Groundwater-controlled phosphorus release and transport from sandy aquifer into lake

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Abstract

Awareness of groundwater-borne dissolved inorganic phosphorus (DIP) loadings into lakes and its role in lake eutrophication is increasing, albeit DIP of natural origin is often ignored. Release of geogenic DIP from an adjacent aquifer and its transport with groundwater into a eutrophic lake is described by combining hydrogeochemical data collected in this study (sampling of piezometers, hydrogeochemical profiles, and seepage meters) with groundwater flow and discharge rates from earlier studies. The major part of the DIP that entered the lake with discharging groundwater was mobilized from iron hydroxides reduced by organic matter buried in the sediments of the old lake bottom. This is indicated by the correlation between DIP and ferrous iron (Fe²⁺) concentrations, with a DIP/Fe²⁺ molar ratio of 0.06, and an increase in pH. One-dimensional reactive transport modeling indicated that high discharge rates (> 0.1 m d⁻¹) of anoxic groundwater upwelling in areas adjacent to the lakeshore prevent downward diffusion of oxygen into the aquifer and do not leave enough time for DIP to become rebounding to the mineral phases at the sediment-water interface. The groundwater-controlled DIP input into the lake calculated along a two-dimensional cross-section averaged 0.01 mol DIP m⁻² yr⁻¹. A 2 m wide offshore high discharge zone delivered approximately 13% of the DIP into the lake. The continuous, external loading of geogenic DIP sustains lake eutrophication and explains the failure of two previous lake restoration attempts.

Groundwater transport of phosphorus into surface waters has been the subject of many studies (Vanek 1993; Kang et al. 2005; Lewandowski et al. 2015; Meinikmann et al. 2015). Groundwater-borne dissolved inorganic phosphorus (DIP) discharge into lakes can be higher than previously thought (Kang et al. 2005; Lewandowski et al. 2015; Meinikmann et al. 2015). High internal and external DIP inputs into lakes often result in lake eutrophication and complicate lake restoration efforts (Phillips et al. 1994; Kang et al. 2005; Katsev and Dittrich 2013). DIP transport and loading have mainly been studied in the context of anthropogenic pollution (Vanek 1993; Heathwaite and Dils 2000; Spiteri et al. 2007; Meinikmann et al. 2015). Also, some of the previous investigations do not clearly state the source of phosphorus (Katsev and Dittrich 2013; Kidmose et al. 2013; Knights et al. 2017). The importance of natural external phosphorus sources (located within the connecting aquifer) for lake eutrophication is rarely mentioned. Heathwaite and Dils (2000) noted that phosphorus-rich Triassic deposits underlying Pleistocene sand in the Pistern Hill catchment (United Kingdom) may be an additional DIP source in the aquifer, which is also influenced by nutrient loading from the arable lands. Regional groundwater flow in a sandy Pleistocene aquifer in Finland delivers DIP to lakes located low in the landscape and determines their trophic state (Ala-aho et al. 2013). In south-central Wisconsin (United States), anthropogenic acidification led to the weathering of phosphate-rich minerals and resulted in elevated DIP concentrations in Cambrian aquifers (McGinley et al. 2016). Thus, a closer focus on the potential role of discharge of DIP of natural origin in lakes eutrophication is needed, especially in the cases of lake restoration and management planning.

DIP mobilization in freshwater aquifers due to saltwater intrusion (coastal environments) is, on the other hand, well documented. DIP desorbs from ferric iron hydroxides along pH and salinity gradients (Spiteri et al. 2008). DIP mobilization from phosphorus-bearing minerals and organic matter at the sediment-water interface (Fillos and Swanson 1975; Löfgren and Boström 1989; Ahlgren et al. 2011; Shaw et al. 2013) and

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wetlands (Carlyle and Hill 2001; Hoffmann et al. 2006) in freshwater environment have also been widely investigated as a part of an internal phosphorus cycle working mainly on an intra-annual timescale. However, up until now, no studies describe DIP mobilization and transport from natural sources (minerals, organic matter) within freshwater sandy aquifers, not influenced by saltwater intrusion, and as a role of an external groundwater-borne natural DIP input in lake eutrophication. Meinikmann et al. (2015) suggested that part of DIP discharged to the eutrophic Lake Arendsee may be released by natural processes. However, due to the anthropogenic DIP inputs to the lake, the natural DIP mobilization processes occurring in the aquifer could not be specifically described.

Lakes with elevated DIP concentrations occur also in post-glacial aquifers (Ala-aho et al. 2013). Groundwater can be enriched in reactive DIP released from mineral phases in aquifers, that is, aluminum, iron, and manganese hydroxides, calcite, hydroxyapatite, vivianite, and organic carbon (Reddy et al. 1999; Lewandowski et al. 2015). The transport of released DIP to the aquifer-lake interface is enhanced under oxidizing conditions (Lewandowski et al. 2015) and occurs mostly along deep circulation flow paths discharging into lakes located low in the landscape, common in postglacial areas (Ala-aho et al. 2013). Prior to groundwater discharge into the lake, a DIP resorption onto the sediments occurs mostly if the conditions at the sediment-water interface are oxic (Vanek 1993; Lewandowski et al. 2015). During anaerobic conditions, DIP can be precipitated as hydroxyapatite and vivianite (Slomp and van Cappellen 2004). However, even if groundwater is saturated with phosphorus-bearing minerals, their precipitation might be kinetically hindered (Lewandowski et al. 2015). We hypothesize that the release and transport of phosphorus in postglacial sandy aquifers can lead to eutrophication of lakes in many countries. Our study sheds new light on the importance of external, aquifer-borne DIP transport into lakes and shows how groundwater-lake interactions affect the loading of DIP into lakes.

Our study was conducted at Lake Væng (Denmark) where groundwater-lake interactions have been the subject of studies by Kidmose et al. (2013), Sebok et al. (2013), and Kazmierczak et al. (2016). Lake Væng has been eutrophic for at least 250 yr due to a high phosphorus concentration (Anderson and Odgaard 1994). Two bio-manipulation attempts, in 1986–1988 and 2007–2009, resulted in only a short-term improvement of water quality (Meijer et al. 1994; Sendergaard et al. 1998, 2016). Kidmose et al. (2013) indicated a relation between the average total phosphorus (TP) concentration of 0.162 mg L⁻¹ in groundwater discharging to the lake and the TP concentrations in the lake water, which in the period from 2008 to 2009 ranged between 0.036 and 0.196 mg L⁻¹. However, the sources of phosphorus to the groundwater and the processes responsible for its release and transport in the aquifer were not resolved.

The objectives of the article are: (1) to identify the sources of DIP discharging into a groundwater-dominated lake, (2) to understand the hydrogeochemical mechanisms responsible for phosphorus mobilization, transport, and discharge, (3) to address, via modeling, the relationship between groundwater discharge rates and DIP retention at the sediment-water interface, and (4) to quantify groundwater-borne DIP loads to a lake and to show its implications for lake eutrophication.

