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Positive and negative impacts of five Austrian gravel pit lakes on groundwater quality

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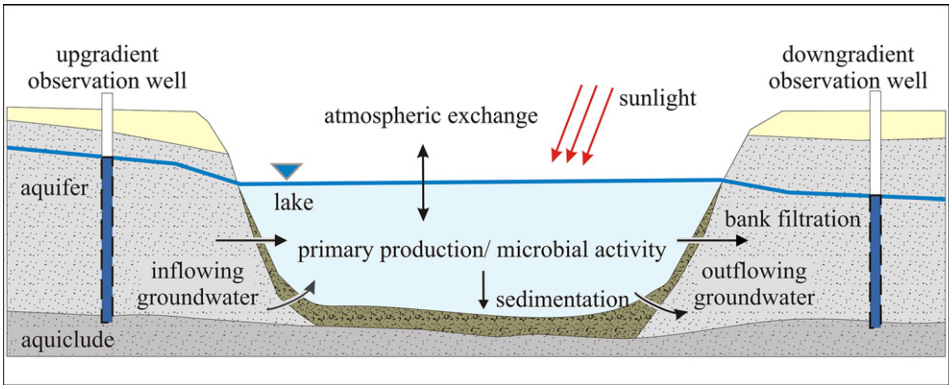
HIGHLIGHTS

- ► Groundwater fed gravel pit lakes might be in conflict with groundwater protection.
- ► Gravel pit lakes change biological, organic, and inorganic parameters of the groundwater.
- ► Gravel pit lakes might reduce nitrate, organic micropollutants, and hardness of the downgradient groundwater.
- ► Nitrate degradation rates were independent of the post excavation age.
- ► The anthropogenic post excavation usage has to be addressed critically.

GRAPHICAL ABSTRACT



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ABSTRACT

Groundwater-fed gravel pit lakes (GPLs) affect the biological, organic, and inorganic parameters of inflowing groundwater through combined effects of bank filtration at the inflow, reactions within the lake, and bank filtration at the outflow. GPLs result from wet dredging for sand and gravel and may conflict with groundwater protection programs by removing the protective soil cover and exposing groundwater to the atmosphere. We have investigated the impact on groundwater of five GPLs with different sizes, ages, and mean residence times, and all having low post-excavation anthropogenic usage. The results revealed highly active biological systems within the lake water, in which primary producers significantly reduced inflowing nitrate concentrations. Decalcification also occurred in lake water, reducing water hardness, which could be beneficial for waterworks in hard groundwater areas. Downgradient groundwater nitrate and calcium concentrations were found to be stable, with only minor seasonal variations. Biological degradation of organic material and organic micropollutants was also observed in the GPLs. For young GPLs adequate sediment deposits may not yet have formed and degradation processes at the outflow may consequently not yet be well established. However, our results showed that within 5 years from the cessation of excavation a protective sediment layer is established that is sufficient to prevent the export of dissolved organic carbon to downgradient groundwater.

GPLs can improve groundwater quality in anthropogenically (e.g., pesticides and nitrate) or geologically (e.g., hardness) challenging situations. However, post-excavation usage of GPLs is often dominated by human activities such as recreational activities, water sports, or fish farming. These activities will affect lake and groundwater quality and the risks involved are difficult to predict and monitor and can lead to overall negative impacts on groundwater quality.

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1. Introduction

Gravel pit lakes (GPLs) result from the extraction of construction materials, often excavated in the vicinity of urban areas where demand is high for both mineral resources and groundwater for human consumption. This can result in land-use conflicts since the impacts of GPLs on groundwater are of concern if the groundwater is used as drinking water, and also because of the precautionary principle (i.e., proof that an action or measure has no harmful impacts to the environment) that applies under, for example, the EU water framework directive.

Sand and gravel are non-renewable mineral resources. The European demand in 2010 was estimated to be three billion metric tons, representing a turnover of about € 20 billion (UEPG, 2012). Sand and gravel are required for many important applications such as building construction, highways, sewers, railroad beds, and water catchment management. The excavation of these natural materials is, in many cases, restricted by urban sprawl (Johnson, 2001), nature conservation, and groundwater protection legislation (Botta et al., 2009), rather than by the extent of the resource. The exclusion of close-to-demand mining areas through such restrictions results in exploitation of more distant mining areas (Arbogast et al., 2000). Gravel and sand are consequently imported from further away, which leads to adverse environmental impacts such as increased CO_2 emissions due to the longer transport distances. Excavation of sand and gravel from Quaternary fluvial sediments close to the demand is therefore ideal, both ecologically and economically, as the quality of the excavated material (Botta et al., 2009) and the transport distances are both optimized.

Important groundwater resources are, however, also often located in Quaternary sediments and GPLs can therefore endanger drinking water supplies (Apaydin, 2012). Excavation is achieved through either dry or wet dredging. The latter is performed below the groundwater table, providing a better quantitative use of the resource and minimizing land consumption. However, wet dredging may cause conflicts with drinking water providers since GPLs can impact on downgradient groundwater quality (Bertleff et al., 2001; Drew et al., 2002; Stichler et al., 2008). These artificial lakes are also often used post-excavation as recreational areas (Yehdegho and Probst, 2001), introducing the possibility of additional environmental threats as a result of these activities (Gołdyn et al., 2010).

A schematic cross-section of a groundwater-fed GPL and its interactions with upgradient and downgradient groundwater is shown in Fig. 1. The downgradient groundwater is rendered more vulnerable to contamination due to the loss of its protective soil cover and its exposure to the atmosphere. This may result in exposure to airborne contaminants (Couillard et al., 2008), surface runoff (Bach et al., 2001), water-borne contaminants (Pitois et al., 2000), oxidation of aquifer minerals (Marques et al., 2012), lake water-related pathogens (Brookes et al., 2004), changes in chemical processes (Sprenger et al., 2011), and nutrient concentration (Nizzoli et al., 2010). In addition to these processes anthropogenic use of the lake, for example for fish farming, recreational areas, theme parks, and related activities, will also affect the quality of the groundwater in the lake. The effects to be expected from such usage will depend to a large degree on the intensity of usage, the precautionary measures that are in place, and on compliance inspections relating to any restrictions that are imposed, and hence they need to be addressed on a case by case basis.

