Journal of Hydrology 524 (2015) 214-226

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

Phosphorus in groundwater discharge – A potential source for lake eutrophication

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ARTICLE INFO

Article history: Received 19 August 2014 Received in revised form 13 February 2015 Accepted 16 February 2015 Available online 26 February 2015 This manuscript was handled by Corrado Corradini, Editor-in-Chief, with the assistance of Ming Ye, Associate Editor

Keywords: Contamination Groundwater phosphorus loading Urban areas Groundwater surface water interaction Lacustrine groundwater discharge Groundwater pollution

SUMMARY

Lake eutrophication has long been mainly associated with phosphorus (P) inputs from overland flow. The present study gives evidence that also groundwater can carry significant loads of dissolved P. We quantified P loads from groundwater to Lake Arendsee using near-shore measurements of P concentrations at a high spatial resolution and volume fluxes of lacustrine groundwater discharge (LGD) derived from a previous study. Results show that LGD accounts for more than 50% of the overall external P load, thus fuelling the eutrophication of the lake. Several different approaches of groundwater sampling (groundwater observation wells, temporary piezometers, and domestic wells) reveal a broad spatial heterogeneity of P concentrations in the subsurface catchment of the lake. The highest P concentrations (above $4 \text{ mg } l^{-1}$) were found below a settled area along the southern lake shore. Contrary to expectations, other parameters (dissolved iron, ammonium, etc.) were not correlated with P, indicating that natural processes are superimposed by heavy contaminations. Both the intensity of the contamination and its proximity to the lake inhibit nutrient retention within vadose zone and aquifer and allow significant P loads to be discharged into the lake. Although the groundwater quality was investigated intensely, the results eventually give no clear evidence of the location and sources of the pollution. As a consequence, measures to decrease LGD-derived P loads cannot target the contamination at its source in the catchment. They need to be implemented in the riparian area to eliminate groundwater P directly before it enters the lake.

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1. Introduction

Phosphorus (P) overloads are still a major threat to lake ecosystems worldwide. As a limiting nutrient P often controls the trophic state of temperate freshwater systems (Heathwaite et al., 2005; Sondergaard and Jeppesen, 2007). After the significant reduction of P from point sources to improve freshwater quality it became more and more obvious that diffuse transport of P also has a critical ecological relevance. Nowadays, many studies claim agriculture is the main source of diffuse P in freshwater systems (Heathwaite et al., 2005; Orderud and Vogt, 2013; Withers and Haygarth, 2007), especially since sewage discharges from point sources have been eliminated to a large extent (Orderud and Vogt, 2013). Depending on site conditions (i.e. inclination, sediment retention capacity, etc.) diffuse P transport occurs as particulate or dissolved P in overland flow, channelized surface runoff, drainage, or

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groundwater. In groundwater natural dissolved P concentrations are usually low, since potentially mobile P (i.e. in general orthophosphate) is adsorbed in the soil and sediment matrix either in the vadose or the saturated zone. As a consequence groundwater was evaluated to be of "low source strength" by Edwards and Withers (2007). However, it needs to be accepted that dissolved P concentrations can increase largely above natural background conditions in groundwater. Interestingly, studies have again found wastewater to cause heavy groundwater P contaminations (Ptacek, 1998; McCobb et al., 2003; Robertson, 2008; Roy et al., 2009), although this was considered to be eliminated as a nutrient source with the reduction of point sources. However, especially among practitioners it still is a common paradigm that P is completely immobile in groundwater. This might also be supported by a generally low data basis on this issue. Since P is non-hazardous for human health it is often not regularly monitored, neither in drinking water nor in groundwater. This is one of the reasons why lacustrine groundwater discharge (LGD) is often dismissed as a major source of external P inputs to lakes. In recent years the awareness of groundwater P is growing and it is becoming more and more accepted that groundwater can indeed have P concentrations







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exceeding thresholds of ecological relevance (e.g. Burkart et al., 2004; Holman et al., 2010; Kidmose et al., 2013).

Studies on groundwater P often deal with the determination of P concentrations on the catchment scale in order to determine natural background concentrations and to separate them from contamination-derived concentrations. Based on these findings thresholds are raised and discussed for groundwater discharging into surface waters (Burkart et al., 2004; Lewandowski et al., 2015). So far only a few studies tried to actually quantify groundwater-borne P loads to lakes and rivers and to evaluate the impact on their trophic state (Ala-aho et al., 2013; Jarosiewicz and Witek, 2014; McCobb et al., 2003; Ouyang, 2012; Shaw et al., 1990). However, the quantification of LGD-derived P loads is difficult. Usually LGD volume fluxes and nutrient concentrations are determined separately and are subsequently multiplied. Both, hydrological (i.e. LGD volume fluxes) and geochemical (i.e. nutrient concentrations) factors may be affected by spatial and temporal heterogeneities, which impede the empirical determination of representative values. Simplification and upscaling of point measurements are often necessary to approximate nutrient loads. In many studies the groundwater path is simply considered as the residual in budget calculations (Rosenberry et al., 2015) or even is completely neglected.

With the present study we aim to provoke an intensified discussion on the potentially harmful contribution of groundwater to lake nutrient budgets and to demonstrate that groundwater P can fuel eutrophication of lakes. The study site is Lake Arendsee in Northern Germany where the mean total phosphorus (TP) concentrations in the lake water showed a gradual increase in the past decades to more than $150 \,\mu g \, l^{-1}$. First investigations indicated a large spatial variability of near-shore groundwater P

concentrations, with concentrations of soluble reactive P (SRP) higher than 1000 μ g l⁻¹ at one site. These results enforced the effort to better understand and quantify LGD and its contribution to the nutrient budget of Lake Arendsee.

As a first step towards the determination of groundwater-borne P loads detailed investigations on LGD volume fluxes and patterns were conducted (Lewandowski et al., 2013; Meinikmann et al., 2013). To incorporate spatial heterogeneity of LGD, the shoreline was subdivided into sections of about 200 m length, for which individual volume fluxes of LGD were calculated. Based on these results P loads were calculated by applying P concentrations of four nearshore groundwater observation wells (sites 1-4 in Fig. 1). This resulted in a groundwater-derived P load of 425 kg yr^{-1} . However, it was hypothesized that detailed spatial information on groundwater P concentrations increases the accuracy of P load calculations. The present study focuses on groundwater P concentrations as the second factor of groundwater-borne P loads (volume fluxes \times concentration) to Lake Arendsee. We hereby aim to (1) localize crucial areas for P input by detailed measurements of P concentrations in near-shore groundwater, (2) calculate LGD-derived P loads and evaluate them within the context of overall P inputs to the lake, as well as (3) localize the origin of the P contamination in the catchment of the lake.