**Study area**

**Site description**

Lake Væng, with its topographical catchment of 9.8 km² (Kidmose et al. 2013), is located in the upper part of the Gudenå river catchment, central Jutland, Denmark (Fig. 1a). The lake has a surface area of 0.16 km², and a maximum water depth of 1.9 m (Jeppesen et al. 1998). The lake is located in a Pleistocene erosional valley filled mainly with sand and gravel of late Pleistocene to early Holocene age (Fig. 2). Based on the geomorphology of the near-lake area two sedimentation terraces can be distinguished: a terrace (II) with a top at the elevation of approximately 40 m a.s.l. and a younger terrace (I) with a top at the elevation of approximately 30 m a.s.l. (Figs. 1c, 2). The lake level is rather stable at 26.4 m a.s.l.

Terrace I was probably formed during the early Holocene, when lake stages in northern Europe were up to 4 m higher than modern water levels (Kaiser et al. 2012). The erosional valley cuts through the sand and clay of previous glacial and interglacial periods underlain by Miocene lacustrine quartz sand traversed with coal layers and fine sand, silt, and clay deposited during Miocene marine transgression-regression stages (Houmark-Nielsen 1999, 2011; Rasmussen et al. 2010). Except near the shore zones, the lake bottom is covered by a low-permeable Holocene gyttja layer (Fig. 1c) with a thickness of up to 11.5 m (Kazmierczak et al. 2016).

The lake catchment is used primarily for agriculture (67%) and forestry (20%). Miocene quartz sand is extracted in a sand-pit located 400 m west from Lake Væng. The extraction base is at approximately 40 m a.s.l. Mining activities have led to the partial exposure of the Miocene coal layers.

**Groundwater-lake interactions**

Lake Væng is a groundwater-dominated lake, with groundwater constituting 74% of the water budget (Kazmierczak et al. 2016). Discharge from the lake takes place at its southern side, and only via a surface water outlet and not via groundwater flow. The aquifer interacting with the lake is mainly unconfined and at a steady-state with heads varying between 26.4 m a.s.l. at the lake to 45 m a.s.l. at the groundwater divides (Fig. 1b; Kazmierczak et al. 2016). The aquifer interacting with the lake is underlain by a continuous Miocene clay layer at an elevation of −10 m (bottom of the cross-section in Fig. 2). Regional groundwater flow occurs along horizontal flow paths (Kazmierczak et al. 2016) (Fig. 1b). The gyttja layer covering the lake bottom acts as a flow barrier. Therefore, the regional groundwater flow
system splits up into four groups of flow paths (Fig. 2) identified by hydraulic head measurements, hydrogeological modeling, and hydrogeochemical tracers (Kidmose et al. 2013; Kazmierczak et al. 2016). Flow path 1 upwells within a 20 m wide seepage face adjacent to the western lakeshore, flow path 2 seeps through the gyttja layer, and flow path 3 passes underneath the lake’s gyttja layer and discharges through the eastern sandy lakebed and at an eastern seepage face, both are flow convergence zones. The deepest flow, path 4, passes underneath the lake and terminates in the Gudenå river, located east of Lake Væng (Fig. 2). High spatial and temporal heterogeneity of groundwater fluxes occurred at the eastern sandy lakebed (flow path 3, Sebok et al. 2013; Kazmierczak et al. 2016). Seepage rates ranged between 0.02 m d\(^{-1}\) close to the sand/gyttja border 20 m offshore and 0.62 m d\(^{-1}\) in a narrow zone located 5–7 m offshore (referred to as the high discharge zone; Kazmierczak et al. 2016). Flow rates reached up to 7.4 m d\(^{-1}\) in single groundwater springs in the lakebed (Kidmose et al. 2013).

TP concentrations in the lake water during the period of 1985–2015 varied between 0.036 and 0.196 mg L\(^{-1}\) (Meijer et al. 1994; Søndergaard et al. 1998, 2016). High TP concentrations in the lake water of up to 0.16 mg L\(^{-1}\) were also estimated for the period of 1770–1990, based on diatom analysis (Anderson and Odgaard 1994).

Methods

DIP mobilization, transport, and loading to the lake were investigated by sampling 11 catchment wells, 100 piezometers, 9 hydrogeochemical profiles, 5 seepage meter samples, and 1 soil water sample (Table 1).

Aquifer

Catchment wells

The relation between Fe\(^{2+}\) and DIP at the catchment scale along the regional flow paths was investigated by sampling of 11 catchment wells (Fig. 1b) at households and waterworks in May 2012. Screens had a length of 1–12 m and were installed 9–103 m below the terrain surface.

Piezometers and piezometer transects

One hundred stainless steel piezometers with an inner diameter of 20 mm and a 0.1 m long screen were permanently installed for monitoring in five transects perpendicular to the lakeshore (E1 to E4 and W), around the lakeshore outside the transects (nearshore single piezometers), and below an 11 m thick gyttja layer (piezometer E2.1) (Fig. 1c). The transects were installed parallel to the regional groundwater flow paths, covering the areas with the highest groundwater discharge (Kidmose et al. 2013; Sebok et al. 2013). Transects E1 to E4 were located along the eastern shore and consisted of 5 on-
Fig. 2. DIP, ferrous iron (Fe$^{2+}$), and ammonium (NH$_4^+$) concentrations increased along the anoxic groundwater flow paths indicating DIP release from iron hydroxides reduced in the anoxic part of an aquifer by organic matter. The highest DIP concentrations were in the sediments of terrace I. The size of each circle with the central point of the circle at the location of the piezometer screen is proportional to the concentration of component in groundwater sampled at each of the piezometers. Circles for the chosen concentrations are shown in the cross-section legends. The figure shows all data for piezometers in transect W and E2, but only the top and bottom samples of profiles P1–P7 and samples located each 2 m in hydrogeochemical profile P8. For the profiles P3–P7 an average DIP, Fe$^{2+}$, and NH$_4^+$ concentrations for all profiles were used. Detailed DIP and Fe$^{2+}$ concentrations in profiles P1, P7, and P8 are plotted in Fig. 5. Location of the cross-section is indicated in Fig. 1c. Flow paths and geology were adapted from Kazmierczak et al. (2016). The dashed part of the flow lines is out of the horizontal scale and represents a stretch of 300 m.
Table 1. Field installation at Lake Væng. Numbers in parentheses refer to number of wells, samples in hydrogeochemical profiles, seepage meter samples, or soil water samples. Sampling sites used to solve the detailed objectives (*) in Transects and Hydrogeochemical profiles sections are listed after each objective.

| Monitoring method          | Objectives                                                       | Sampling date |
|----------------------------|------------------------------------------------------------------|---------------|
| Catchment well (11)        | Fe$^{2+}$ vs. DIP—catchment scale (Figs. 4, 6)                   | May 2012      |
| Transect                   | DIP mobilization and transport near the lake (Figs. 2, 3, 6, 7)  |               |
| W (52)                     | *processes in groundwater inflowing from the catchment,          | Jun 2013      |
| E1 (10)                    | W and E1–E4                                                      | Jan 2013      |
| E2 (9)                     | *processes along deep circulation flow paths, E1–E4              | Sep 2013      |
| E3 (10)                    | *processes at the flow convergence zone, E1–E4                   | Jan 2013      |
| E4 (10)                    | *processes at the high discharge zones, W and E2                 | Nov 2012      |
| Single piezometer E2.1 (1) | Fe$^{2+}$ vs. DIP below the thick gyttja layer (Fig. 2)         | Sep 2013      |
|                            | Processes along deep circulation flow paths                     |               |
| Nearshore single piezometer (8) | Fe$^{2+}$ vs. DIP—areas of minor groundwater discharge to the lake (Figs. 4, 6) | Dec 2012      |
| Hydrogeochemical profile   | DIP mobilization and vertical transport near the lake (Figs. 5, 8; Table 2) |               |
| P1 (9)                     | *processes at the flow convergence zone (P1, P2)                 | Sep 2013      |
| P2 (9)                     | *processes at the on-land high discharge zone (P2)               | Sep 2013      |
| P3–P7 (5 profiles × 14 samples) | *processes at the offshore high discharge zone (P3–P7)        | Sep 2013      |
| P8 (15)                    | *DIP concentration vs. recharge area (P8, P9)                    | Jan 2012      |
| P9 (13)                    | *processes along deep circulation flow paths (P1–P9)            | Nov 2011      |
| Seepage meter P3–P7 (5)    | DIP loading at the offshore high discharge zone (Table 2)       | Sep 2013      |
| Soil water sample P2 (1)   | DIP loading at the on-land high discharge zone (Table 2)        | Sep 2013      |