While the possible negative impacts of GPLs have been discussed in published literature (e.g., Marques et al., 2012; Yehdegho and Probst, 2001; Pitois et al., 2000), potential positive effects have rarely been considered. Groundwater-fed GPLs can alter the biologic, organic, and inorganic parameters of groundwater through a combination of bank filtration at the inflow, reactions within the lake itself, and bank filtration at the outflow. The positive aspects of bank filtration on groundwater quality through abiotic and biotic processes are well recognized (Kedziorek et al., 2008; Massmann et al., 2008; Wiese et al., 2011). In addition to the effects of bank filtration, water quality may also be improved through the biologically highly active water column in the lake itself (e.g., the activity of primary producers and microorganisms), as well as through atmospheric exchange. Biogenic decalcification within the lake may also be beneficial for waterworks that are dependent on hard groundwater (Kinsela et al., 2012). Moreover, a shift in the redox environment (from oxic groundwater, to anoxic conditions in the bank filtration zone) could, for example, enhance the degradation of pesticides or other organic micropollutants.

The aim of this study was to elucidate the influence of GPLs on downgradient groundwater quality. Five GPLs differing in size, post-excavation age, and mean lake water residence time, have been investigated. To exclude possible overlapping impacts from post-excavation anthropogenic usage, the GPLs selected for investigation were restricted to lakes that had no intensive usage and as little as possible anthropogenic disturbance. In addition to the lake water quality, upgradient and downgradient groundwater quality was also analyzed in terms of physico-chemical parameters, selected water constituents, and microbiological parameters. We assessed the risks and benefits to the downgradient groundwater quality by comparing the data from the five selected lakes with published data from other GPLs.

2. Material and methods

2.1. Research areas

The five research areas selected are characteristic of Austrian shallow foreland basin aquifers with respect to, for example, their aquifer materials, hydraulic gradients, and dissolved O_2 (>2 mg L^{-1}). The investigated lakes are typical of Austrian GPLs in terms of depth (<10 m), surface area (<20 ha), and usage (recreational fishing only). The locations of the five gravel pit lakes in the states of Lower Austria,

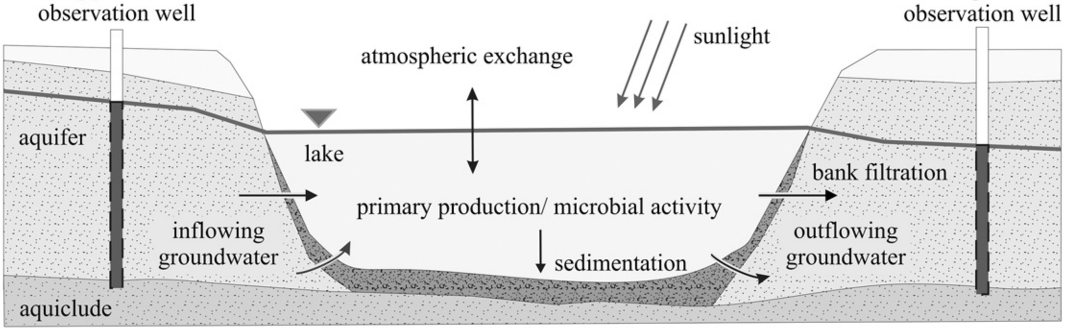

Fig. 1. Schematic cross-section of a groundwater-fed gravel pit lake, and locations of the hydraulically upgradient and downgradient observation wells installed for this study.

Upper Austria, and Styria, are shown in Fig. 2, together with a detailed view of each lake. To avoid major effects from post-excavation anthropogenic usage, this study was restricted to lakes that only allowed recreational fishing (fish stocking maximum 150 kg ha^{-1}, no fish feeding permitted). GPLs with public access for recreation (e.g., for swimming and water sports) or other activities were excluded. The lakes were surrounded by a vegetation buffer with no buildings, housing, or public roads (see Supplementary material, Supp. 1). Land use in the vicinity of the GPLs was dominated by agriculture. All lakes were groundwater-fed and had no surface water inflow. The surface areas of the GPLs ranged from 38,000 to 164,000 m^2, and the time period since excavation ceased ranged from 1 year to 28 years. The maximum depth of the lakes was limited by their geological settings to between 5 and 10 m. Both lake water and inflowing groundwater were oxic.

The surrounding porous aquifers consisted of carbonate-rich Quaternary fluvial deposits (mainly sand and gravel) that are situated geologically within the Austrian Molasse basin, a foreland basin. The GPL 1 (Marchfeld) aquifer had its origin in a geological depression (a pull apart basin) and is dominated by river sediments from the Danube River, with a minor contribution from the March River, while the GPL 2 (Tullner Feld) aquifer was formed under the influence of the Traisen, Kamp, Krems, and Danube rivers. The GPL 3 (Leibnitzer Feld) aquifer is dominated by deposits of the Mur River, the GPL 4 (Ybbser Scheibe) aquifer is influenced by sediments from the Danube and Ybbs rivers, and the GPL 5 (Welser Heide) aquifer comprises sediments from the Traun River. Because of their different catchment areas, these river sediments consist of a wide range of minerals, but the source lithologies are dominated by the rocks of the Northern Limestone Alps and, in the case of GPL 3, by those of the Central Eastern Alps. The hydraulic conductivities ranged from 1.5×10^{-2} to 5×10^{-3} m s^{-1}, and hydraulic gradients from 0.3 to 2.9‰. The aquifer thickness was around 40 m for GPL 1 and ranged between 5 and 10 m for the other four study areas (GPLs 2–5). With the exception of GPL 1, all GPLs were fully excavated down to an aquiclude. Geological profiles and information on aquifer characteristics are provided in the Supplementary material (Supp. 2). The annual rainfall in 2009 ranged from 0.56 to 1.31 m and exceeded the potential evaporation (calculated after Penman, as described by DVWK, 1996) for all GPLs except GPL 1. The mean residence time of the lake water varied between 0.2 and 1.5 years (Weilhartner et al., 2012), based on stable water isotope $\delta^{18}O$ analysis and numeric groundwater flow simulation. The most important characteristics of the selected GPLs are summarized in Table 1.

2.2. Groundwater and lake water sampling

The research areas were located in climate zones with dimictic lake types, and sampling was therefore performed twice during circulation phases (April and September, 2009) and twice during stagnation phases (July and December, 2009). Groundwater observation wells (inner diameter: 0.05 m, high-density polyethylene) were installed upgradient and downgradient from the lake (Fig. 1). The downgradient observation wells were a maximum of 25 m from the lake shorelines (Fig. 2). The hydraulic connections between the downgradient groundwater observation wells and the lakes were tested by analyzing stable water isotopes ($\delta^{18}O$), as reported by Stichler et al. (1986).

Groundwater samples were collected with a submersible pump (Grundfos® MP 1), after stabilization of field parameters and after at least three times the well volume had been exchanged. Lake water was sampled from a boat equipped with a submersible pump (Gigant® 12 V) at influent and effluent locations, and in the center of the lake. The lake water samples were collected from three depths in each part of the lake: 0.5 m below the water surface, the middle zone of the lake water column, and 0.5 m above the lake floor.

