DISSERTATION

Titel der Dissertation

„Biogeochemistry and biofilms in gravel pit lakes and effects on the outflowing groundwater quality"

Verfasser

Mag. rer. nat. Andreas Weilhartner

angestrebter akademischer Grad

Doktor der Naturwissenschaften (Dr. rer. nat.)

Wien, 2014

Studienkennzahl lt. Studienblatt:	A 091
Dissertationsgebiet lt. Studienblatt:	Ökologie
Betreuerin / Betreuer:	Univ. Prof. Dr. Tom J. Battin

Contents

Introduction 2

Study site description and methods 4

Ecology and biogeochemistry of gravel pit lakes 6

Publication 1 6

Publication 2 9

Publication 3 11

Conclusion 15

Publications forming the basis for this PhD thesis 16

References 17

Contributions to publications 18

Acknowledgements 19

Scientific publications and manuscripts 20

1. Gravel pit lake ecosystems reduce nitrate and phosphate concentrations in the outflowing groundwater 20

2. Positive and negative impacts of five Austrian gravel pit lakes on groundwater quality 28

3. Physiological profiles and community metabolism of benthic biofilms in gravel pit lakes 39

English Abstract 71

Deutschsprachige Kurzzusammenfassung 72

Curriculum Vitae 73

Introduction

Sand and gravel are essential natural resources obtained through various dredging methods but mainly through wet dredging from the groundwater aquifer. Many industries depend on the continuous supply of this non-mineral natural resource in applications such as concrete for housing, sewage facilities, water dams and channels but also ceramic elements for dental practices for instance (Botta et al., 2009; Drew et al., 2002).

Mining activities may lead to potential changes in biological, inorganic and organic parameters as well as changes of biogeochemical processes in the groundwater aquifer due to removal of protective soil coverage and exposure to the atmosphere (Muellegger et al., 2013). Hence dredging activities may pose direct harm to groundwater quality (Drew et al., 2002; Langer et al., 2001). Groundwater resources are often located in Quaternary sediments (Apayadin, 2012), which are sought after by the mining industries. However, public interest in safeguarding groundwater quality is especially high in urbanized areas were groundwater is increasingly used for drinking water supply. Hence conflicts between resource extracting industries and national authorities, working in the public interest of groundwater safety, are in the long term inevitable.

The aim of this study was to investigate effects of post-excavation gravel pit lakes (GPLs) on the long-term development of groundwater quality in the effluent areas of the lakes as well as understand key processes shaping this diverse man-made ecosystem. Various biogeochemical parameters as well as metabolic and physiological parameters of microorganisms in the GPL water, at the interfaces and in the lake sediments were measured and studied to gain knowledge of how these complex systems interact with the groundwater aquifer after mineral resource extraction.

In general, GPLs may affect hydrodynamic conditions in the groundwater aquifer by causing groundwater to deviate from its original pathway (Peckenham et al., 2009). Hence effects such as interface clogging and changes in lake water discharge and recharge are fundamental problems after dredging the deposits (Peckenham et al., 2009; Muellegger et al., 2013). In addition, the exposure of groundwater to the atmosphere significantly affects parameters such as water temperature, electric conductivity, pH and various biogeochemical processes. An increase in biological activity due to groundwater-derived nutrients leads to a build up of organic biomass in the GPLs (Weilhartner et al., 2012). However, with increasing post-dredging age of GPLs, groundwater – lake water interactions decrease due to sedimentation processes and subsequent clogging of the GPL interfaces and bottom. This is a critical point in the evolvement from young recently dredged and well-connected GPLs to old GPLs that are increasingly disconnecting from the adjacent groundwater aquifer, prone to eutrophication. Metabolic processes in GPLs, especially at the interfaces affect redox-sensitive parameters as well as dissolved organic carbon (DOC) and nutrient concentrations in the inflowing groundwater (Figure 1). These processes, mainly caused by microbial activity, occur at the inflow and outflow interfaces as well as in the lake water. GPLs represent a diverse and complex ecosystem comparable to natural seepage lakes due to similar connectivity of the lake to the adjacent groundwater aquifer and possibly similar effects of groundwater derived nutrients on the metabolic activity and biogeochemical processes in the lakes. Due to the massive build up in organic biomass and the slow disconnection from the groundwater aquifer, GPLs will with time evolve from oligotrophic to potentially eutrophic lakes. However, if respected and managed accordingly GPLs may add immense recreational value and biodiversity to the typically dull areas, mainly reined by agriculture, in which they exist.