2. Methods

2.1. Study site



Fig. 1. Subsurface catchment of Lake Arendsee including hydraulic head contour lines (m above sea level) and resulting groundwater flow directions (grey arrows). Black dots depict locations equipped with one, two, or three groundwater observation wells, respectively (see also Table 1). White circles represent rates of lacustrine groundwater discharge (LGD) determined from temperature measurements in the lake sediment (Meinikmann et al., 2013).

Lake Arendsee in Northern Germany is 5.14 km² in size. As already described in previous studies (e.g. Hupfer and

Lewandowski, 2005; Meinikmann et al., 2013) it is a deep stratified lake (max. depth 49 m, mean depth 29 m) which was originally solely groundwater-fed. Currently, four ditches draining adjacent agricultural fields discharge into the lake and an artificial runoff channel transports water out of the lake (Fig. 1). Since the middle of the last century the lake is eutrophied. The annual mean TP concentration from 2009 to 2013 ranged between 179 and 199 μ g l⁻¹ resulting in mass developments of phytoplankton dominated by cyanobacteria. Due to its morphometric characteristics the lake has a large volume (147 M m³) resulting in a water residence time of 50–60 years. Accordingly the lake reacts with significant delay to changes of external nutrient loads.

In March 2010 two to three groundwater observation wells with screens in different depths were installed at four different sites along the southern shoreline, where most of the LGD was expected to occur (Fig. 1). Groundwater sampling revealed a contamination with SRP. especially at site 3. where the shallower well had a mean SRP concentration of $1210 \,\mu g \, l^{-1}$ (Meinikmann et al., 2013). The subsurface catchment mainly expands south of the lake. Surface inclination is generally low in the catchment. However, a steep slope of up to 6 m can be found at the north-western shoreline. Groundwater exfiltration occurs along the western, southern, and (north-) eastern shoreline, while lake water infiltration into the aquifer primarily takes place at the northern and northwestern shoreline (Fig. 1). Hydraulic head contour lines indicate generally northern groundwater flow directions, with main LGD occurring along the southern shoreline. LGD rates derived from point measurements of sediment temperatures confirmed these findings, but revealed significant heterogeneity at the medium scale of the shoreline segments (Fig. 1, Meinikmann et al., 2013). Aquifer sediments are dominated by Saalian and Elstarian substrates above Miocene sands (Fig. 2). Spatial information on hydraulic conductivity is scarce. It is assumed that within the geologic layers of relatively high values $(3-6 \cdot 10^{-4} \text{ m s}^{-1})$ lenses of significantly lower ones are frequent (Fig. 2), introducing some spatial heterogeneity in groundwater flow velocity and exfiltration on the medium scale (Fig. 2). The predominant land use type in the subsurface catchment is agriculture (pasture and croplands, 18% and 35%. respectively), followed by forestry (35%). Settled areas are focused on the city of Arendsee which is situated all along the southern, southeastern, and -western shoreline, and accounts for 14% of the subsurface catchment.

2.2. Near-shore groundwater quality

2.2.1. Groundwater observation wells

Due to the first results of high SRP concentrations at near-shore site 3 (Fig. 1), a monitoring program was setup to investigate temporal variations in groundwater chemistry at those shoreline sites. In order to track back the potential SRP plume, which enters the lake in the vicinity of site 3, seven additional wells were established at four different locations south of site 3 in November 2011. They represented the general groundwater flow direction, and covered the settled area of the city (sites 5–7) as well as the agricultural background (site 8, Fig. 1). While at site 7 one well was installed, at sites 5, 6, and 8 two wells had been built in different aquifer depths, respectively (Table 1).

Groundwater observation wells at sites 1–4 (Fig. 1) were sampled monthly from April 2010 to April 2011 and bimonthly until October 2012. Monthly investigations at site 3 were continued. In 2012 SRP concentrations at sites 5–8 were measured monthly while afterwards the sampling frequency was reduced (see also Table 1). In the following sections, wells will be referred to as shallow, deep, or middle due to their position in the aquifer when compared to other wells at a specific site.

2.2.2. Temporary piezometers

To increase spatial information on SPR concentrations between the four near-shore groundwater observation sites, hand-drilled temporary piezometers were installed along a section of the shoreline where exfiltration occurred. With a drilling-set of Eijkelkamp Agrisearch Equipment boreholes (with a maximum depth of 2.5 m below ground surface) were drilled in close proximity to the shoreline. Then a 1-in.-diameter bottom-screened (20 cm filter length) polyethylene-pipe was put into the borehole. With a peristaltic pump groundwater was extracted until the water turbidity allowed its filtration with 0.45 µm syringe filters. This was usually the case after 10–30 min. The spatial distance between the



Fig. 2. Geological cross-sections along the southern shore including groundwater observation sites 1–4 (a) and perpendicular to the southern shore including groundwater observation sites 3, 5, 6, and 8 in Fig. 1 (b). Mean SRP concentrations (grey values) result from regular investigations as documented in Table 1.

Table 1
Characteristics of groundwater observation wells at sites 1–8 in Fig. 1.

Site	ID	Max. depth of filter screen [m below ground surface]	Filter screen length [m]	Location of filter screen [m above sea level]	Investigation period	Number of measurements
1	1a	10.8	7	21.4-14.4	04/2010-12/2013	22
	1b	27.8	9.9	7.4 to -2.5		
2	2a	9.3	2	17.2–15.2	04/2010-12/2013	22
	2b	21.9	9.6	11.8-2.2		
	2c	31.1	6	-1.2 to -7.2		
3	3a	10	8	22.1-14.1	04/2010-12/2013	33
	3b	17.6	5.4	11.8-6.4		
4	4a	3.9	1.8	22.5-20.7	04/2010-12/2013	22
	4b	22.9	8.9	10.5-1.6		
	4c	34	5.8	-3.8 to -9.6		
5	5a	12.2	2	20.6-18.6	12/2011-12/2013	15
	5b	17.2	2	15.7–13.7		
6	6a	10.2	2	22.3–20.3	12/2011-12/2013	15
	6b	17.2	2	15.2–13.2		
7	7	15.8	2	15.5-13.5	12/2011-12/2013	15
8	8a	8.1	2	23.9-21.9	12/2011-12/2013	15
	8b	13.9	2	18.1-16.1		

boreholes was generally about 300 m, but spacing was decreased at sites with extraordinary high SRP concentrations. In some sections of the shoreline, manual drilling and/or groundwater pumping was not possible, either due to sediment characteristics (fine grained sediments with very low hydraulic conductivity) or inaccessibility of the shoreline (private property). In total, groundwater was sampled from 44 temporary boreholes.