Polyethylene (PE) sampling bottles were pre-conditioned in the laboratory. All bottles were rinsed three times with ultrapure water ($\leq$0.06 -μS cm^{-1}, Millipore® Elix 5), conditioned for 48 h with 1 mL HNO_3 (6 M Merck®, ultra-pure) per 100 mL, and then rinsed again three times with ultrapure water before drying. In the field, each bottle was rinsed three times with the sample water and then filled so that it was free of air bubbles and had no headspace.

Samples for the main anions (Cl^-, NO_3^-, and SO_4^{2-}), and also for NH_4^+ and NO_2^- were filtered on site through 0.2 μm Millipore® cellulose acetate filters. Samples for the main cations (Ca^{2+}, Mg^{2+}, Na^+,

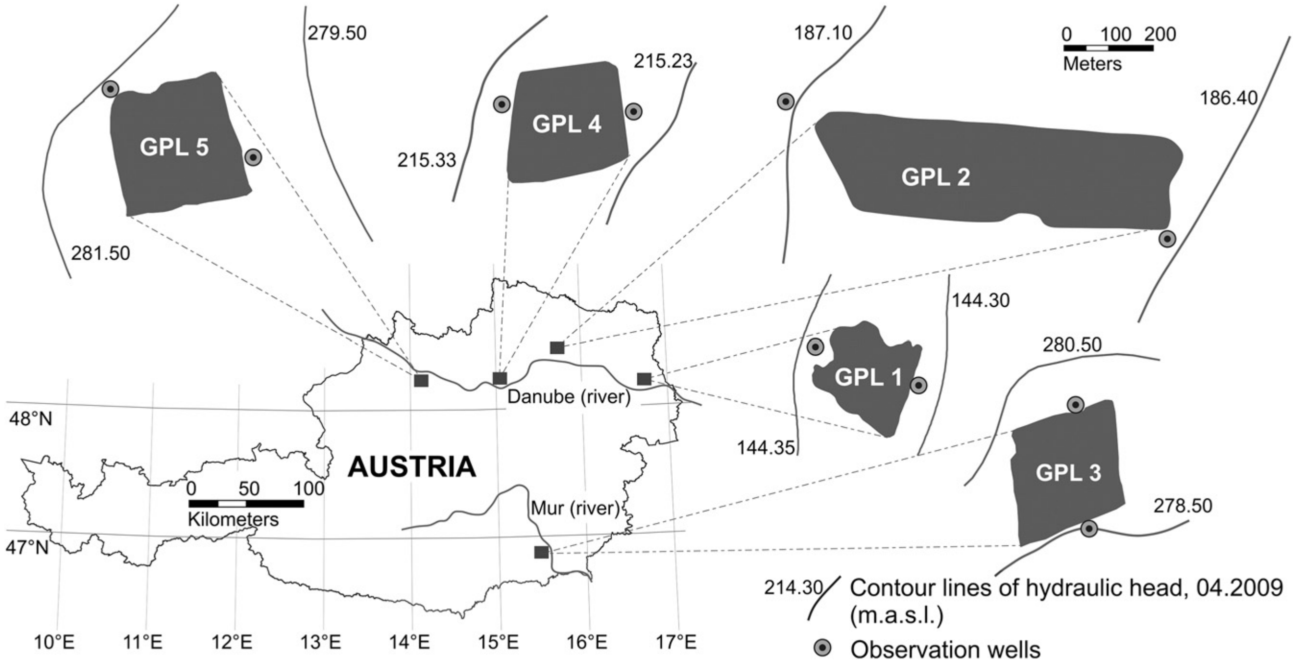

Fig. 2. Locations of the five gravel pit lakes and detailed views of each of the lakes, showing contour lines for the hydraulic heads and the locations of upgradient and downgradient observation wells.

Table 1
Characteristics of the investigated GPLs and the surrounding aquifers.

Lake	Age [a]	Surface area [m^2]	Max. water depth [m]	Mean lake water residence time [a]	Groundwater inflow [m^3 d^{-1}]	Total annual precipitation (2009) [m]	Potential evaporation (2009) [m]	Hydraulic gradient [‰]	Hydraulic conductivity [m s^{-1}]
GPL 1	1	38,000	9.6	1.4	423	0.56	0.79	0.3	5×10^{-3}
GPL 2	5	164,000	10.1	1.5	1954	0.69	0.67	0.8	5×10^{-3}
GPL 3	10	59,000	5.0	0.2	1500	1.32	0.73	1.5	$1–5\times10^{-3}$
GPL 4	17	60,000	9.2	1.1	790	1.05	0.70	0.4	5×10^{-3}
GPL 5	28	86,000	6.3	0.3	3582	0.90	0.61	2.9	$1–1.5\times10^{-2}$

and K^+), Fe^{2+}, Mn^{2+} and trace elements (Ni, Cr, Cu, Zn, Pb, Cd, and Al) were filtered on site through 0.45 μm Millipore® cellulose acetate filters and acidified with HNO_3 (6 M Merck®, ultra-pure) to pH<2. Samples for dissolved organic carbon (DOC) and microbial abundance were collected in 500 mL bottles, and samples for $\delta^{18}O$ were collected in 100 mL bottles. Additional water samples were collected immediately after pesticides had been applied in the agriculture-dominated surroundings of GPLs 1, 2 and 4, from upgradient and downgradient groundwater observation wells and from the center of each of the three lakes (0.5 m below lake water level). Sample bottles (5000 mL Duran amber glass, Schott®) were sealed with PTFE-tape. All samples were stored in a cooling box at approximately 4 °C and shipped to the laboratory within 4 h.