Hydrogeochemical profiles

Hydrogeochemical profiles were obtained by a temporary installation of nine stainless steel push-down wells (P1 to P9, Fig. 1c). Wells P1 and P2 were located on-land, at the eastern side of the lake near transect E2. Profile P1 was installed near the eastern groundwater divide and profile P2 at the on-land high discharge zone to better understand flow distribution and changes in groundwater chemistry at the flow convergence zone (Kazmierczak et al. 2016). The profiles were sampled with intervals of 0.25–0.5 m to a depth of 3 m below surface. Wells P3–P7 were located in the offshore high discharge zone to investigate the relationship between high groundwater flow rates and DIP loading into the lake. Samples in this area were taken at an interval of 0.1–0.25 m to the depth of 2 m below the lakebed. Hydrogeochemical profiles P8 and P9 were installed at the side of the lake where most of the topographical catchment of the lake is located, to relate the changes in DIP concentration and groundwater chemistry over depth to the groundwater recharge areas. Push-down well P8 was installed close to transect W and P9 north of transect W. The wells P8 and P9 were sampled at 1–4 m depth interval and their maximum screening depth reached 28 m and 27.5 m below surface, respectively.

Groundwater sampling

Prior to the sampling of groundwater for hydrogeochemical analysis, single piezometers and piezometers in transects W and E1–E4 were clean-pumped and left for at least 2 months for equilibration. The push-down wells P1–P9 were sampled...
immediately after reaching each target depth. Groundwater sampling was conducted in November 2011 for profile P9 and in January 2012 for profile P8. Transect E4 was sampled in November 2012, nearshore single piezometers in December 2012, transects E1 and E3 in January 2013, and transect W in June 2013. Samples from profiles P1–P7, single piezometer E2.1, and transect E2 were obtained in September 2013 (Table 1).

Piezometers and wells were sampled using a peristaltic pump, except profiles P8 and P9 where water was driven to the surface by pressurizing the well tube equipped with a check valve using N₂ gas (Appelo and Postma 2005). Three volumes of the water inside the well were exchanged prior to sampling. Samples were collected with a 60 mL syringe connected to silicon tubing. Electrical conductivity (EC), pH, and dissolved oxygen (DO) were measured in the field in a flow cell.

Sediment-water interface and seepage faces

Six water samples were taken in September 2013 at hydrogeochemically active sediment-water interface and at seepage face on land to check the influence of these interfaces on the chemistry of groundwater discharging at high discharge zones. Groundwater at the eastern seepage face, at the location of P2, was sampled with a soil water sampler made of Teflon. The sampler was placed just below the wetland surface and connected by nylon tubing to a 60 mL syringe collecting the groundwater.

Groundwater samples from the offshore high discharge zone were taken with the use of five seepage meters (Lee 1977) installed at the sandy lakebed at the location of P3–P7. The flow rates were estimated using the method described by Lee (1977) and prior to sampling the valve at the seepage meter remained open for a time, allowing exchange of at least two volumes of the water inside the seepage meter. After flushing of the seepage meter, the valve was closed and groundwater sample was taken with a 60 mL syringe connected to the seepage meters by silicon tubing. A 15 mL aliquot was transferred into a 20 mL polypropylene vial in order to measure the groundwater EC, pH, and DO.

Chemical analysis

DO, pH, and EC were measured using a Standard Luminescent/Optical Dissolved Oxygen Probe, a PHC101 Standard Gel Filled pH Electrode, and a CDC401 Standard Conductivity Probe, respectively. All were of the HACH-LANGE IntelliCAL™ type, and connected to a HQ40d Portable Multi-Parameter Meter.

All water samples collected in the field were immediately filtered through Sartorius Minisart 0.2 μm cellulose-acetate syringe filters into 20- and 50-mL bottles and stored in the refrigerator. Prior to filtration, the filters were flushed with N₂ gas to prevent formation of iron hydroxides and coprecipitation of DIP. Samples for DIP and cation analysis were preserved with sulfuric acid and 2 vol% of 7 mol L⁻¹ nitric acid, respectively. Field analysis of ferrous iron (Fe²⁺) concentrations was conducted using the Ferrozine method (Stookey 1970). The absorbance at 562 nm of the Fe²⁺-Ferrozine complex was measured using a HACH-LANGE DR2800™ Portable Spectrophotometer. Alkalinity was measured in the field using the Gran-titration method (Appelo and Postma 2005).

Calcium (Ca²⁺), magnesium (Mg²⁺), sodium (Na⁺), potassium (K⁺), manganese (Mn²⁺), and iron (Fe_total) concentrations were analyzed using inductively coupled plasma optical emission spectroscopy. Sulfate (SO₄²⁻), chloride (Cl⁻), and nitrate (NO₃⁻) concentrations were determined using ion chromatography. DIP was measured by the molybdenum-blue spectrophotometric method (Hansen and Koroleff 1999). Nitrite (NO₂⁻) and ammonium (NH₄⁺) were analyzed spectrophotometrically on a flow injection system QuickChem 8500 Series, Lachat Instruments.

DIP loading into the lake

DIP loading into the lake in the studied two-dimensional (2D) cross-section (Fig. 1c) was calculated based on the flow rates modeled by Kazmierczak et al. (2016) and average DIP concentrations in the groundwater discharge areas obtained during the present study. Only advective DIP transport was considered. Average DIP concentrations in anoxic groundwater were calculated for: (1) the area of upwelling of anoxic groundwater at the nearshore zone of transect W, P8, and E2.1, (2) P3–P7 installed at the high discharge offshore zone, and (3) transect E2, including P1 and P2. All piezometers in each of the groundwater discharge zones had a similar groundwater chemistry and hydrogeological conditions (Kazmierczak et al. 2016). Thus, for simplification, we assumed that each zone had uniform DIP mobilization processes resulting in transport of a calculated average DIP concentration. No DIP retention in the wetlands/seepage faces, gyttja deposits covering the lake bottom and at the sediment-water interface was considered, as we assumed that it is a part of an internal DIP cycle in a lake, where DIP is adsorbed and remobilized on an intra-annual timescale (Fillos and Swanson 1975; Vanek 1993; Hoffmann et al. 2006; Shaw et al. 2013).