2.3. LGD-derived P loads

The sub-section LGD volume fluxes presented in Meinikmann et al. (2013) were multiplied with the SRP concentrations derived from temporary piezometers to achieve SRP loads for single shoreline segments. In cases where more than one SRP concentration was available a weighted mean concentration based on the represented length of the shoreline section was calculated. Eventually, sub-sectional SRP loads were summed up to an overall LGDderived SRP load.

2.4. Groundwater P concentrations in the catchment

To achieve an overview on groundwater quality in the catchment, as many groundwater samples as possible were included in the monitoring program. This was done to localize the source of groundwater pollution.

2.4.1. Groundwater observation wells

Overall, at 15 additional sites groundwater observation wells were available. At most of these sites only one well existed. However, at two sites two wells were available with screens in different aquifer depths. This resulted in a total of 17 groundwater observation wells. Most of these wells were sampled seven to nine times between September 2010 and December 2013. Due to access constraints some of them were only monitored four times or less.

2.4.2. Domestic wells

To further improve the overview on groundwater P concentrations in the catchment, the citizens of the catchment were asked to bring water from their private wells for chemical analyses. After a successful campaign in September 2011, this was repeated a second time in August 2012. At a central public location in the city of Arendsee citizens could get 250 ml-PE-bottles and a leaflet with instructions for the sampling procedure as well as questions regarding location and depth of the well. Participants were asked to discard at least 201 of water before collecting the sample to avoid sampling of standing pipe water. Furthermore, participants were instructed to not leave a head space to prevent oxidation and precipitation. Afterwards, they were asked to store samples in refrigerators and return samples within 24 h.

2.5. Other sources of external P loads

To evaluate the relative importance of groundwater P for the trophic state of Lake Arendsee additional paths of P import were quantified:

2.5.1. Atmospheric deposition

To quantify P import by atmospheric deposition, which comprises wet and dry deposition, bulk samplers were installed. Between 2009 and 2012 sampling stations were located around the lake (up to six stations), at a landing stage at the lake shore (one station) and on the lake itself (up to four stations). Installation and sampling of the samplers were done following the recommendations of the German Working Group of the Federal States on Water (LAWA, 1998). Sampling details are reported in Lewandowski et al. (2011). Samples were collected monthly.

2.5.2. Water fowl

During the winter half-year different geese species and some other water fowl stay overnight on Lake Arendsee. Their numbers were counted 80 times from 1994 to 2010. Average numbers were multiplied by five months (duration of stay) and literature values for the P concentration of their excrements (Lewandowski et al., 2011).

2.5.3. Drainage from agricultural areas

Large parts of the agricultural subsurface catchment are drained by a ditch system, resulting in four drainage ditches discharging into the lake. For a one-year-period (August 2010 to July 2011), daily measurements of discharge and P concentrations were conducted to quantify P loads from agricultural drainage. As already described in Meinikmann et al. (2013) two of the ditches were equipped with V-weirs and pressure sensors recording water levels in 30 min-intervals. Discharge in a third ditch was determined with an ultrasonic flow measurement device. Three of the ditches drain parts of the subsurface catchment which is mainly characterized by agricultural land use. The fourth ditch drains a pasture which is situated to the west of the lake outside the subsurface catchment. Discharge here was also measured with a pressure sensor recording water levels in a 30 min-interval, which were translated into discharge via a water stage-discharge relation. SRP was measured from each single daily sample while total phosphorus (TP) was measured from samples that were mixed due to similar discharge rates and SRP values of several consecutive days. Daily (SR)P loads were calculated by multiplying the concentrations with 24 h-summed up discharge volumes for each drainage ditch.

2.5.4. Storm water discharge into the lake

Wastewater is mostly collected and treated in a centralized wastewater treatment plant outside of the lake's catchment. However, during heavy rainfalls storm water overflow is discharged into the lake. Discharge was measured with an ultrasonic flow measurement device and, in case of an overflow event, samples were taken for SRP and TP analysis. Additionally rainwater discharge is considered, although only 1.7 ha of paved area is directly discharging into the lake (data provided from public authorities).

2.5.5. Overland flow

There is no significant inclination in the catchment of Lake Arendsee. Thus overland flow was expected to be low. However, P load from overland flow was modelled based on the ABAG approach, which represents an adaption to the USLE (universal soil loss equation, Wischmeier and Smith, 1965) to German conditions (Gebel et al., 2010).

2.5.6. Bathers

According to a study by Schulze (1981), bathers introduce 94 mg P per person and day into a lake. Based on this value and current numbers of bathing tourists at the lake P inputs were calculated.

2.6. Evaluation of external P loads estimations by mass balance

External P loads (P_{load}) equal the sum of P retention in the lake sediment (P_{sed}), P export from the lake by surface and groundwater outflow (P_{exp}), and changes in P inventory of the lake water (ΔP_{lake}):

$$P_{load} = P_{sed} + P_{exp} + \Delta P_{lake} \tag{1}$$

This equation was used to validate external P load determinations described above. Hupfer and Lewandowski (2005) calculated P_{sed} from dated sediment cores taken at different water depths and referred it to the lake area deeper than 30 m (3.0 km²).

 P_{exp} was estimated based on mean epilimnic P concentrations from 1993 until 2013. However, since no hydrological data were available for surface and groundwater outflow from the lake (Q_{out}) this term was calculated from the lake's water balance:

$$Q_{out} = Q_{in} - E_{lake} \tag{2}$$

Water inflow to the lake (Q_{in}) is the sum of all hydrological input paths. Water loss from the lake surface by evaporation (E_{lake}) was determined as a long-term value for the period from 1990 until 2009. Q_{out} and P_{exp} are cumulated values for water and P losses from the lake, respectively, allowing no distinction between groundwater and surface water outflow. ΔP_{lake} was derived from the mean linear trend of lake water P content from 1993 until 2013.