2.3. Chemical, physical and microbial analyses

Field parameters (pH, dissolved O_2, electric conductivity, and water temperature) were measured using an airtight continuous-flow chamber with WTW® measuring equipment (pH320, OxiCal-SL, Cond340i). The alkalinity of the groundwater samples was determined in the field with the Gran plot method (Stumm and Morgan, 1996), using at least four titration points between pH 4 and pH 3 by adding HCl (0.1 M Merck® ultra-pure). A Continuous Flow Analyzer (Alliance instruments®) was used to determine NO_3^-, NO_2^- and NH_4^+; the limit of quantification (LOQ) was 100 μg L^{-1} for NO_3^-, and 10 μg L^{-1} for NO_2^- and NH_4^+. Major cations and Fe^{2+} were measured by Inductively Coupled Plasma-Optical Emission Spectrometry using a PerkinElmer® Optima 5300DV ICP-OES (LOQ 100 μg L^{-1} for Mg^{2+}, Ca^{2+}, Na^+ and K^+, and 5 μg L^{-1} for Fe^{2+}). Trace elements and Mn^{2+} were measured with Inductively Coupled Plasma–Mass Spectrometry using a PerkinElmer® Elan 6100 ICP–MS (LOQ 0.02 μg L^{-1} for Cd, 0.1 μg L^{-1} for Cu, Ni, and Zn, 0.2 μg L^{-1} for Pb, 1 μg L^{-1} for Cr and Mn^{2+}, and 10 μg L^{-1} for Al). Ion chromatography was used to measure Cl^- and SO_4^{2-} using a Dionex® IC 1000 IC System (LOQ 100 μg L^{-1}). A Picarro® L1115-i Isotopic Liquid Water and Water Vapor Analyzer, with a precision of ±0.1‰, was used to measure $\delta^{18}O$. DOC samples were filtered (GF/F Whatman®, 0.45 μm) and analyzed using a Sievers 900 Portable TOC Analyzer (GE Analytical Instruments®), with a working range of 0.03 μg L^{-1} to 50 mg L^{-1} and 3% accuracy. For microbial abundance, 10 mL of samples were transferred into sterile triplicate vials containing formaldehyde (2.5% final concentration), and then 10 μL of DNA/RNA dye (SYTOX® Green) was added to 990 μL of the water sample (5 μM final concentration) and incubated for 15 min in the dark. Microbial abundance was measured using flow cytometry (Beckman Coulter® Quanta cytometer) and epifluorescence microscopy (Zeiss® Axioimager microscope). Pesticides and metabolites were analyzed by Liquid Chromatography–Mass Spectrometry (Varian® 320-MS-detector, Reprosil Pur® C18-AQ phase 3 μm 150×2.0 mm column). The LOQ was 0.025 μg L^{-1} for desphenylchloridazone, methyldesphenylchloridazone, metolachlor, metolachlor ethane sulfonic acid (ESA), metolachlor oxanilic acid (OA), dimethachlor ESA, metazachlor ESA, metazachlor OA, and chlorthalonil ESA. For 2,6-dichlorobenzamide and terbuthylazine the LOQ was 0.02 μg L^{-1}, and for bentazone it was 0.05 μg L^{-1}.

3. Statistical analyses and calculations

In order to determine the influence of GPLs on the downgradient groundwater quality, changes in field parameters (pH, dissolved O_2, and electric conductivity), microbiological parameters (microbial abundance and DOC), and chemical parameters (major cations, major anions, NH_4^+, NO_2^-, Fe^{2+}, Mn^{2+}, and trace metals), were statistically analyzed using the Wilcoxon matched pairs test (Jürgen and Laatz, 2005). The threshold p-value for statistical significance was set at 0.01. The calculated p-values are documented in the Supplementary material (Supp. 3). Differences between the upgradient and downgradient groundwater quality were tested to assess the influence of GPLs on groundwater parameters. The lake water quality was also compared to the downgradient and upgradient groundwater qualities in order to determine whether changes took place within the lake itself, or during bank filtration. The relevant sets of parameter (n=20) were based on seasonal groundwater measurements and average values from seasonal lake water measurements.

Annual average concentrations for all four seasons and the standard deviations were calculated from seasonal measurements of upgradient groundwater (n=4), downgradient groundwater (n=4), and lake water (n=36).

The average calcite saturation indices were calculated for upgradient groundwater (n=4), downgradient groundwater (n=4), near-surface lake water (n=4, central location) and near-bottom lake water (n=4, central location), using the PHREEQC thermodynamic equilibrium model, version 2.17 (Parkhurst and Appelo, 1999).

A mass balance was calculated from the solute transport of Ca^{2+} and NO_3^-, based on groundwater inflow and outflow and atmospheric deposition. Information regarding the calculations can be found in Weilhartner et al. (2012), and in the Supplementary material (Supp. 4).

4. Results

4.1. Isotope data

Enriched $\delta^{18}O$ values in the lake water relative to the upgradient groundwater indicated the influence of evaporation (Fig. 4a). The enrichment was between 1.5 and 3.6‰ for the GPLs with a mean residence time more than one year and less than 1.5‰ for the GPLs with a shorter mean residence time (≤0.3 year). Seasonal isotopic variations in the lake water were shown to be very low (Fig. 3a–e). Only the summer bottom-water samples from GPLs 1 and 4 showed lower $\delta^{18}O$ enrichment than the near-surface lake water. In spring, autumn, and winter, GPLs 1 and 4 were fully mixed. The downgradient groundwater observation wells proved to be 88–100% lake water influenced, calculated after Stichler et al. (1986). All $\delta^{18}O$ values and calculated hydraulic connections of the downgradient observation wells to the lake water are provided in the Supplementary material (Supp. 5).

4.2. Field parameters

The pH values were significantly higher in the lake water (+1.0±0.3 pH units on average) than in the upgradient groundwater (Fig. 4b).