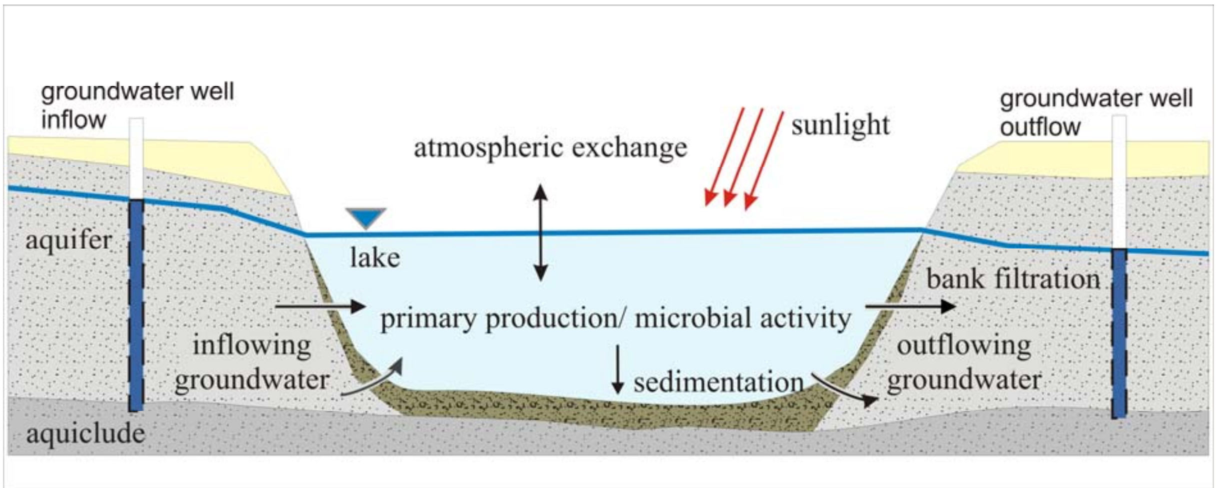
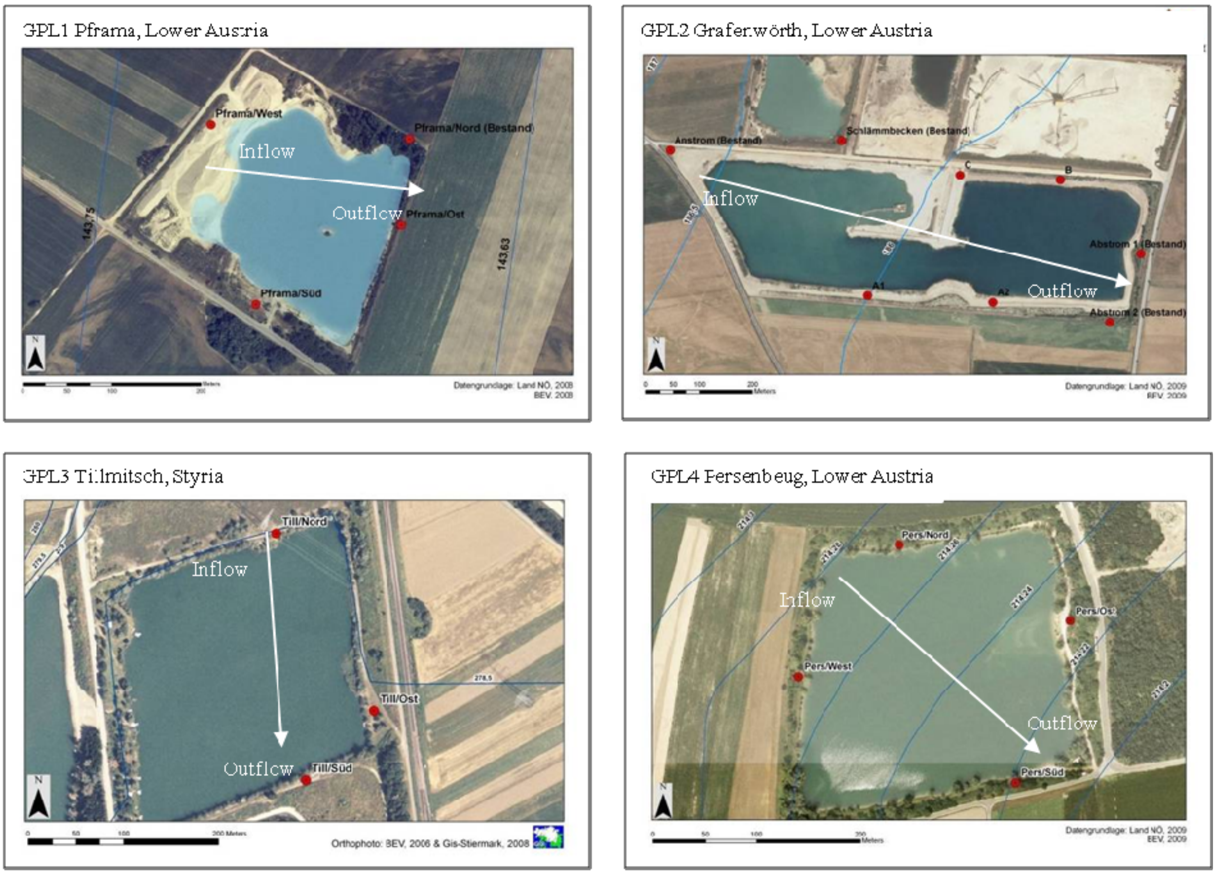