Hydrogeochemical modeling

Calculation of aqueous speciation, electrical balances, and mineral saturation indices (SIs) in all water samples, and one-dimensional (1D) reactive transport modeling at the offshore high discharge zone were conducted using PHREEQC 2.0 (Parkhurst and Appelo 1999).

The influence of the (upward) discharge velocity of ferrous groundwater across the lakebed on the transport of groundwater-borne DIP into the oxic lake water column at P3–P7 was investigated by reactive transport modeling. The 1D conceptual reactive transport model was set up to understand the role of the high discharge zones in prevention of
DIP retention by iron hydroxide formation in the lakebed. The model comprised a 0.2 m long column, discretized into 20 cells. The inflowing and initial solution of all cells resembled the anoxic groundwater in P3–P7 (temperature 8°C, pH 6.5, alkalinity 1 meq L\(^{-1}\), Fe\(^{2+}\) 55 μmol L\(^{-1}\) and DIP 2.1 μmol L\(^{-1}\)). The hydrogeochemical composition of this solution was an average for all groundwater samples taken at P3–P7, except for pH where the median value was used. The upper boundary condition was oxic lake water containing 1 mol Cl\(^{-}\) L\(^{-1}\) as a tracer, no Fe\(^{2+}\) and DIP and with O\(_2\) of −0.68. For all cells, an effective diffusion coefficient of 0.3 × 10\(^{-9}\) m\(^2\) s\(^{-1}\), and a dispersivity of 0.001 m were applied. Ferrihydrite (Fe(OH)\(_3\)) in the database was allowed to precipitate. Adsorption/coprecipitation of phosphate to ferrihydrite was simulated, taking into account the oxidation kinetics of groundwater-delivered Fe\(^{2+}\) by O\(_2\) transported diffusively from the upper boundary (lake water) against the direction of flow, and the subsequent DIP adsorption onto precipitated iron hydroxides. We used Dzombak and Morel (1990) surface complexation model for hydrous ferric oxide (HFO), which is available in PHREEQC. The number of moles of weak and strong sites per mol Fe equaled 0.2 and 0.005, respectively, and the surface area was set to 4.6 × 10\(^4\) m\(^2\) mol\(^{-1}\). The HFO amount was linked to the amount of Fe(OH)\(_3\) precipitated. To cover the variety of discharge velocities at Lake Væng (Kazmierczak et al. 2016), the model was run for pore-water velocities of 0.001, 0.01, 0.1, and 1 m d\(^{-1}\). The kinetics of the oxidation of dissolved Fe\(^{2+}\) with O\(_2\) were simulated using the rate equation (Davis and Seed 1983):

\[
\frac{dm_{\text{Fe}}(\text{II})}{dt} = k \times (a\text{OH}^+)^2 \times pO_2 \times m_{\text{Fe}}(\text{II})
\]

where \(t\) is time, \(a\text{OH}^+\) activity of hydroxyl ions, \(pO_2\) oxygen partial pressure, and \(m_{\text{Fe}}(\text{II})\) is total molality of Fe\(^{2+}\) in solution. Two reaction rate constants (\(k\)) were tested: \(k = 8 \times 10^{13} \text{ mol}^{-2} \text{ atm}^{-1} \text{ min}^{-1}\) (Singer and Stumm 1970) and \(k = 2 \times 10^{13} \text{ mol}^{-2} \text{ atm}^{-1} \text{ min}^{-1}\) (Davis and Seed 1983). The rate constant given by Singer and Stumm (1970) is perhaps the most classical choice, although it was determined for iron oxidation in acid mine drainage. The rate described by Davison and Seed (1983) was developed for natural freshwaters in the pH range 6.5–7.4.

Changes in DIP concentration along the flow paths

Anoxic zone: DIP vs. Fe\(^{2+}\) and NH\(_4^+\)

DIP and Fe\(^{2+}\) concentrations in the anoxic part of the aquifer increased along the flow paths and were highest in the sediments of terrace I (Figs. 2, 4). The trend was visible in the area of transect W, where groundwater that flowed toward the lake was enriched in up to 3.7 μmol DIP L\(^{-1}\) and up to 57 μmol Fe\(^{2+}\) L\(^{-1}\) after it crossed the border between terrace II and I (anoxic flow path 1 in Fig. 2). High DIP (3.4 μmol L\(^{-1}\)) and Fe\(^{2+}\) (57 μmol L\(^{-1}\)) concentrations similar to those in the groundwater in the nearshore piezometers of transect W were also in piezometer E2.1 installed below the gyttja sediments in the central part of the lake (Fig. 2).

The groundwater of the deep-circulation flow paths (flow path 3) was further enriched with DIP and Fe\(^{2+}\) (Fig. 2). DIP and Fe\(^{2+}\) concentrations in groundwater that discharged at the eastern side of the lake reached 4.11 μmol L\(^{-1}\) and 76 μmol L\(^{-1}\), respectively (Figs. 2, 6). The pore-water concentrations of DIP and Fe\(^{2+}\) in the upper 2 m of the lakebed sediments at the eastern offshore high discharge zone (P3–P7) were nearly constant over depth, fell within similar ranges in all profiles, and averaged 2.2 ± 0.4 μmol L\(^{-1}\) and 53 ± 6 μmol L\(^{-1}\), respectively (P7 in Fig. 5). Groundwater in transects with the highest pH values (E1, E2, and P1, P2) showed an irregular DIP distribution with an average DIP concentration 1.6 μmol L\(^{-1}\). That was slightly lower than in the remaining eastern transects (E3 and E4), where DIP concentrations averaged 2.2 μmol L\(^{-1}\). The increase in DIP and Fe\(^{2+}\) concentration in the anoxic part of an aquifer was followed by an increase in NH\(_4^+\) concentration (Fig. 2). However, this trend was uneven and NH\(_4^+\) concentration in the wells of transect W located furthest from the lake was also relatively high (Fig. 2).

Seepage faces and the sediment-water interface were an additional source of DIP in discharging groundwater. The highest DIP and NH\(_4^+\) concentrations were in the surface discharged at transects E1–E4 and P1–P7 had a higher Cl\(^-\), Ca\(^{2+}\), and Na\(^+\) concentrations than groundwater of flow paths 1 and 2 at the western side of the lake (Kazmierczak et al. 2016). Groundwater of transects E1 and E2 and P1 and P2 was also enriched in HCO\(_3^-\) (Kazmierczak et al. 2016). These differences in the composition of groundwater were paralleled by differences in pH. The pH values ranged from 6 to 7 at the western side of the lake and up to 8.34 at the eastern side of the lake (Fig. 3). The pH values in anoxic groundwater of terrace I at transect W increased along the flow paths while Ca\(^{2+}\) and HCO\(_3^-\) concentrations were nearly constant. The thickness of the oxic zone (DO > 0.026 mmol L\(^{-1}\)) was approximately 7 m and 1 m at the western and eastern sides of the lake, respectively (Kazmierczak et al. 2016; Fig. 2). The sediment-water interface in the area of the offshore high discharge zone (P3–P7 in Fig. 8) was also under anoxic conditions.