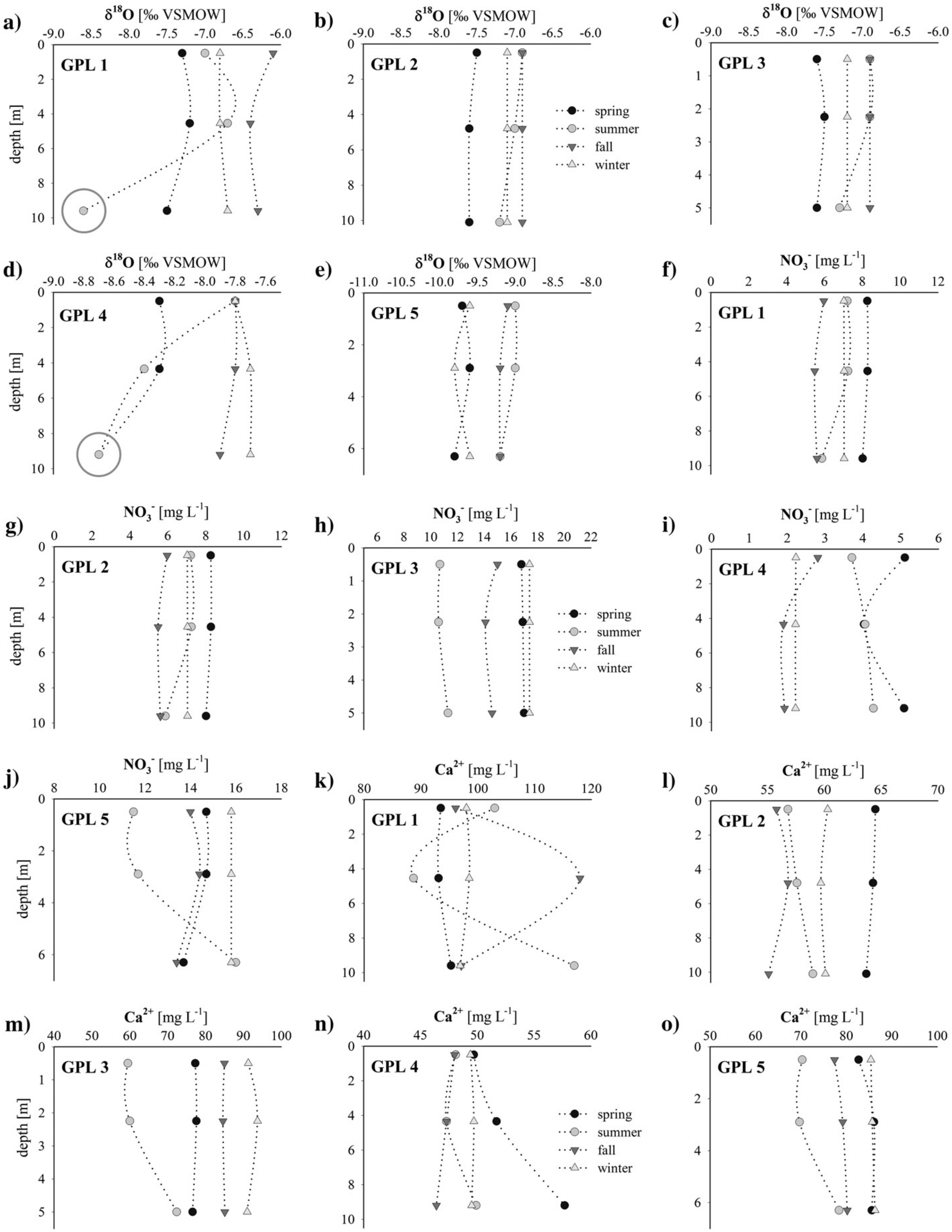

Fig. 3. Vertical lake water profiles for $\delta^{18}O$, NO_3^- and Ca^{2+}, from all five GPLs in all four seasons (from central locations, and showing depth below water surface).

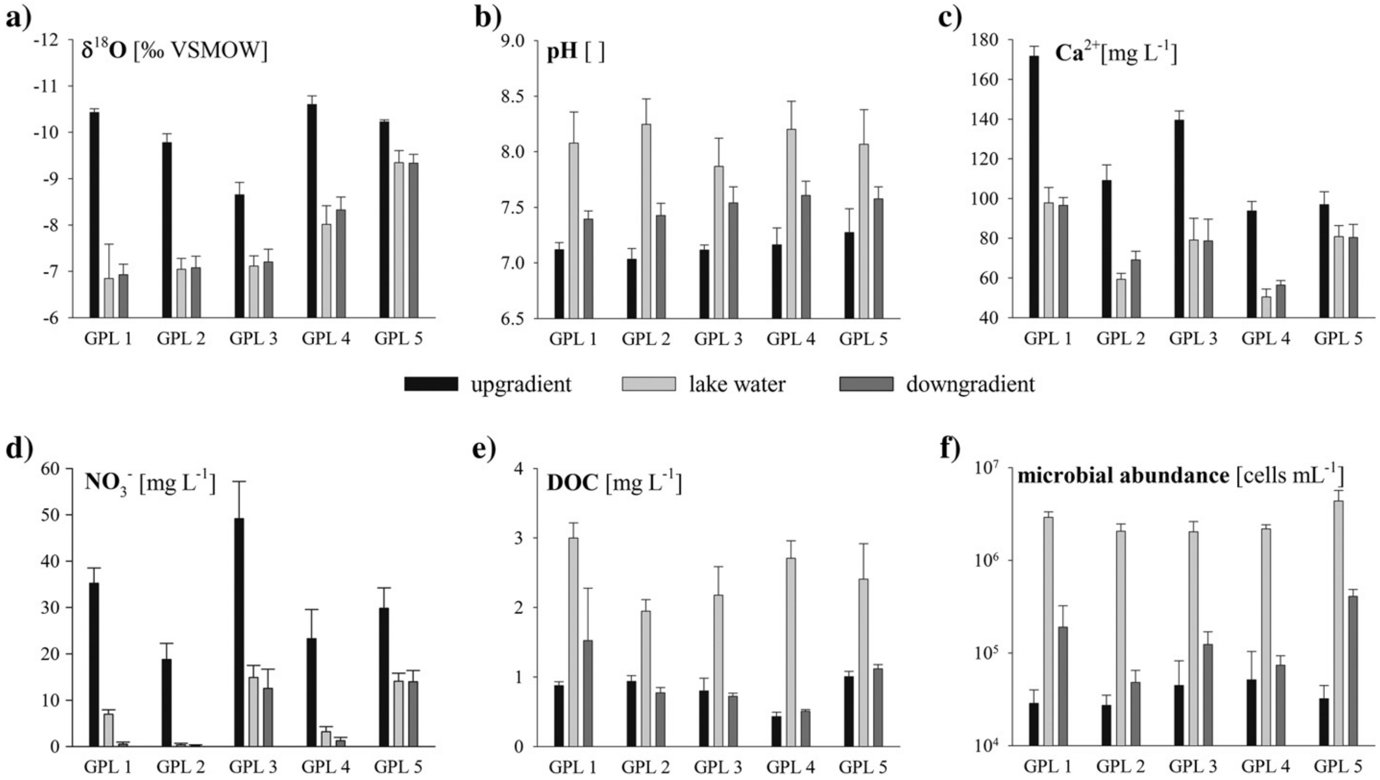

Fig. 4. Annual average hydrochemical (pH, Ca^{2+}, NO_3^-, $\delta^{18}O$), and microbial (DOC, microbial abundance) data along the groundwater flow gradient of all GPLs, with associated standard deviations, for upgradient groundwater (n = 4), downgradient groundwater (n = 4), and lake water (n = 36).

Downgradient of the lakes the pH values decreased again, but remained significantly higher than in the upgradient groundwater (+0.4 ± 0.2 pH units on average). Dissolved O_2 concentrations were significantly lower (down to anoxic conditions) in the downgradient groundwater than in the upgradient groundwater or the lake water. Dissolved O_2 was >2 mg L^{-1} in the upgradient groundwater and the lake water, for all GPLs and all seasons. Downgradient groundwater temperatures were up to 7.2 °C higher in summer and up to 6.9 °C lower in winter than upgradient groundwater temperatures. In summer, lake water temperatures close to the surface reached up to 27.3 °C. Electric conductivity was significantly lower in the lake water (−234 ± 132 μS cm^{-1} on average) than in the upgradient groundwater. The downgradient groundwater electric conductivities were similar to those of the lake water. Measurements of dissolved O_2, groundwater temperature, and electric conductivity along the groundwater flow gradients, from upgradient groundwater to downgradient groundwater, are presented in Table 2. Results for the lakes are provided in the Supplementary material (Supp. 6).