Figure 1: Graphical abstract of a post-excavation GPL ecosystem.

Study site description and methods

Only GPLs exposed to extensive use were chosen to serve as sample lakes in this study. Chosen GPLs had no surface water inflows, were not located in contaminated areas and had no risk of flooding. Out of a series of 29 literature surveyed GPLs, 12 were actively surveyed and, in accordance with the project stakeholders, 5 were chosen as sample lakes. GPLs were characteristic for the respective provinces of Austria and were located in Tillmitsch (Styria), Hörsching (Upper Austria), Grafenwörth, Persenbeug and Pframa (Lower Austria) (Figure 2).



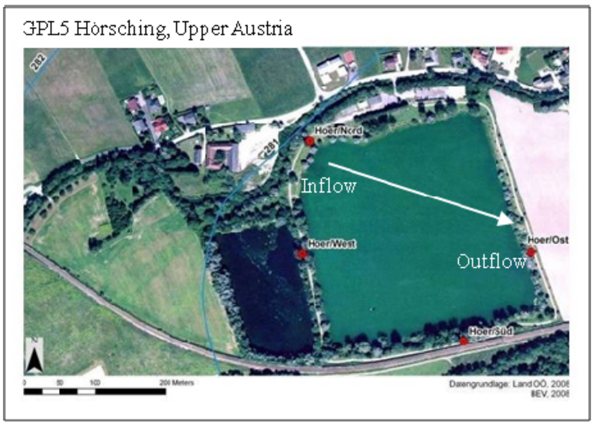


Figure 2: Satellite images of GPL 1-5 in combination with groundwater contour lines indicating the groundwater flow direction. Red dots were the location of the groundwater wells used for extraction of groundwater samples. Inflow and Outflow indicate inflow and outflow interfaces of each GPL, respectively were stones for biofilm analysis were sampled.