2.7. Chemical analysis

SRP samples were filtered using a 0.45 μ m syringe filter (cellulose acetate). P concentrations were determined with the ammonium molybdate spectrometric method with a limit of quantification (LOQ) of 25 μ g l⁻¹. Domestic well samples were additionally digested and analyzed for total phosphorus (TP, DIN EN ISO 6878).

Although the present study focuses on P, some additional parameters were determined in all groundwater samples. Analysis included the two most relevant N-fractions (ammonium and nitrate), dissolved iron, boron, and redox potential. The latter could not be determined for domestic wells since the redox potential has to be measured on-site during sampling in flow-through cells.

Nitrate-N concentrations were determined by ionchromatography (DIN EN ISO 10304-1), while ammonium-N was measured photometrically (DIN EN ISO 11732). Boron and dissolved iron concentrations were determined via inductively coupled plasma optical emission spectrometry (ICP-OES). Redox potentials of well samples were measured on-site in a flow-through cell with a potentiometry probe (Multi3430, WTW).

3. Results

3.1. Near-shore groundwater quality

3.1.1. Groundwater observation wells

Mean SRP concentrations at the eight monitoring sites (Fig. 1) vary by orders of magnitudes (Fig. 3). Most remarkable are the results of sites 3 and (upgradient to it) site 5 where the shallow wells have mean SRP concentrations of 1600 and 3900 μ g l⁻¹, respectively. The deeper wells at these sites show concentrations of 650 and 610 μ g SRP l⁻¹, respectively. At near-shore sites 2 and 6 SRP concentrations also decrease with increasing aquifer depths. At both sites the shallowest wells still have SRP concentrations with a potential relevance for lake eutrophication (210 and 170 μ g l⁻¹ at 2a and 6a, respectively). The pattern of decreasing SRP concentrations with depth is not valid at all monitoring sites. At sites 1, 4, and 8 SRP concentrations are slightly higher in the deeper wells than in the shallower ones. Thus, there is no consistency in P concentrations with regard to aquifer depth.

With one exception, time series of SRP concentrations in the ten groundwater observation wells at sites 1 to 8 (Fig. 1) from April 2010 to December 2013 demonstrate that no significant changes take place (Fig. 4). Variations over time may be driven by seasonal factors (e.g. weather conditions) or analytical errors but do not seem to be caused by general changes in groundwater chemistry. However, at well 5a which has the highest SRP concentrations, a decrease occurred. In January 2012 a maximum concentration of 4500 μ g l⁻¹ was measured, followed by an almost continuous decrease until a final concentration of 3630 μ g SRP l⁻¹ was recorded in December 2013. In contrast, the deeper well at site 5b revealed an ongoing increase of SRP concentrations from 510 μ g l⁻¹ at the beginning of the monitoring period to 770 μ g l⁻¹ in December 2013.

3.1.2. Temporary piezometers

Samples from temporary near-shore piezometers in the upper part of the aquifer reveal a large heterogeneity of SRP concentrations (Fig. 5a). Concentrations range from less than 25 to above 4000 μ g SRP l⁻¹ in overall 44 piezometer samples. The results show that SRP concentrations of more than 100 μ g l⁻¹ almost exclusively occur in a 1.9 km long section along the southern and southeastern shoreline, including sites 2 and 3, where increased concentrations are also found in the deeper observation wells (Fig. 3). The section, where LGD is heavily contaminated with P,



Fig. 3. Mean concentrations and standard deviations (error bars) of soluble reactive phosphorus (SRP in μ g l⁻¹) in groundwater observation wells at sites 1–8 (sites 1, 2, and 4: *n* = 22, site 3: *n* = 33 in a period from April 2010 to December 2013; sites 5–8: *n* = 15 from December 2011 to December 2013). Letters (a, b, and/or c) represent shallow, middle, and/or deep well according to Table 1.



Fig. 4. Time series of concentrations of soluble reactive phosphorus (SRP) in groundwater observation wells at sites 1–8. Letters (a, b, and/or c) indicate shallow, middle, and/ or deepest well at a specific site (see Table 1). Note the differing scales at sites 3 and 5.

is restricted to urban areas of the city of Arendsee. Concentrations up to 4060 μ g SRP l⁻¹ are found in this reach. There are only two sites outside the area where near-shore groundwater has concentrations of more than 100 μ g SRP l⁻¹. They are located at the western shoreline, where a settlement of vacation cottages is situated (Fig. 5a).

3.2. LGD-derived P loads

The largest portion of LGD-derived P loads enters the lake along a 1.4 km long reach where not only SRP concentrations are high, but also LGD rates are largest (Meinikmann et al., 2013, Fig. 1). Standardized SRP loads in the shoreline sections range from less



Fig. 5. (a) Near-shore groundwater concentrations of soluble reactive phosphorus (SRP) in groundwater observation wells (big outlined circles) and temporary piezometers (small circles), and (b) resulting standardized SRP loads (g SRP entering the lake along one meter of shoreline per year) for shoreline segments (based on hydrological data by Meinikmann et al., 2013).

than 1 to 1060 g SRP discharging to the lake along one meter of shoreline per year (g SRP m⁻¹ yr⁻¹, Fig. 5b), with a median of 12 g m⁻¹ yr⁻¹. Segmented SRP loads sum up to an overall ground-water-borne load of 830 kg SRP yr⁻¹. Of this, 94% enters the lake along 23% of the shoreline where exfiltration occurs.

3.3. Groundwater P concentrations in the catchment

Mapping of SRP concentrations at sites 1–8 indicates a plume which encompasses groundwater observation sites 2, 3, and 5 (Fig. 6a). Site 6 with a mean of 170 μ g l⁻¹ might also be part of this plume, while sites 7 and 8 are not considered to be impacted by a contamination (<100 μ g SRP l⁻¹). However, in the settled area of the city of Arendsee, another well with a concentration of 1900 μ g SRP l⁻¹ occurs north of site 7 (Fig. 6b). In the remaining, mostly rural parts of the catchment, SRP concentrations are relatively low. There are only two groundwater observation wells in the south and at the eastern border of the subsurface catchment with SRP concentrations of more than 100 μ g l⁻¹ (140 and 190 μ g l⁻¹, respectively). However, these concentrations are relatively low compared to some found in the urban area (Fig. 6b).