4.3. Hydrochemical parameters

The Ca^{2+} and Mg^{2+} concentrations were significantly lower in the lake water than in the upgradient groundwater (−48.7 ± 20.9 mg L^{-1} and −3.4 ± 3.3 mg L^{-1} respectively, on average; see Fig. 4c and Supplementary material, Supp. 7). The concentrations downgradient from the lake were similar to those in the lake water. Mass balance calculations for Ca^{2+} indicate retention rates between −0.16 and −0.52 kg m^{-2} a^{-1}; downgradient concentrations were up to 47% lower than upgradient groundwater concentrations. (Table 3). The HCO_3^- concentrations were significantly lower in the lake water (−113 ± 46.6 mg L^{-1} on average) than in the upgradient groundwater; they increased again downgradient but were still significantly lower than the upgradient concentrations (−94 ± 42.2 mg L^{-1} on average). Calculated calcite saturation indices indicated near equilibrium conditions for both upgradient and downgradient groundwater. In contrast, the lake water calcite saturation indices indicated supersaturation, with average values near the lake surface of 0.8 ±

Table 2
Development of dissolved oxygen, groundwater temperature, and electric conductivity for all GPLs, along the groundwater flow gradient from upgradient groundwater to downgradient groundwater.

		Dissolved oxygen [mg L^{-1}]				Water temperature [°C]				Electric conductivity [μS cm^{-1}]			
		sprIng	Summer	Fall	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall	Winter
GPL 1	Upgradient	2.4	2.6	2.8	3.0	11.4	11.9	12.1	11.3	1460	1445	1361	1423
	Downgradient	1.3	<0.1	2.1	0.3	8.0	19.1	19.3	15.6	1042	1036	994	1008
GPL 2	Upgradient	5.7	5.3	7.8	5.7	11.1	11.8	13.9	11.8	839	860	956	836
	Downgradient	2.0	1.1	1.5	1.1	9.0	14.4	19.8	15.0	677	649	599	615
GPL 3	Upgradient	9.8	8.2	8.0	8.4	10.9	14.5	14.4	10.7	906	807	775	768
	Downgradient	5.9	0.4	<0.1	4.9	12.1	20.9	21.5	9.8	550	517	577	601
GPL 4	Upgradient	9.3	9.0	6.8	6.9	11.6	12.7	13	10.7	627	586	572	590
	Downgradient	0.4	<0.1	<0.1	0.2	10.0	15.8	18.1	15.4	404	426	399	410
GPL 5	Upgradient	10.6	8.0	4.7	7.2	10.4	11.8	13.9	11.5	638	654	615	588
	Downgradient	2.0	3.6	1.5	6.2	15.5	14.5	19.7	4.6	551	532	528	581

Table 3
Mass balance results for Ca^{2+} and NO_3^-, for all five GPLs.

Lake	Groundwater inflow [kg a^{-1}]	Atmospheric deposition[a] [kg a^{-1}]	Groundwater outflow [kg a^{-1}]	Retention rates[b] [kg m^{-2} a^{-1}]	Decrease[c] [%]
Ca^{2+}					
GPL 1	26,493	23	14,049	−0.33	47
GPL 2	77,734	98	49,366	−0.17	37
GPL 3	76,361	35	45,760	−0.52	40
GPL 4	27,015	36	17,429	−0.16	36
GPL 5	126,649	52	107,021	−0.23	16
NO_3^-[d]					
GPL 1	5437	57	69	−0.14	99
GPL 2	13,383	246	147	−0.08	99
GPL 3	26,913	89	7301	−0.33	73
GPL 4	6705	90	375	−0.11	94
GPL 5	38,982	129	18,624	−0.24	52

[a] Leder (2008).
[b] Retention rates per m^2 lake surface (negative values indicate a sink).
[c] Compared to upgradient groundwater concentrations.
[d] Weilhartner et al. (2012).

0.1 and average values near the bottom of the lake of 0.5 ± 0.1 (Fig. 5). Average NO_3^- concentrations decreased significantly along the flow path from upgradient groundwater to lake water (−23.3 ± 8.7 mg L^{-1}), and from the lake water to downgradient groundwater (−2.2 ± 2.5 mg L^{-1}, Fig. 4d). Mass balance calculations for NO_3^- reveal retention rates between −0.14 and −0.33 kg m^{-2} a^{-1}; downgradient concentrations were up to 99% lower than upgradient groundwater concentrations (Table 3). Downgradient NO_2^- concentrations were ≤0.01 mg L^{-1} and the NH_4^+ concentrations ≤0.18 mg L^{-1}, for all sampling dates, (see also Weilhartner et al., 2012). For SO_4^{2-}, Cl^-, K^+, Na^+, Fe^{2+}, and Mn^{2+}, downgradient groundwater concentrations did not differ significantly from upgradient groundwater or lake water concentrations. The Fe^{2+} concentrations were always ≤0.12 mg L^{-1}, and the Mn^{2+} concentrations were always ≤0.18 mg L^{-1}, the only exception being the downgradient groundwater at GPL 1, where concentrations were up to 0.29 mg L^{-1} for Fe^{2+} and up to 0.95 mg L^{-1} for Mn^{2+}. Trace metal concentrations were similar in downgradient groundwater to upgradient groundwater and lake water (≤0.04 μg L^{-1} for Cd, ≤14.2 μg L^{-1} for Zn, ≤1.7 μg L^{-1} for Cr, ≤8.0 μg L^{-1} for Cu, ≤8.1 μg L^{-1} for Ni, ≤4.4 μg L^{-1} for Pb, and ≤88 μg L^{-1} for Al). Although Ni concentrations decreased consistently, the downgradient decrease was on average only 1.1 ± 0.8 μg L^{-1}. Results for Mg^{2+}, K^+, Na^+, HCO_3^-, Cl^-, SO_4^{2-}, Fe^{2+}, Mn^{2+}, and trace metals from all GPLs are provided in the Supplementary material (Supp. 7, 8, 9).