GPLs differed in size (3.8 – 16.4 hectares), depth (5 – 10 meters), and post-dredging age (1-28 years), thus allowed the study of potential effects of both, size and age on the outflowing groundwater quality. Groundwater conditions were monitored using self-installed and already existing groundwater wells. Bathymetry was used to elaborate the geomorphology of each GPL. Based on a combination of mean groundwater table measurements, bathymetric results and groundwater contour maps, provided by the regional governments, a numerical groundwater model was constructed to assess mean residence times of all GPLs. Results of this model were independently verified using stable isotope analysis ($\delta^{18}O$). Both methods yielded matching results. Mean water residence times of the GPLs ranged from 0.2 to 1.5 years (Muellegger et al., 2013).
GPLs were monitored seasonally during the year 2009 for lake and groundwater temperature, electric conductivity, dissolved oxygen, pH, anions, cations, heavy metals, DOC, nutrients and microcystin. Additionally we took seasonal samples of lake-biota, chlorophyll *a* and measured bacterial secondary production (BSP), microbial abundance and unsaturated fatty acid contents. At the GPL interfaces we focused our research on biofilm metabolism, microbial abundance and differences in biofilm physiological profiles between the inflow and outflow interfaces. Lake sediments were analyzed for heavy metals concentrations and biomarkers as part of a research study by LIPTOX (Lipid and Toxicology Research Group) of the WasserCluster Lunz – Biologische Station GmbH.
In order to evaluate the effects of GPLs on the outflowing groundwater quality based on the results of previously published studies we performed a database-driven meta-analysis. Based on criteria pertinent to the study GPLs, we obtained detailed insight into 128 existing studies that formed our database, which helped us gain a broad understanding of relevant issues concerning the study of GPL ecosystems on a worldwide scale. To conclude the project, results from all workgroups and from the meta-analysis were published in the final project report, which was delivered to the government stakeholders in the year of 2011.

Ecology and biogeochemistry of gravel pit lakes

Here I will detail my specific research and contributions to the study of GPLs in the framework of the overall project as described above with a special focus on the biogeochemistry and microbial ecology of gravel pit lakes as part of my PhD thesis.

Publication 1:

Gravel pit lake ecosystems reduce nitrate and phosphate concentrations in the outflowing groundwater (published in Science of the Total Environment, 2012)

The first publication shows the importance of GPLs in their ability to sequester nutrients from the inflowing groundwater and to contribute to groundwater amelioration due to immense metabolic activity of microbial communities in the lake water as well as at the inflow and outflow interfaces of the GPLs.

First, we performed seasonal groundwater and lake water sampling campaigns where subsequent results led to the elaboration of water and solute mass balance models describing nutrient ($N\text{-}NO_3$, $P\text{-}PO_4$) and DOC fluxes in GPLs. We used custom-made microcosms (Figure 3A) to measure biofilm respiration and production. Biofilms were collected from stones, sampled at specific inflow and outflow areas of the GPLs that were previously selected (Figure 3B). The study was rounded up including lake microbial metabolism, measured as bacterial secondary production (BSP) and elaborating a model for whole-ecosystem metabolism that was based on the combination of epilithic microbial metabolism, pelagic BSP measurements and published relationships for pelagic and benthic metabolism. One of the key finding of this study was that GPLs evolve from being net sources to net sinks for organic carbon as they mature showing a significant relationship with residence time and a positive although not significant trend with post-excavation age (Figure 4A). This process was mainly driven by enhanced in-lake metabolism at the interfaces and in the lake water due to high fluxes of nutrients from the inflowing groundwater. Highest inflows of nitrate and phosphate were encountered in GPL5, the oldest lake, however all GPLs turned out to be a sink for both nitrate and phosphate. DOC fluxes showed mixed results as GPL1, 4 and 5 were generally sources whereas GPL2 and 3 were sinks of DOC to the outflowing groundwater.