The call for groundwater samples from domestic wells was successful and resulted in 56 additional samples. Most of them are from the city of Arendsee. Only a few came from other small villages in the subsurface catchment (6c). At first glance, P concentrations confirm the existence of a P plume in the area south and southeasterly of the impacted sites 3 and 5. Concentrations of more than 500 μ g P l⁻¹ are found south of site 7, which was previously not considered to be located in the potential P plume. Furthermore, the area around site 6 as well as south and west of site 7 is dominated by P concentrations between 100 and $200 \ \mu g \ l^{-1}$. Although these concentrations are relatively low the agglomeration of slightly increased P concentrations may also indicate a contamination of this area. Compared to the eastern part of the city, information on groundwater quality west of the transect is scarce. Geological conditions are assumed to be dominated by sediments of low hydraulic conductivity. The installation of groundwater wells, at least for private water abstraction, is presumably not worthwhile in that area. As a consequence, no samples are available from the central part of the city of Arendsee. Alternatively, many samples were brought from the southwestern part of the city of Arendsee (Fig. 6d). Except one, they all show P concentrations of less than 100 μ g l⁻¹.

Although the results indicate a P plume reaching the lake from southeast of site 3, the focus here should also be on medium to small scale results. There is considerable heterogeneity in groundwater P concentrations in this area. Two wells north of site 7 reveal a discrepancy of P concentrations within a small distance. One of them had a concentration of 1900 μ g l⁻¹, while the other well (although located 50 m away) had 40 µg P l⁻¹. Both wells had similar depths of about 8 m below ground surface. Furthermore, two domestic wells in even closer proximity to site 7 were found to have the same depth (9 m) but significantly different P concentrations (400 and 35 μ g l⁻¹, respectively) (Fig. 6d). According to the owners these two wells are located less than 20 m apart from each other. Also around near-shore site 2 P concentrations are heterogenic. Within a distance of 130 m two samples collected in six and three meters depth below ground, respectively, have concentrations of 3200 and less than 25 μ g P l⁻¹. Near-shore well 2a in close proximity to them has a mean P concentration of about 220 μ g l⁻¹ but is with 9 m below ground deeper than the other ones (Table 1).

Although no general dependency on aquifer depth can be identified, concentrations of more than $1000 \ \mu g \ P \ l^{-1}$ are restricted to wells with depths ranging from 6 to 12 m below top ground surface (Fig. 6d). At those of the heavily contaminated sites which are equipped with a shallow and a deep well, a decrease of P concentrations with increasing well depths is determined (e.g. sites 3 and 5, Fig. 3).

To summarize, the investigation reveals an area south of nearshore site 3 which seems to be impacted by a P plume. However, its origin is not traceable. Furthermore, upgradient of near-shore observation site 2 another plume exists. Within the contaminated areas there are sites in close proximity to heavily impacted wells which do not show any increase in P concentrations.



Fig. 6. Spatial variation of phosphorus (P) concentrations in the catchment of Lake Arendsee and stepwise increase of investigation extent and its spatial resolution. (a) Most shallow groundwater observation wells at sites 1–8; (b) in addition groundwater observation wells in and close to the subsurface catchment of the lake; and (c) in addition domestic wells and temporary piezometers. (d) Enlargement of the rectangle in (c) which depicts the urban area of the city of Arendsee. It includes well depths (m below ground surface, coloured according to the corresponding P concentration) to additionally visualize results from different wells at the same place and/or sampling depths.

3.4. Correlations of phosphorus with other groundwater parameters

With the exception of boron, P concentrations show hardly any correlation with other groundwater parameters. The majority of coefficients of determination (R^2) are less than 0.02 (Fig. 7). Boron shows a slightly positive correlation with P (R^2 = 0.16, Fig. 7e). In some samples with P concentrations of less than 250 µg l⁻¹, both, ammonium-N and dissolved iron increase with increasing P concentrations, indicating a dependency on the redox potential. However, at higher P concentrations this positive relation is not valid anymore (Fig. 7a and b). Redox potential data themselves do not show any correlation with P concentrations (Fig. 7d). Increased P concentrations occur at both, high and low redox potentials. It is noteworthy that out of the five highest P concentrations four occur at positive redox potentials of more than 50 mV. Nitrate-N concentrations also do not correlate with P concentrations. High and low nitrate concentrations occur together

with high P concentrations, while ammonium and dissolved iron have concentrations predominantly below the LOQ at high P concentrations.

3.5. External phosphorus inputs into Lake Arendsee

Overall, P inputs from external sources sum up to 1560 kg yr⁻¹ (Table 1). Due to the results presented above, LGD accounts for 53% of this value which is equivalent to 161 mg m⁻² yr⁻¹ (referred to the whole lake area). This is followed by atmospheric deposition (19%), water fowl (13%), and drainage from agriculture (12%). Rainwater and storm water overflow discharge, overland flow, as well as bathers did not contribute significantly to the overall external P load (Table 2). To evaluate these results, additional calculations were performed with a background concentration of 50 µg P l⁻¹ in LGD (generally discussed as maximum background P concentrations in areas without anthropogenic impact;



Fig. 7. Concentrations of phosphorus (P) vs. concentrations of Fe² (a), NH₄⁺-N (b), NO₃⁻-N (c), B (e) and redox potential (d). a, b, c and e include median concentrations of time series of groundwater observation wells as well as results from domestic wells which were sampled once. Data depicted in (d) contain only results from groundwater observation wells, since no redox potential measurements were possible for domestic well samples. Note log-transformation of *x*-axis.

Table 2

External phosphorus (P) loads to Lake Arendsee.

P input path	Actual P input	Actual P input ^a			Background P input ^b		
	kg yr $^{-1}$	%	$\mathrm{mg}~\mathrm{m}^{-2}~\mathrm{yr}^{-1}$	$kg yr^{-1}$	%	$\mathrm{mg}\mathrm{m}^{-2}\mathrm{yr}^{-1}$	
Groundwater	830	53	161	70	9	14	
Atmospheric deposition	300	19	58	300	38	58	
Waterfowl	200	13	39	200	25	39	
Drainage ditches	180	12	35	180	23	35	
Bathers	20	1	4	20	3	4	
Overland flow	10	1	2	10	1	2	
Storm water overflow	10	1	2	10	1	2	
Rainwater discharge	10	1	2	10	1	2	
Sum of P inputs	1560	100	304	800	100	156	

^a Groundwater P load based on measured data presented in this study.

^b Groundwater P loads based on a theoretical maximum background concentration of 50 µg P l⁻¹.