Results

Groundwater chemistry near the lake

EC in the aquifer interacting with Lake Væng ranged from 105 μS cm\(^{-1}\) in the shallow, oxic groundwater at the western side to 476 μS cm\(^{-1}\) in anoxic groundwater that discharged at the eastern side of the lake. The most abundant anions were HCO\(_3^-\) (0.21−2.56 mmol L\(^{-1}\)) and SO\(_4^{2-}\) (0.03–0.73 mmol L\(^{-1}\)). The dominant cation was Ca\(^{2+}\) (up to 1.9 mmol L\(^{-1}\)). Anoxic groundwater of deep circulation flow paths (flow path 3) that...
discharge at the eastern, sandy lake bottom (P3–P7) and at the adjacent seepage face in the wetland (P2 in Table 2). Groundwater sampled from the eastern seepage face contained 4.3 μmol DIP L⁻¹ and 46 μmol Fe²⁺ L⁻¹ (P2 in Table 2). Concentrations of these two constituents were also high at the sediment-water interface at the offshore high discharge zone (P3–P7 in Table 2) and ranged between 46 and 68 μmol Fe²⁺ L⁻¹ and 2.3 and 9.7 μmol DIP L⁻¹. NH₄⁺ concentration varied significantly (Table 2), was three to eight times higher at the interfaces than in the aquifer, and on average increased from 4 to 22 μmol L⁻¹.

DIP and Fe²⁺ concentrations increased simultaneously in the anoxic groundwater (DO < 1 mg L⁻¹) (Figs. 2, 5, 6). The DIP and Fe²⁺ concentrations in the area of transect W increased from 0.3 to 3.8 μmol L⁻¹ and from 0 to 57 μmol L⁻¹, respectively. Assuming a causal interdependency, 3.5 μmol DIP L⁻¹ was mobilized in the aquifer per release of 57 μmol Fe²⁺ L⁻¹ (Fig. 6a). The clear relationship between the DIP and Fe²⁺ concentration faded at the discharge zone of the deep circulation flow paths (group 3, Fig. 2) upwelling at the eastern transects E1–E4 and P1–P7 was enriched in Cl⁻, Na⁺, and Ca²⁺ (red and black dots). Groundwater in profiles P1 and P2 and transects E1 and E2 had additionally high HCO₃⁻ concentration (black dots). Gray dots indicate shallow single piezometers installed around the lake and P9 installed in the sediments of terrace I in the north-western area of the lake. Similar color code is used in Figs. 6, 7.

Oxic zone: DIP vs. Ca²⁺

In the oxic zone at transect W, Ca²⁺ and DIP concentrations increased simultaneously (Fig. 7a). The oxic groundwater contained 0.2–3.4 μmol DIP L⁻¹, negligible Fe²⁺ concentrations and

Fig. 3. Saturation indices of groundwater for vivianite (a) and hydroxyapatite (b) increased with an increasing pH. Groundwater at the eastern side of the lake, enriched in HCO₃⁻ was supersaturated for vivianite and hydroxyapatite. Location of transects, piezometers, and hydrogeochemical profiles is shown in Fig. 1c. Data were divided into four groups, based on the piezometer location, screening depth, and hydrogeochemical types of groundwater at Lake Væng described in detail by Kazmierczak et al. (2016). Transect W, piezometer E2.1 and P8 represent groundwater of the regional flow system with EC < 300 μS cm⁻¹ that flowed across the boundary between terraces I and II (white dots). Groundwater of the deep circulation flow paths (group 3, Fig. 2) upwelling at the eastern transects E1–E4 and P1–P7 was enriched in Cl⁻, Na⁺, and Ca²⁺ (red and black dots). Groundwater in profiles P1 and P2 and transects E1 and E2 had additionally high HCO₃⁻ concentration (black dots). Gray dots indicate shallow single piezometers installed around the lake and P9 installed in the sediments of terrace I in the north-western area of the lake. Similar color code is used in Figs. 6, 7.

Fig. 4. Highest DIP concentrations in topographical catchment of the lake were in the anoxic aquifer near the lake. Average DIP concentrations are plotted for transects W, E1, E2, E3, E4 and profiles P1, P2, P3–P7, PB and P9. The size of the circle is proportional to DIP concentration as in Fig. 2.
showed no gradients for DIP concentration along the flow paths. Approximately 2 μmol DIP L\(^{-1}\) was mobilized in the aquifer per 1 mmol Ca\(^{2+}\) L\(^{-1}\) (Fig. 7a). This relation faded in the areas of the aquifer (Fig. 7b), where mixing with groundwater enriched in Ca\(^{2+}\) occurred (Kazmierczak et al. 2016).

### Fig. 5. DI P (red dots) and Fe\(^{2+}\) (gray dots) concentrations increased simultaneously in the anoxic part of an aquifer and were nearly constant at the offshore high discharge zone (P7). Groundwater in the major part of an aquifer was subsaturated for calcite (white dots), hydroxyapatite (light blue dots) and vivianite (dark blue dots). The hydrogeochemical profiles were installed at: western seepage face (P8), offshore high discharge zone (P7), and eastern seepage face (P1). For the flow directions, see Fig. 2.

**DIP vs. K\(^{+}\) and NO\(_3^−\)**

There was no relation in the aquifer between the DIP, K\(^{+}\), and NO\(_3^−\) concentrations, which are components of N-P-K fertilizers (Cooke and Williams 1973). The highest K\(^{+}\) concentration of 0.17 mmol L\(^{-1}\) was in a sample with 0.2 μmol DIP L\(^{-1}\).
In the remaining samples, the K⁺ concentration ranged from 0.01 to 0.07 mmol L⁻¹ and remained unchanged while DIP concentration increased. The sample with the highest NO₃⁻ concentration (1 mmol L⁻¹) contained 0.4 μmol DIP L⁻¹. The NO₃⁻ concentration in the remaining samples from the oxic zone ranged from 0 to 0.5 mmol L⁻¹ while DIP concentration increased from 0.2 to 3.4 μmol L⁻¹. Anoxic groundwater contained 0–0.26 mmol NO₃⁻ L⁻¹ and 0.17–4.11 μmol DIP L⁻¹. The highest NO₃⁻ concentrations were in samples with DIP concentration < 1.5 μmol L⁻¹, in both oxic and anoxic zones.

Saturation of groundwater with DIP-bearing minerals

Groundwater at the eastern side of the lake was saturated with respect to DIP-bearing minerals (vivianite, hydroxyapatite, and calcite). Changes in the saturation states with respect to DIP-bearing minerals were driven by changes in pH (Fig. 3), which was coupled to calcite dissolution and changes in partial CO₂ pressure. According to the PHREEQC calculations, groundwater became supersaturated for vivianite and hydroxyapatite when pH increased above neutral. Groundwater at transects E1, E2 and P1, P2 had a SI of up to 1.9 for vivianite and of up to 2.6 for hydroxyapatite (Fig. 3 and P1 in Fig. 5). In addition, the groundwater in this part of the aquifer was supersaturated for calcite (median SI of 0.15) and had a low partial CO₂ pressure (median P₃CO₂ 1.3 mbar). Groundwater at the remaining areas of the aquifer had a higher partial CO₂ pressure (median PCO₂ 10.5 mbar) and was subsaturated with respect to vivianite (SI from −10.0 to −0.80), hydroxyapatite (SI from −13 to −0.71) and calcite (SI from −2.8 to −0.38).