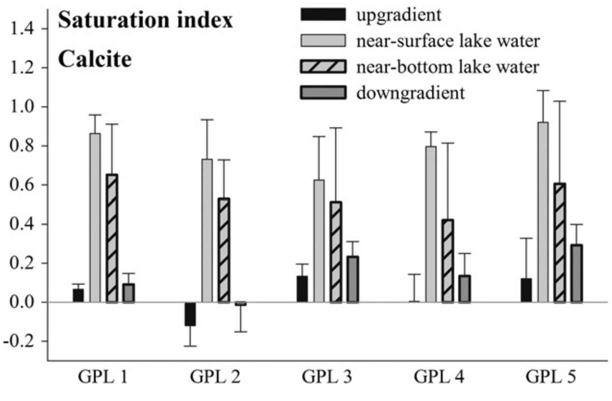

Fig. 5. Annual average calcite saturation indices along the groundwater flow gradient of all GPLs, with associated standard deviations, for upgradient groundwater (n = 4), near-surface lake water (n = 4), near-bottom lake water (n = 4) and downgradient groundwater (n = 4).

4.4. Microbial parameters

DOC concentrations were significantly higher in the lake water (1.64 ± 0.55 mg L^{-1} on average) than in the upgradient groundwater, but decreased again downgradient (Fig. 4e). Upgradient and downgradient groundwater therefore had comparable DOC concentrations, and no DOC export could be observed from the older lakes. Higher downgradient DOC concentrations were only recorded at the youngest lake (GPL 1). Microbial abundances in upgradient water samples were consistently low (Fig. 4f) but increased significantly in all GPLs (+2.7 ± 1.1 × 10^6 cells mL^{-1}, on average). Microbial abundances decreased again rapidly downgradient, but were still high compared to upgradient groundwater abundances (+1.3 ± 1.5 × 10^5 cells mL^{-1}, on average).

4.5. Pesticides and metabolites

The metabolite desphenylchloridazone was detected in the upgradient groundwater at all GPLs where the examination for pesticides and metabolites was carried out (0.10 μg L^{-1} at GPL 1, 0.03 μg L^{-1} at GPL 2, 0.05 μg L^{-1} at GPL 4). Desphenylchloridazone was, however, no longer detectable in the lake waters. The downgradient observation well for GPL 2 was situated on agricultural land where the pesticide chloridazone was used; the transformation product desphenylchloridazone was present at a concentration of 0.04 μg L^{-1}. None of the other pesticides or metabolites for which we tested were detected at any of the GPL systems investigated.

5. Discussion

Groundwater can be endangered by GPLs and the loss of its protective soil cover. However, the chemical, physical, and microbial processes operating within the lake and during bank filtration can also improve the quality of the inflowing groundwater and be beneficial to waterworks in situations that pose anthropogenic (e.g., pesticides and nitrates) or geological (e.g., water hardness) challenges. A good understanding of the potential impacts of GPLs is thus crucial, especially when downgradient groundwater is used as drinking water.

5.1. Lake water mixing and redox conditions

The investigated GPLs are groundwater-fed systems in which isotope fractionation modifies $\delta^{18}O$ through lake water evaporation. Vertical isotopic lake water profiles provide insights into lake water mixing, stratification and, in particular, into deep groundwater inflows into lakes (Perini et al., 2009). Seebach et al. (2010) and Stichler et al. (2008) have previously reported significant stratification in GPLs, but the lakes that they considered were much deeper than those that we investigated. In our study, only at GPL 1 (Fig. 3a) and GPL 4 (Fig. 3d) was a near-bottom groundwater flow with less $\delta^{18}O$ enrichment seen in summer, which is typical of a groundwater-influenced colder base-flow. At all other times of the year the nearly homogeneous $\delta^{18}O$ values of the lake water clearly indicated a wind and density driven mixing of the lake water throughout the entire water column, preventing any stable thermal or chemical stratification of the lake water (Fig. 3a–3e).

In downgradient groundwater the dissolved O_2 was depleted by microbial degradation of organic matter at the lake-aquifer interfaces, as described by various studies related to bank filtration (Sharma et al., 2012; Hoffmann and Gunkel, 2011; Kedziorek et al., 2008). This is also supported by the observed pH decrease in downgradient groundwater (Fig 4b). With time, biomass sedimentation may build up a thick layer at the interface between the lake and the aquifer (Weilhartner et al., 2012). However, dissolved O_2 was depleted downgradient not only in the older GPLs (3–5), but also in the younger GPLs (1–2), and similar redox conditions were found in GPLs of all ages (Table 2). This may be the result of highly productive lakes causing a rapid build-up of the sediment layers, followed by microbial O_2 consumption at the interfaces.

5.2. Groundwater temperature

As discussed by Sprenger et al. (2011), the rate of biochemical processes increases with water temperature. Water temperature also influences the survival time of microorganisms and the inactivation of viruses (Brugger et al., 2001). The water temperature in lakes follows atmospheric weather conditions and has a clear effect on downgradient groundwater temperatures. However, Stichler et al. (2008) reported a rapid return to upgradient groundwater temperatures within 200 m downgradient of a GPL, even though the $\delta^{18}O$ signal clearly indicated lake water origin. In this study a similar rapid temperature adjustment was noted at downgradient observation wells, although downgradient groundwater temperatures clearly indicated the influence of the lake water (Table 2).

5.3. Microbial abundance

Alfreider et al. (2001) reported little difference in microbial abundance downgradient from older GPLs; microbial abundance was only affected downgradient from a lake that was still being dredged. In contrast, our own results indicated a significant increase in microbial abundance at the downgradient observation wells for all GPLs throughout the seasons. However, the microbial abundance at downgradient observation wells (well-shoreline distance <25 m) was already between 6.1 and 6.7 log units smaller than in the lake water (Fig. 4f), proving that bank filtration is a powerful mechanism for reducing microbial abundance. Groundwater temperature variations showed little influence on microbial abundance.

5.4. Dissolved organic carbon

DOC forms a substrate for microbial metabolism and growth (Battin, 1999). In groundwater, DOC is mainly soil-derived, originating from sources such as plant and microbial biomass (Baker and Lamont-Biack, 2001). In lake water, additional inputs such as algal biomass or leaf litter from vegetation surrounding the GPLs, contribute to the DOC composition. High DOC values can be critical in drinking water supplies due to, for example, the possible formation of toxic disinfection byproducts as result of chlorination (Zhang et al., 2012), increased pathogens in distribution networks, or increased microbial growth (Lee et al., 2006). DOC concentrations increased in all of the investigated GPLs, but decreased again downgradient to background values (Fig. 4e). In general, GPLs appeared to have no significant influence on downgradient DOC concentrations. Only at the youngest lake (GPL 1), where dredging was completed just one year ago, an elevated DOC concentration in the downgradient groundwater was observed, probably due to the lake sediments not yet being fully developed.