Lewandowski et al., 2015). In this scenario LGD accounts for only 9% of the overall external P load to Lake Arendsee (Table 2).

3.6. Phosphorus mass balance

 Q_{in} (Eq. 2) sums up the total runoff in the catchment (as presented Meinikmann et al., 2013), precipitation on the lake surface, discharge of a ditch draining pastures west of the subsurface catchment (see Fig. 1 and Section 2.5), and groundwater abstraction for drinking water supply (Table 3). Subtracting water losses due to evaporation of lake water (E_{lake}) yields the amount of water leaving the lake with groundwater outflow and surface runoff (Q_{out} in Eq. 2 and Table 3). The long-term epilimnetic P concentration is 134 µg l⁻¹, resulting in a P_{exp} of 355 kg P yr⁻¹. 1400 kg P yr⁻¹ are retained in the lake sediment (P_{sed} in Eq. 1). Between 1993 and 2013 ΔP_{lake} increased on average by 215 kg yr⁻¹. P_{exp} , P_{sed} , and ΔP_{lake} sum up to 1970 kg yr⁻¹ (Eq. 1) compared to an external P load (P_{load}) of 1560 kg yr⁻¹ determined by summing up all input paths (Table 2).

Table 3

Water balance of Lake Arendsee with water inflow to the lake (Q_{in}), evaporation of lake water (E_{lake}), and resulting outflow of the lake (Q_{out}) based on Eq. (2) (in M m³ yr⁻¹).

Q _{in}	6.03
Precipitation on lake surface	3.00
Total runoff in subsurface catchment	2.35
Discharge from drainage ditch outside of subsurface catchment	1.00
Groundwater abstraction for drinking water supply	-0.32
Elake	-3.38
Q _{out}	2.65

4. Discussion

4.1. The role of LGD at Lake Arendsee

Groundwater P concentrations found in the catchment of Lake Arendsee partly exceed ecological thresholds discussed in literature by far (Burkart et al., 2004; Holman et al., 2010; Lewandowski et al., 2015). Moreover, main LGD takes place where the groundwater is most contaminated. As a result, LGD-derived P loads from the segmented approach account for 53% of all quantified external P inputs to Lake Arendsee, compared to only 9% based on natural background concentrations of P. Temporary piezometer investigations increased the spatial resolution of SRP concentrations along the shore significantly. Accordingly, the application of the results to LGD rates also increased the accuracy of P load determinations and led to a groundwater-borne P load of 830 kg yr⁻¹. A first approach by Meinikmann et al. (2013) based on only four nearshore groundwater concentrations yielded a P load of 425 kg yr⁻¹. The underestimation of about 50% can be attributed to the large heterogeneity in near-shore SRP concentrations which was not captured by the four near-shore observation sites alone.

However, both approaches showed that LGD contributes the largest proportion of external P loads to the lake. This confirms that groundwater P drives the ongoing eutrophication of Lake Arendsee. The area P loading via LGD is 161 mg m^{-2} yr⁻¹. Values reported for other lakes range from 6 to about 2900 mg P m⁻² yr⁻¹ via LGD (e.g. Belanger et al., 1985; Brock et al., 1982; Kang et al., 2005; LaBaugh et al., 1995; Lewandowski et al., 2015; McCobb et al., 2003; Misztal et al., 1992; Ommen et al., 2012; Shaw et al., 1990; Vanek, 1991). Other studies also found LGD as a major contributor to lake P budgets. For example, Ommen et al. (2012) showed for oligotrophic Lake Hampen in Denmark that groundwater accounts for 85% of external P loads, with groundwater P concentrations ranging from 4 to 52 μ g l⁻¹. However, while LGD in Lake Hampen had a much higher proportion of the P budget than at Lake Arendsee, its eutrophication potential is significantly lower due to generally lower groundwater P concentrations. Nevertheless, the authors still attributed the potential for lake eutrophication to LGD derived P loads. There are probably many other lakes where LGD significantly enhances eutrophication.

Common neglect of LGD in lake nutrient budgets has several reasons. Groundwater is an invisible input path, and the quantification of its contribution to lake nutrient budgets is challenging (Lewandowski et al., 2015). Temporal and especially spatial heterogeneities in LGD and nutrient concentrations have to be carefully considered, to minimize uncertainties in the nutrient budget. This has recently been confirmed for groundwater-borne N inputs to a lake by Kidmose et al. (2014). But in contrast to N, P has long been assumed to be immobile in the aquifer and thus generally low groundwater P concentrations are expected (Lewandowski et al., 2015). This paradigm has changed within the last years and as an indicator for contrary findings the USGS (2014) issued the following statement on its webpage: "Phosphorus Doesn't Migrate in Ground Water? Better Think Again!". The results of the present study show that groundwater P concentrations can increase far beyond natural values and by that alter the trophic condition of surface waters. Lake Arendsee might represent a "worst case" where extremely high P concentrations coincide with the area of main LGD volume fluxes. Our findings should encourage scientists and practitioners dealing with surface water eutrophication to also take groundwater into account as a significant source of external P. Furthermore, it needs to be considered that in close proximity to surface waters water tables are usually low. Consequently, nearshore groundwater is especially prone to contaminations: The thickness of the vadose zone and by that its adsorption and retention capacities decrease with decreasing distance to the shoreline. Moreover, the closer a contamination source is to surface water the less time and flow path length is available for restoration and retention of pollutants during the passage of the saturated zone.

time with more or less constant intensity. Since no improvement of groundwater quality could be determined during almost four years of monitoring it cannot be excluded that the contamination source is still active. Moreover, increasing SRP concentrations at well 5b indicate, that at least for deeper parts of the aquifer, the maximum extent of the plume might not have reached the lake yet. The generally low temporal variability at the near-shore sites supports the approach to use a one-time-sampling of groundwater from temporary piezometers for representative P load calculations. These results also support the utilization of one-time-measurements of P concentrations from private domestic wells.