**Fig. 6.** DIP and Fe²⁺ concentrations increased simultaneously in the anoxic groundwater near the lake indicating DIP release from iron hydroxides reduced in the anoxic part of an aquifer. (a) Data from the western lakeshore, where groundwater of regional horizontal flow paths crossed the border between terraces I and II (transect W, piezometer E2.1 and P8). (b) Data from the catchment, single shallow piezometers around the lake, and from the eastern lakeshore (transects E1–E4, P1–P7) which was a flow convergence zone where mixing of different groundwater types occurred. The red dot with bars is an average concentration for the profiles P3–P7. The bar length shows ± 1 standard deviation (SD). Color code of the samples is as in Fig. 3.

![Fig. 6](image1)

**Fig. 7.** A relation between DIP and Ca²⁺ concentrations in oxic groundwater near the lake indicates DIP release from calcite or hydroxyapatite. (a) Data from the western lakeshore, where groundwater of regional horizontal flow paths crossed the border between terraces I and II (transect W and P8). (b) Data from P9, single shallow piezometers around the lake, and from the eastern lakeshore (transect E1 and E4, P1) which was a flow convergence zone where mixing of different groundwater types occurred. Color code of the samples is as in Fig. 3.

![Fig. 7](image2)
DIP retention controlled by flow velocities

DIP retention by iron hydroxide formation in the lakebed strongly depended on the velocity of discharging groundwater, as shown in the results of the conceptual model (Fig. 8). Concentrations of O₂ and Fe²⁺ showed an inverse pattern with increasing depth below the surface of the lakebed, as Fe²⁺ in the upward discharging groundwater became oxidized by O₂ that diffused downward into the lakebed against the direction of water flow. Iron hydroxide precipitation and, consequently, DIP retention within the lakebed sediment (Fig. 8, right panel) occurred at progressively shallower depth with increasing flow velocity. Accordingly, the concentration of groundwater-borne DIP that reached the lake water column increased with increasing flow velocity and ranged from 0.07 μmol DIP L⁻¹ to 1.85 μmol DIP L⁻¹ for the flow rates 0.001 m d⁻¹ to 1 m d⁻¹, respectively. Elevated flow rates allowed too little time for downward diffusion of oxygen, and for the oxidation of upward transported Fe²⁺ to occur within the lakebed sediment or in the connected aquifer (Fig. 8). At flow rates above 0.1 m d⁻¹, more than 73% of the groundwater DIP discharged directly into the lake. At flow rates below 0.01 m d⁻¹, the combined diffusive oxygen transport and Fe²⁺ oxidation kinetics at an increased residence time resulted in DIP sorption onto iron hydroxides within the lakebed. At flow rates around 0.001 m d⁻¹, the front of sorption of DIP onto iron hydroxides was located at a greater depth below the lake bottom (Fig. 8). The effect of using different reaction rate constants (Singer and Stumm 1970 vs. Davison and Seed 1983) was minor as compared to the effect of the flow rate. The modeled concentrations and DIP retention were nearly equal for both constants.

Annual groundwater-borne external DIP loading into Lake Væng equaled 0.01 mol DIP m⁻². The average DIP concentrations in the studied 355 m long cross-section (Figs. 1c, 2) equaled: (1) 2.0 μmol L⁻¹ for the nearshore area of transect W and piezometer E2.1, (2) 2.2 μmol L⁻¹ in P3–P7 installed below the sandy lake bottom, and (3) 1.9 μmol L⁻¹ at the eastern seepage face and over the distance 0–3 m offshore (transect E2 and P1 and P2). The corresponding groundwater discharge equaled 2.56 m³ d⁻¹ (54%) at the western seepage face, 0.78 m³ d⁻¹ (16%) through the gyttja layer, 1.03 m³ d⁻¹ (22%) at the sandy lakebed (in this 0.59 m³ d⁻¹ at the high discharge zone), and 0.39 m³ d⁻¹ (8%) at the eastern seepage face (Kazmierczak et al. 2016). Thus, groundwater-controlled DIP input into the lake in the studied 2D cross-section equaled 3.58 mol yr⁻¹, out of which 2.17 mol yr⁻¹ discharged at the seepage faces and 0.84 mol yr⁻¹ at the sandy lakebed. Thirteen percentage of DIP loading through the sandy lakebed (0.47 mol DIP yr⁻¹) took place at the 2 m wide offshore high discharge zone, which covered less than 1% of the lake bottom in the studied 2D cross-section (Fig. 9).

Discussion

The present study shows that DIP released from the phosphorus-bearing minerals in the aquifer may lead to the maintenance of lake eutrophication. The DIP mobilization in the aquifer interacting with Lake Væng was influenced by: (1) accumulation of the phosphorus-rich iron hydroxides and organic matter within the part of the aquifer that represents the old lake bottom, (2) the anoxic conditions, and (3) the...
flow system, including flow rates. Anoxic groundwater discharged at high rates through the old lake bottom and transported released DIP into the lake.

**DIP origin**

Previous studies have reported on the mobility of DIP of natural origin in sandy (Ala-aho et al. 2013) or bedrock aquifers (McGinley et al. 2016). Likewise, the DIP in the aquifer interacting with Lake Væng must have a natural origin. The transport of DIP from the upstream arable lands could be excluded, because there were no correlations between DIP, K\(^+\), and NO\(^{-3}\) concentrations in the groundwater, ions typical for N-P-K fertilizers, livestock excreta, and domestic wastes (Cooke and Williams 1973) (see “DIP vs. K\(^+\) and NO\(^{-3}\)” section). Furthermore, based on diatom analysis, Lake Væng had been eutrophic for at least 250 yr (Anderson and Odgaard 1994) which was prior to the application of fertilizers started in 1950s and an inflow of sewage into the lake from 1964 to 1983. Thus, prior to the 1950s, the DIP load was transported either by a surface runoff from an eroded catchment (Anderson and Odgaard 1994) or by discharging groundwater from phosphorus-bearing minerals in the aquifer.

The lowest groundwater DIP concentrations in the anoxic zone were in the catchment wells (Figs. 4, 6) and the piezometers of transect W (anoxic flow path 1 in Fig. 2) situated at the upstream part of the lake. Consequently, part of the DIP may have been transported from the brown coal layers exposed to weathering in the nearby sand pit or from Miocene aquifer containing DIP (Figs. 2, 4). The subsequent increase of DIP toward the lakeshore suggests that additional DIP mobilization took place in the deposits of the old lake bottom (Kazmierczak et al. 2016) at terrace I (Fig. 2). Therefore, our hypothesis is that DIP in the anoxic part of the aquifer was of natural origin and was released from iron hydroxides, which typically are abundant in lacustrine sediments (Katsev and Dittrich 2013; Lewandowski et al. 2015). The relation between DIP and Ca\(^{2+}\) concentration in the oxic part of the aquifer (Fig. 7) suggests calcite dissolution as a main source of DIP, and thus also a natural DIP origin.

