.; project administration, S.J., O.B. and J.K.; funding acquisition, S.J. and J.K.

**Funding:** This research was funded by Geocenter Denmark, grant number 6-2015.

**Acknowledgments:** The authors are grateful to the estate of Brahetrolleborg and Catharina Reventlow-Mourier for kindly providing access to Nørresø. Thanks are also given to Rikke Orloff Holm (SDU) and Carina Kronborg Lohmann (SDU) for assistance with the sequential extraction of the sediment and analysis of TDP.

**Conflicts of Interest:** The authors declare no conflict of interest.

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