4.3. Spatial variability of phosphorus concentrations in the catchment

Groundwater observation and domestic wells reveal a large degree of spatial heterogeneity in the urban area. Several locations with low P concentrations were found in closest proximity to severely contaminated sites. In some cases these heterogeneities can be explained by different depths of well screens, since plumes have a limited horizontal as well as vertical extent. A vertical concentration gradient within the plume might be responsible for differing measured P concentrations at neighboring sites when the lengths of the screens differ. An example are strongly differing SRP concentrations at sites 3 and 5, which are located only 150 m apart from each other. Flow directions indicate that groundwater first passes site 5 before it reaches the lake at site 3 (Figs. 1 and 2). Mean SRP concentrations of about 3900 μ g l⁻¹ at well 5a compared to 1600 μ g l⁻¹ at well 3a (Fig. 3) might imply that the maximum extent of the contamination has not reached the lake vet, but actually well 5a covers only 2 m of the upper vertical extent of the aquifer while well 3a covers 8 m of the aquifer (Table 1 and Fig. 2b). Samples from well 5a are likely taken from the more contaminated upper part of the aquifer, while samples from well 3a are diluted with less contaminated deeper groundwater. Thus, drilling depths and screen lengths should be considered when evaluating spatial groundwater quality data.

A vertical gradient might also be responsible for relatively low P concentrations at well 7 (arithmetic means $25 \ \mu g \ l^{-1}$), although surrounding wells indicate a P plume in that area. Since here groundwater is sampled from 9 m below the water table, the maximum P concentration within the vertical aquifer extent might not be captured. In addition, spatially varying aquifer substrates can cause heterogeneous P concentrations due to differences in hydraulic conductivities. A sediment layer with a larger hydraulic conductivity compared to surrounding sediments can function as a preferential flow path for groundwater and its constituents. Also, the commonly higher retention capacity of sediments with low hydraulic conductivity might reduce groundwater P concentrations more efficiently than sediments of large hydraulic conductivity. Nevertheless, since retention capacities are exhaustible this effect will be suspended at one point.

Although the number of available monitoring sites is quite high in the present study, it still is not possible to identify a contamination site. The spatial variety of P concentrations indicates that the pollution is caused not only by one but by several contamination sources.

However, the detailed picture of groundwater quality below the city of Arendsee could only be accurately assessed due to the inclusion of domestic wells into the investigation. They provide a fast, simple and cheap supplement of traditional investigations based on groundwater observation wells.

4.4. Correlations with other parameters

4.2. Temporal variability of phosphorus concentrations

Low temporal dynamics of P concentrations at near-shore site 3 indicate a contamination source that has been active for a long

Ammonium-N, dissolved iron, and P are usually known to occur under anaerobic conditions (i.e. at negative redox potentials). In contrast, at higher redox potentials nitrogen exists as nitrate-N, while P mobility is decreased due to adsorption to iron(oxy)hydroxides. In the present study, none of these assumptions seems to be valid; P concentrations do not correlate with other parameters (Fig. 7). Moreover, in several cases there are even contrasting findings. High P concentrations go along with high redox potentials, and with low ammonium and dissolved iron concentrations. In several cases high P concentrations occur in combination with high nitrate concentrations. We suspect that the following processes are responsible for this:

Organic matter enters the unsaturated zone from an unknown source and is mineralized. Nutrients mobilized by mineralization underlie different mechanisms and processes: Nitrogen is percolated with the groundwater down the unsaturated zone as nitrate-N, as long as the redox potential is positive. In contrast, under oxic conditions, P derived from the degradation of organic matter is predominantly immobilized in the vadose zone by sorption onto different mineral surfaces (e.g. Fe(III)-containing oxides or hydroxides) and therefore, does not reach the groundwater. However, with ongoing pollution these retention capacities of the unsaturated zone become exhausted and freshly delivered P starts to constantly travel towards the saturated zone, even though the redox potential is clearly positive. At some sites with negative redox potentials, the usual pattern of co-existence between redox-dependent species are still visible, i.e. increased P concentrations correlate with increased ammonium and dissolved iron concentrations. However, this seems to be only valid for groundwater with P concentrations less than 250 μ g l⁻¹ (Fig. 7). Heavier contaminations (P concentrations > 250 μ g l⁻¹) are restricted to oxic conditions, indicating already exhausted retention capacities at those sites.

Additionally, spatial separation of plume constituents during the passage of the aquifer might cause discrepancies between P concentrations and other contamination indicators at a single site. It is known that P travel times are at least one magnitude lower than actual groundwater flow velocity while boron or nitrate show nearly no retardation in the aquifer.

Overall we assume that the present distribution of nutrients and other compounds in the aquifer of the subsurface catchment results from a complex overlay of different processes. Furthermore, we interpret these findings as resulting from the immense impact of a severe pollution.

4.5. Origins of the groundwater P contamination

4.5.1. Agricultural or urban origin?

The intense investigation of the groundwater quality in the subsurface catchment of Lake Arendsee leads to the conclusion that the sources of the P contamination are located somewhere in the urban area of the city of Arendsee. In particular, results from near-shore temporal piezometers did not reveal increased SRP concentrations in nonsettled areas. There is no evidence that agriculture is a significant source of P enrichment of the aquifer in the catchment of Lake Arendsee. In fact, according to an independent modelling approach based on land use types (Gebel et al., 2010) diffuse P loads from agriculture accounts for only 13% of the overall P loads calculated in this study. Even less (3% of overall P load) are delivered by forested areas.

Higher P concentrations in urban groundwater compared to agricultural or other land use types have been reported in several other studies before (Holman et al., 2008; Qian et al., 2011), demonstrating a potential vulnerability of urban aquifers to P contamination.

4.5.2. Potential sources

According to paleoecological investigations a change from a mesotrophic to a eutrophic state happened in Lake Arendsee in the middle of the 20th century (Scharf, 1998). This was mainly attributed to the discharge of untreated communal and industrial wastewater into the lake. Furthermore, the drainage of an adjacent lake to reclaim arable land and the overall intensification of agriculture in the catchment probably also contributed to increased nutrient loads.

Since the end of the 1970s a sewage system transports wastewater to a treatment plant outside of the catchment. It was assumed that this measure would eliminate the largest portion of external P. However, the trophic state of the lake did not recover, which at the time was explained by the very long water residence time of Lake Arendsee. Nevertheless, TP concentrations still increased during the subsequent decades. Results from the present study now reveal that it is mainly P contaminated groundwater from settled areas at the southern shore that contributes to the ongoing lake eutrophication.