**DIP mobilization in the aquifer**

The simultaneous increases of DIP, Fe\(^{2+}\) (Figs. 2, 5, 6a), and pH (Fig. 3) in the anoxic groundwater indicate that DIP was released from iron hydroxides reduced by organic matter (Katsev and Dittrich 2013):

**Table 2.** Average DIP, Fe\(^{2+}\), and NH\(^{4+}\) concentrations at the seepage faces (P2) and at the sediment-water interface (P3–P7) were higher than in corresponding groundwater (profiles P2–P7) and indicate an additional DIP release under anoxic conditions.

| Sampling point       | DIP (μmol L\(^{-1}\)) | Fe\(^{2+}\) (μmol L\(^{-1}\)) | NH\(^{4+}\) (μmol L\(^{-1}\)) |
|----------------------|-----------------------|-------------------------------|-------------------------------|
|                      | Profile | Surface discharge | Profile | Surface discharge | Profile | Surface discharge |
| P2 (nearshore land)  | 1.7     | 4.3              | 38      | 46               | 3.0      | 10.5              |
| P3 (offshore)        | 2.0     | 9.7              | 52      | 55               | 4.6      | 38.6              |
| P4 (offshore)        | 2.1     | 5.4              | 60      | 68               | 4.2      | 15.3              |
| P5 (offshore)        | 2.3     | 2.7              | 53      | 46               | 4.2      | 15.2              |
| P6 (offshore)        | 2.1     | 4.2              | 51      | 61               | 4.0      | 15.4              |
| P7 (offshore)        | 2.2     | 2.3              | 53      | 54               | 4.4      | 26.7              |
| Avg. ± 1 SD (offshore)| 2.1 ± 0.1 | 4.9 ± 3.0              | 53.8 ± 3.6 | 56.8 ± 8.2       | 4.3 ± 0.2 | 22.2 ± 10.4       |

**Fig. 9.** Groundwater-controlled external DIP loading into the lake through the different components of the environment (wetlands/seepage faces, gyttja layer, and the sandy lakebed) maintains lake eutrophication. Total groundwater-borne DIP inputs equaled 3.58 mol yr\(^{-1}\) in the studied 2D cross-section (Kazmierczak et al. 2016), out of which 0.47 mol yr\(^{-1}\) discharged through the narrow high discharge zone (HDZ) at the sandy lakebed.
Organic matter reduction is also consistent with the slightly increased \( \text{NH}_4^+ \) concentrations toward the lake and at the sediment-water interface (Fig. 2, Table 2).

The approximate molar DIP/Fe\(^{2+} \) ratio of 0.06 (Fig. 6a) resulting from DIP release from early Holocene littoral sediments into groundwater at Lake Væng was 4–9 times lower than the ratios of 0.2–0.5 reported for sediment-water interface in recent lake sediments (Fillos and Swanson 1975; Lijklema 1980; Gunnars et al. 2002; Katsev and Dittrich 2013). DIP adsorbed to the iron minerals at the sediment-water interface is more easily released than DIP buried in the deeper parts of an aquifer, more permanently bound to mineral phases, which results in lower DIP/Fe\(^{2+} \) molar ratios (Katsev and Dittrich 2013; Lewandowski et al. 2015; O’Connell et al. 2015).

DIP could also be released during the oxidation of organic matter (Katsev and Dittrich 2013). Because the changes of \( \text{NH}_4^+ \) were unrelated to those of DIP, while a distinct relation between the Fe\(^{2+} \) and DIP concentrations existed (Figs. 2, 6a), it is more probable that organic matter was not a main DIP source and that the major part of DIP was released from the iron hydroxides (Eq. 2).

Vivianite dissolution (Postma 1981):

\[
\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O} \rightleftharpoons 3\text{Fe}^{2+} + 2\text{PO}_4^{3-} + 8\text{H}_2\text{O} \quad (3)
\]

was another potential DIP source, although of minor importance at Lake Væng. The presence of vivianite in Danish aquifers was reported by Walpersdorf et al. (2013). If DIP in groundwater only came from vivianite, the DIP/Fe\(^{2+} \) ratio should equal 0.67 (Eq. 3), which contrasts the aquifer DIP/Fe\(^{2+} \) ratio of 0.06 (Fig. 6a). The high concentration of DIP (median of 1.8 \( \mu \text{mol L}^{-1} \)) at the eastern side of the lake (Fig. 4) and the increase of SI for vivianite along the anoxic flow paths from 4.2 to 1.8 (Fig. 3) were more likely a result of the reduction of iron hydroxides (Walpersdorf et al. 2013) rather than of DIP release from vivianite. Vivianite dissolution has minor importance as compared to DIP desorption from iron hydroxides in freshwater environments (Katsev and Dittrich 2013).

Dissolution of hydroxyapatite (Guidry and Mackenzie 2003):

\[
\text{Ca}_5(\text{PO}_4)_3(\text{OH}) + \text{H}^+ \rightleftharpoons 5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{H}_2\text{O} \quad (4)
\]

and a DIP-containing calcite (House et al. 1986) were unlikely present in the anoxic zone, but occurred at the oxic zone. Anoxic groundwater showed no relation between the Ca\(^{2+} \) and DIP concentrations and the Ca\(^{2+} \) concentration near the western lakeshore was almost constant, while the DIP concentration increased. Groundwater in the oxic zone was saturated with calcite and hydroxyapatite (Fig. 3) and Ca\(^{2+} \) and DIP concentrations were related (Fig. 7a). Kinetics of DIP sorption onto calcite are fast (Sø et al. 2011), and DIP desorption was accordingly possible even at the high groundwater flow rates at Lake Væng.

**DIP fate in the aquifer and at the discharge surfaces**

Partial DIP immobilization occurred in the aquifer interacting with the lake. DIP concentrations decreased in the shallow, nearshore piezometers and at transects E1, E2 and P1, P2 (Figs. 4, 6, 7). Potential DIP sinks were: (1) vivianite, hydroxyapatite, and calcite precipitation, (2) DIP resorption onto iron hydroxides, and (3) binding of DIP into plants at the wetlands.

Groundwater of the deep circulation flow paths (flow path group 3) was supersaturated with vivianite, hydroxyapatite, and calcite (Figs. 3, 5). However, supersaturation by itself does not indicate a precipitation of the mineral (Lewandowski et al. 2015). According to Guidry and Mackenzie (2003), an increase of pH above 7 triggers the precipitation of vivianite and hydroxyapatite, which could be consistent with Fig. 3. Vivianite formed after reduction of iron hydroxides by organic matter and the release of DIP under similar conditions, that is, at Lake Ørn in Denmark (O’Connell et al. 2015). However, groundwater flow rates at the eastern side of the lake exceeded 1 m d\(^{-1} \) (Kazmierczak et al. 2016), which probably did not leave enough time for vivianite formation. Precipitation kinetics of vivianite are slow (Postma 1981) and vivianite equilibration with groundwater took approximately 50 d in laboratory experiments (Walpersdorf et al. 2013). Hydroxyapatite precipitation was also unlikely as below 50 \( \mu \text{mol DIP L}^{-1} \), the precipitation of hydroxyapatite does not occur, even if water is supersaturated with respect to that phase (Sø et al. 2011). Adsorption and coprecipitation of DIP on calcite takes place in freshwater saturated for calcite, with \( < 20 \mu \text{mol DIP L}^{-1} \), approximately 2 mmol Ca\(^{2+} \) L\(^{-1} \) and a pH ranging between 7 and 9.5 (House and Donaldson 1985; House et al. 1986). Similar conditions were at the eastern side of Lake Væng (Figs. 2, 3, 5). Thus, DIP adsorption/coprecipitation on the calcite crystals could potentially occur in that area. However, DIP sorption onto calcite is easily reversed by lowering the aqueous DIP concentrations (Sø et al. 2011). And while hydroxyapatite, vivianite, and calcite potentially can remove DIP under anoxic conditions, the process is less efficient than DIP sorption onto iron hydroxides and coprecipitation with aluminum, calcium, and iron under oxic conditions (Slomp and van Cappellen 2004; Spiteri et al. 2007).