5.5. Nitrogen

Concentrations of NO_3^- were significantly reduced in the downgradient groundwater at all five GPLs investigated (Fig. 4d). Primary producers (i.e., macrophytes, algae) are largely responsible for the observed nitrate reduction in the GPLs via nutrient uptake (Weilhartner et al., 2012; Harrison et al., 2009; Alfreider et al., 2001). A further downgradient nitrate reduction was observed, most likely due to microbial denitrification under anoxic conditions. This downgradient reduction was relatively minor (<6.5 mg L^{-1}, on average) compared to the uptake by primary producers in lake water (up to 34 mg L^{-1}, on average). While the upgradient NO_3^- concentrations ranged up to 57.8 mg L^{-1}, exceeding WHO guidelines for safe drinking water quality (WHO, 2011), downgradient concentrations were always ≤17.1 mg L^{-1}. Only very low NO_2^- and NH_4^+ concentrations were found in the anoxic downgradient groundwater.

The GPLs investigated thus serve as a sink for nitrate and have an important positive effect on groundwater quality. Neither the age of a GPL nor its size appeared to have a significant effect on the observed downgradient NO_3^- concentrations. Nitrate reduction is affected by the lake water residence time. In lakes with a long mean residence time (e.g., GLPs 1, 2, and 4), nitrate was reduced by up to 99%. The highest areal nitrate retention rates were observed at GPL 3 and GPL 5, which had the shortest lake water mean residence times. This indicates that despite initially high retention rates, the lake water mean residence time was likely too short to allow complete removal of nitrate. Longer mean residence time for the lake water may result in increased nitrate uptake and hence in reduced nitrate concentrations downgradient.

5.6. Decalcification

Lake water pH is not only influenced by the inflowing groundwater and by atmospheric exchange, but is also significantly affected by primary producers within the lake through uptake of CO_2 (Stumm and Morgan, 1996). In this study a marked pH increase in the lake water (up to 8.6) was observed, with consequent precipitation of calcite. Lake water calcite saturation indices clearly indicate supersaturation, with differences between near-surface and near-bottom lake water that may be due to variations in primary production (Fig. 5).

Downgradient pH was significantly lower than in the lake water (Fig. 4b), and downgradient calcite saturation indices consequently showed near equilibrium conditions (±0.3) in all locations. However, downgradient Ca^{2+} concentrations were similar to those of lake water, indicating that no re-dissolution of calcite from lake sediments had occurred. The highest precipitation rates per m^2 of lake surface were calculated for the shallow GPL 3, which had a short mean residence time for the lake water (Table 3). There was no relationship between the decrease in Ca^{2+} concentrations and the post-excavation age of the GPLs or the mean residence times of the lake water in general, but the observed decrease was proportional to the initial concentrations (with the exception of GPL 5). The observed decalcification is of major interest for drinking water supply, since calcite precipitation is a critical problem in distribution networks (Kinsela et al., 2012).

5.7. Metals

Microbial respiratory activity can lead to redox conditions in which subsequent dissolution of Mn(III) and Fe(III) (hydr)oxides can occur (Kedziorek et al., 2008). Even though dissolved O_2 was reduced or fully consumed downgradient, SO_4^{2-}, Fe^{2+}, and Mn^{2+} concentrations did not change significantly. The older GPLs (2–5) had no influence on the Fe^{2+} and Mn^{2+} concentrations. Concentrations only increased relative to upgradient values at GPL 1, but they still remained below <1 mg L^{-1}.

The GPLs were not found to have any significant influence on trace metals. Concentrations were within natural background levels (Kunkel et al., 2004). Marques et al. (2012) reported oxidation of reduced GPL sediments in Brazil, which can lead to acidification and subsequent mobilization of trace metals and SO_4^{2-} by pyrite dissolution. This process is a common problem in flooded lignite mines (Schultze et al., 2010) but not relevant to the shallow GPLs that we investigated, since the aquifer sediments did not contain any acid reducing mineral phases such as pyrite.

5.8. Pesticides

Even though the investigated GPLs are situated close to areas of intensive agriculture, no residues of any of the monitored pesticides were recorded in lake water. The vegetation belt surrounding the GPLs could possibly act as a barrier to pesticide inputs from surrounding agricultural areas, both from spray drift and from surface run off. However, desphenylchloridazone was detected in the upgradient groundwater, but this transformation product was not present in the lake water. Different microbial habitats and redox zones can promote the degradation of organic micropollutants. Sampl (1995) reported the biodegradation of atrazine in a groundwater-fed GPL, demonstrating the potential of GPLs to improve groundwater quality. However, the risks of inputs from spray drift or surface runoff still need to be taken into account (Tang et al., 2012), especially in young GPLs, where the absence of lake sediments reduces their ability to purify outflowing groundwater.

6. Conclusion

Although gravel pit lakes pose a potential risk to groundwater, we have in this study demonstrated that gravel pit lakes can also serve to improve the quality of downgradient groundwater through their various microbiological habitats and different redox zones. They provide retention capacity for both nutrients and pollutants. For example, NO_3^- concentrations are reduced though biological uptake by primary producers and may thus contribute to groundwater amelioration in situations where NO_3^- concentrations exceed drinking water guidelines. Furthermore, in areas where groundwater is predominantly hard due to the local geology, decalcification will be of considerable benefit to waterworks. The reduced NO_3^- and Ca^{2+} concentrations observed in this study were remarkably stable downgradient from the GPLs, with low seasonal variability.

We conclude that the biological degradation of organic material and organic micropollutants in gravel pit lakes is similar to well-known processes observed in bank filtration. We also conclude that this reactive zone may not yet be well established in young GPLs, where insufficient lake sediments have been deposited. The results from this study indicate that an adequate protective sediment layer is established within five years of the cessation of excavation. However, sediment deposition and the formation of an active bank filtration zone depend on many factors (e.g., nutrient supply, temperature, depth, and lake usage) and further investigations will be required before this can be established as a general rule.

Gravel pit lakes fulfill important ecological and socio-economic roles, serving for instance as valuable wetland habitats supporting biodiversity in both plants and animals. The use of GPLs, however, is often dominated by human activities. Human activities can affect downgradient groundwater quality by disturbing established food webs (e.g., by fish stocking, or through manipulation of algae growth), and can also result in the direct input of various contaminants (e.g., personal care products, antibiotics used in fish farming, and harmful substances released accidentally). The risk potentials are diverse, and the monitoring and control of these risks remains a challenge; it may even not always be possible. We therefore conclude that, if the downgradient groundwater is to be used as drinking water, either at present or in the future, GPLs should be protected as far as possible from anthropogenic disturbance as it is the major driver and risk for groundwater contamination.

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Appendix A. Supplementary data

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