Contamination of groundwater below urban areas is often caused by leakages from wastewater systems (Bishop et al., 1998; Rutsch et al., 2008; Schirmer et al., 2013; Wakida and Lerner, 2005). This includes on-site septic tank-systems, or sewer channels, with the latter including the municipal sewage system, as well as house connection sewers. Sewage P concentrations range between 9 and 15 mg PO₄-P l^{-1} (Bishop et al., 1998; Holman et al., 2008). However, a part of the wastewater P can be assumed to be retained in the vadose zone matrix during percolation (Gilliom and Patmont, 1983; Zanini et al., 1998). The amount of nutrients and pollutants from leaky sewers that actually reaches the groundwater depends on filtering and retention capacities of the vadose zone. Under oxic conditions P is usually adsorbed as phosphate onto positively charged mineral surfaces, e.g. Al-, Mn(IV)- and Fe(III)-containing oxides and (oxy)hydroxides, and calcite (Ptacek, 1998; Spiteri et al., 2007; Wilhelm et al., 1994; Zanini et al., 1998) or onto solid organic carbon (Harman et al., 1996). Thus, P concentrations do not necessarily increase instantly after a contamination. However, as mentioned above, a long-lasting continuous supply of P exhausts the aforementioned retention capacities. In such a case pollution-derived P is transported through the vadose zone and finally reaches the groundwater. Depending on the thickness of the vadose zone, its retention capacities, and due to slow groundwater flow velocities it might take decades before the groundwater pollution is recognized (McCobb et al., 2003).

Leakages from wastewater facilities within the city of Arendsee would easily explain the observed heterogeneity of the groundwater P concentrations. Especially house connection sewers and onsite septic tanks are known to be malfunctioning (e.g. Katz et al., 2011). Some studies even warn of pumping septic tank leachate from domestic wells since it might cause serious health threats (Bremer and Harter, 2012; Katz et al., 2011).

Other potential sources for P in groundwater are abandoned contaminated sites such as agricultural fertilizer storage units, and/or industrial sites. The excessive application of fertilizers in private gardens may also cause groundwater contaminations (Vanek, 1993; Zhao et al., 2011).

In the case of Lake Arendsee the large heterogeneity of P concentrations prevented the identification of contamination sites and origins. Reasons for this heterogeneity might be the following:

- Small- to medium-scale differences in aquifer material cause preferential flow paths and a heterogenic dispersion of a potential plume.
- The contamination is/was happening at several sites simultaneously (e.g. leaking of wastewater at several malfunctioning sites) causing plumes of varying intensity.
- Incompatible parameters of observation sites (e.g. well depths and screen lengths) or lacking information on them prevented a reliable interpretation of the results.

4.6. Evaluation of external phosphorus load estimations

The sum of separately determined external P loads (Table 2) agrees well with the sum of P retention in the lake sediment, P export from the lake, and changes in lake P inventory (Eq. 1). The good agreement confirms that all relevant P input paths have been considered in the investigations. Discrepancies might result from small errors in individual terms. Uncertainties in LGD arise from the determination of the subsurface catchment, from groundwater recharge calculations, as well as P concentrations in LGD (e.g. due to inappropriate resolution of near-shore measurements along the lake and with depth). One year-measurements of P loads from agriculture via drainage ditches might differ from a long-term mean. Storm water overflows might have been underestimated due to a small and thus non-representative number of discharge events during the experimental period (data not shown). Additionally, P retention in the lake sediment underlies some uncertainty. The relatively good agreement of total P loads (Table 2) with the sum of P_{sed} , P_{exp} , and ΔP_{lake} (Eq. 1) provides significant evidence for the importance of LGD-derived P loads to the lake.

4.7. Implications

Because of the long water residence time an immediate reduction of the P concentration in Lake Arendsee is only possible by internal P inactivation (Schauser et al., 2003). Due to the high external P loads P concentrations in the lake will gradually exceed critical threshold values necessary for controlling primary production within only one decade after a chemical inactivation. Therefore, a restoration is only sustainable when the internal measure is accompanied by a decrease of external P loads. Since the results do not indicate if and when a decrease in groundwater P loads can be expected, further measures should be considered to reduce P loads from LGD. Calculations of section-wise groundwater P loads allow the delineation of a reach at the shore where most groundwater P is entering the lake (Fig. 5b). Thus, it seems promising to establish groundwater remediation measures along this reach. One possibility is the installation of a permeable reactive barrier close to the shoreline to directly remove diffuse P from shallow groundwater before it enters the lake. For this P sorbing materials (e.g. metal cations) are blended with filter sediment material (e.g. zero-valent-iron) and implemented into the soil/ aquifer matrix or, like described for Ashumet Pond in Cape Cod, as a permeable reactive layer directly into the lake bottom (McCobb et al., 2009). Also, the abstraction of contaminated near-shore groundwater to an off-site treatment facility may be a feasible option to remove P from the system. After treatment the water could either be reinserted into the aquifer or directly discharged into the lake. The deviation of the untreated groundwater to a treatment plant outside of the lake's catchment could also be taken into account. However, the resulting shift in the lake water balance should be carefully considered in that case.

5. Summary and conclusions

- 1. Completing the segmented approach introduced by Meinikmann et al. (2013) with near-shore groundwater P concentrations from temporary piezometers enabled us to quantify LGD-derived P loads and to evaluate their impact on the lake's trophic state.
- Groundwater can be a main cause of lake eutrophication, especially when a contamination leads to high nutrient concentrations in those parts of the shoreline where main lacustrine groundwater discharge (LGD) takes place.

- 3. Despite a large number of observation sites it was not possible to clearly locate a contamination site and to identify the source for the severe groundwater pollution.
- 4. It is conceivable that groundwater P pollution is more common than previously thought. Special care should be taken when human settlements are located in close proximity to those reaches of a lake shore where significant groundwater exfiltration takes place. Adsorption and retention potentials of both, vadose and saturated zones usually decrease with decreasing distance to the lake.
- 5. Heavy contaminations may alter natural patterns of co-existence of groundwater constituents. At Lake Arendsee groundwater P concentrations are highest at high positive redox potentials, indicating a severe contamination to superimpose the usual redox dependency of P mobility in groundwater.
- 6. Sustainable restoration of Lake Arendsee will only be achieved by a reduction of the P inventory in the lake on the one hand and external P loads on the other hand. Since groundwater is by far the largest contributor to the overall P load, measures for P elimination from near-shore groundwater should be evaluated for their applicability.

Acknowledgements

Sincere thanks are given to Christine Sturm for groundwater sampling as well as the team of the chemical lab at the Leibniz-Institute of Freshwater Ecology and Inland Fisheries Berlin (IGB). This study was funded by the State Agency for Flood Protection and Water Management Saxony-Anhalt (LHW).

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