Extensive amount of iron hydroxides precipitated at the seepage faces and sediment-water interface at Lake Væng. Therefore the decrease of DIP in groundwater at transects E1 and E2 was probably due to DIP sorption onto iron hydroxides formed during aeration of the anoxic groundwater containing DIP and Fe\(^{2+} \) (Griffioen 2006). The results of the conceptual hydrogeochemical model also showed that significant DIP retention on iron hydroxides could be expected at flow rates below 0.1 m d\(^{-1} \) at the sediment-water interface.
(Fig. 8). Wetlands and seepage faces adjacent to Lake Væng also acted as a buffer for direct DIP inputs into the lake with discharging groundwater. DIP concentrations below wetlands in shallow nearshore piezometers were < 1 μmol L⁻¹ (Figs. 2, 4). Vanek (1993) reported a sorption capacity of 0.08 × 10⁻³ to 1.3 × 10⁻³ mol DIP kg⁻¹ from sand deposits and riparian zones in southern Sweden, while the sorption capacity for sandy sediments may be as high as 0.002 mol DIP kg⁻¹ (Carlsson and Horkeby 1976).

The processes of adsorption of DIP onto iron hydroxides and organic matter and binding into plants at the seepage faces, wetlands and sediment-water interface are temporary (Reddy et al. 1999; Carlyle and Hill 2001). Thus, DIP sorbed onto iron hydroxides and organic matter at the sediment-water interface is released to the lake if conditions turn anoxic (Lewandowski et al. 2015). Changes in nitrate concentration, or the exhaustion of the assimilative capacity of the wetlands may also lead to release of DIP (Löfgren and Boström 1989; Vanek 1993; Hoffmann et al. 2006). These processes are considered by us as a part of the in-lake phosphorus cycle. The occurrence of the in-lake phosphorus cycle at Lake Væng was confirmed by (1) annual fluctuations in TP concentration in the lake water (Søndergaard et al. 1998) and (2) higher DIP and NH₄⁺ concentration in the water sampled as a surface discharge at wetlands (P2) and at the sediment-water interface (P3-P7) than in groundwater in P2-P7 (Table 2).

**Groundwater-borne DIP loading maintaining lake eutrophication**

The estimated external loading of 3.6 mol DIP yr⁻¹ in the studied 2D cross-section gives 0.01 mol DIP m⁻² yr⁻¹ which is at the high end of the range for groundwater-driven external and internal DIP inputs into lakes, 0.0000078–0.03 mol DIP m⁻² yr⁻¹, given by Lewandowski et al. (2015). However, the groundwater-controlled DIP loading at Lake Væng may have been even higher. The groundwater DIP concentrations increased along the flow paths up to 3.7 μmol L⁻¹, while in the calculation average concentrations of 1.9–2.2 μmol L⁻¹ were used. We took into account only advective DIP transport in the thick gyttja layer, while DIP concentrations in discharging groundwater may have increased due to the release of DIP from organic lake sediments under anoxic conditions (Ahlgren et al. 2011). Advevtive DIP transport through the organic-rich lake bottom sediments was also assumed by Kang et al. (2005), who showed that groundwater seepage can deliver 7.8 ± 4.5 × 10⁻⁵ mol DIP m⁻² yr⁻¹ to the in-lake DIP circulation.

Our study shows a flow rate dependent DIP-delivery to the lake water (Fig. 8), which implies a hydrogeological control. High anoxic groundwater seepage rates may lower O₂ level in the lakebed sediment, thereby preventing phosphorus retention and increasing the groundwater-borne DIP loading to lakes (Lewandowski et al. 2015). The nearly constant chemistry of fast upward flowing ferrous DIP-rich groundwater across the uppermost 2 m of the sandy lakebed in the high discharge zone (P7 in Fig. 5) supports such a scenario. Here, a flow rate averaged 0.25 m d⁻¹ (Kazmierczak et al. 2016) and according to the conceptual model, flow rates above 0.1 m d⁻¹ were adequate to maintain anoxic conditions at the sediment-water interface (Fig. 8). The DIP retention at the lakebed, considered here as an in-lake phosphorus cycle, may have changed temporarily, as the location of high discharge zones changed temporally at Lake Væng (Sebok et al. 2013). However, the aquifer interacting with the lake was generally at steady state with groundwater and lake level fluctuations below 0.1 m (Kazmierczak et al. 2016). Thus, the amount of groundwater discharging into the lake, redox boundary in the aquifer, and thereby external DIP loading, remained unchanged.

Our results highlight the need for a dense sampling network and a good understanding of the flow system at various scales for a correct estimation of the external nutrient inputs into the lake as also suggested by Brock et al. (1982). Similar DIP inputs as in the studied 2D cross section are also expected in other areas of the lake, since DIP concentrations were equally high within entire terrace I (Fig. 4). Assuming that the inflow of groundwater containing on average 2.0 μmol DIP L⁻¹ is the only source of DIP to the lake, the resulting DIP concentration in the lake water would approximately be 1.5 μmol L⁻¹. Shallow (mean depth < 3 m) lakes of moderate ecological quality have TP (DIP and organic phosphorus) concentrations of 1.6–3.2 μmol L⁻¹ (Søndergaard et al. 2005). Thus, the groundwater-controlled input of the mobilized DIP is one of the factors maintaining eutrophication of Lake Væng.

**Conclusions**

A freshwater aquifer is an important source of geogenic DIP in groundwater-dominated lake.

Reduction of iron hydroxides by organic matter within the sediments of the old lake bottom results in phosphorus desorption. The high discharge of anoxic groundwater in areas adjacent to the lakeshore and at the sandy lake bottom does not leave enough time for oxygen diffusion into the aquifer, which would cause DIP retention by iron hydroxides formation before groundwater discharge to the lake. Thus, DIP discharges directly into the lake with anoxic groundwater.

In the studied 2D cross-section, 13% of DIP was transported to the lake through an area covering less than 1% of the lake bottom, where discharge rates above 0.1 m d⁻¹ prevent diffusion of oxygen into the aquifer.

Short groundwater residence time in the aquifer limits the potential of the system for DIP immobilization, even though the groundwater was supersaturated for vivianite and hydroxyapatite due to the increase of pH along deep circulation flow paths.

From an ecological perspective, the continuous upwelling of groundwater containing high concentrations of geogenic...
DIP maintains lake eutrophication and could explain the failure of the two previous lake restoration attempts.

Groundwater-borne inputs of DIP of natural origin can undo the positive effects of biomanipulation attempts, as shown at Lake Væng. Knowledge of the DIP mobility in aquifers has recently increased (Lewandowski et al. 2015). Thus, identification of natural DIP sources in lake catchments is crucial for lake management and should be integrated into a common monitoring practice. This is especially important in areas where natural groundwater DIP concentration exceeds the threshold for good ecological quality of lakes.

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Conflict of Interest
None declared.