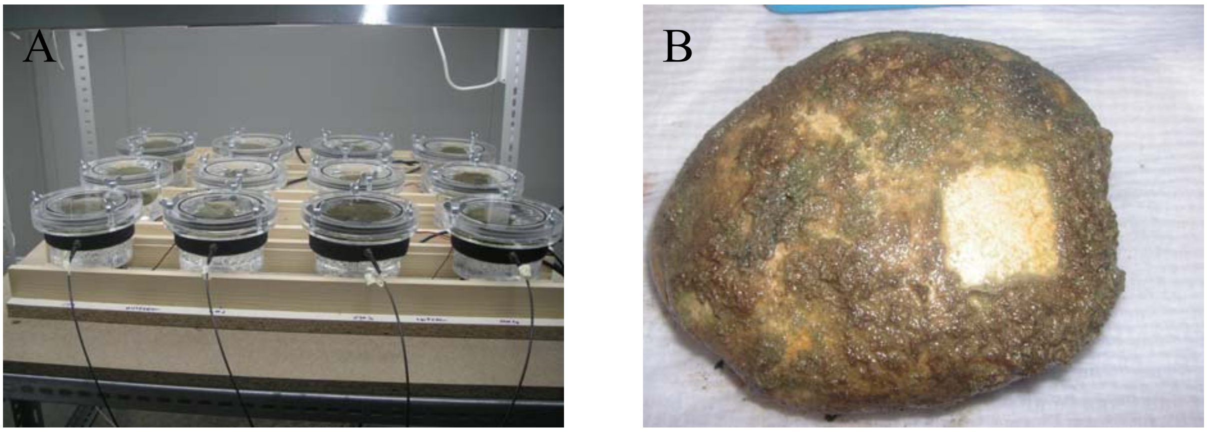


Figure 3: Experimental setup of biofilm respiration chambers (A) and sample stone with biofilm coverage taken at the GPL interfaces (B).

However groundwater derived nutrients foster both benthic and pelagic primary production and lead to the accrual of organic biomass in the GPLs yet, no significant release of nitrate, phosphate or DOC into the outflowing groundwater. The accumulation of organic biomass may finally contribute to clogging of the GPL interfaces and lead to the disconnection of the lake from the adjacent groundwater. These processes may ultimately lead to internal recycling of inorganic nutrients in the lake.

We found that net carbon fluxes and pelagic chlorophyll *a* concentrations are related to post-excavation age of GPLs (Figure 4A, B). All GPLs were net autotrophic as shown by the ratio of R:NPP decreasing with increasing post-excavation age (Figure 4C). Hence GPLs may show a shift towards eutrophication with post-excavation age, a relationship that was also confirmed by increasing chlorophyll *a* concentrations with post-excavation age in the lake water (Figure 4B). Not only do groundwater derived nutrients lead to eutrophication, atmospheric deposition of phosphate for instance was as high as 240% of groundwater derived phosphate loads. This may be of concern especially in agricultural areas were wind drifts increase the input of inorganic nutrients into those lakes. However phosphate concentrations in the outflowing groundwater decreased up to 99% compared to concentrations observed in the inflowing groundwater.

In general our data suggest comparability of GPLs to natural seepage lakes were groundwater subsidizes the lake metabolism. Although GPLs accumulate significant amounts of organic biomass and tend to eutrophication, they significantly contribute to groundwater amelioration especially in areas that are suffering from intense agricultural use and subsequent inputs of inorganic nutrients. Accrual of organic biomass in lake sediments may cause disruption of the groundwater flow up to the point of total disconnection from the groundwater aquifer however we found beneficial effects of GPLs to prevail.

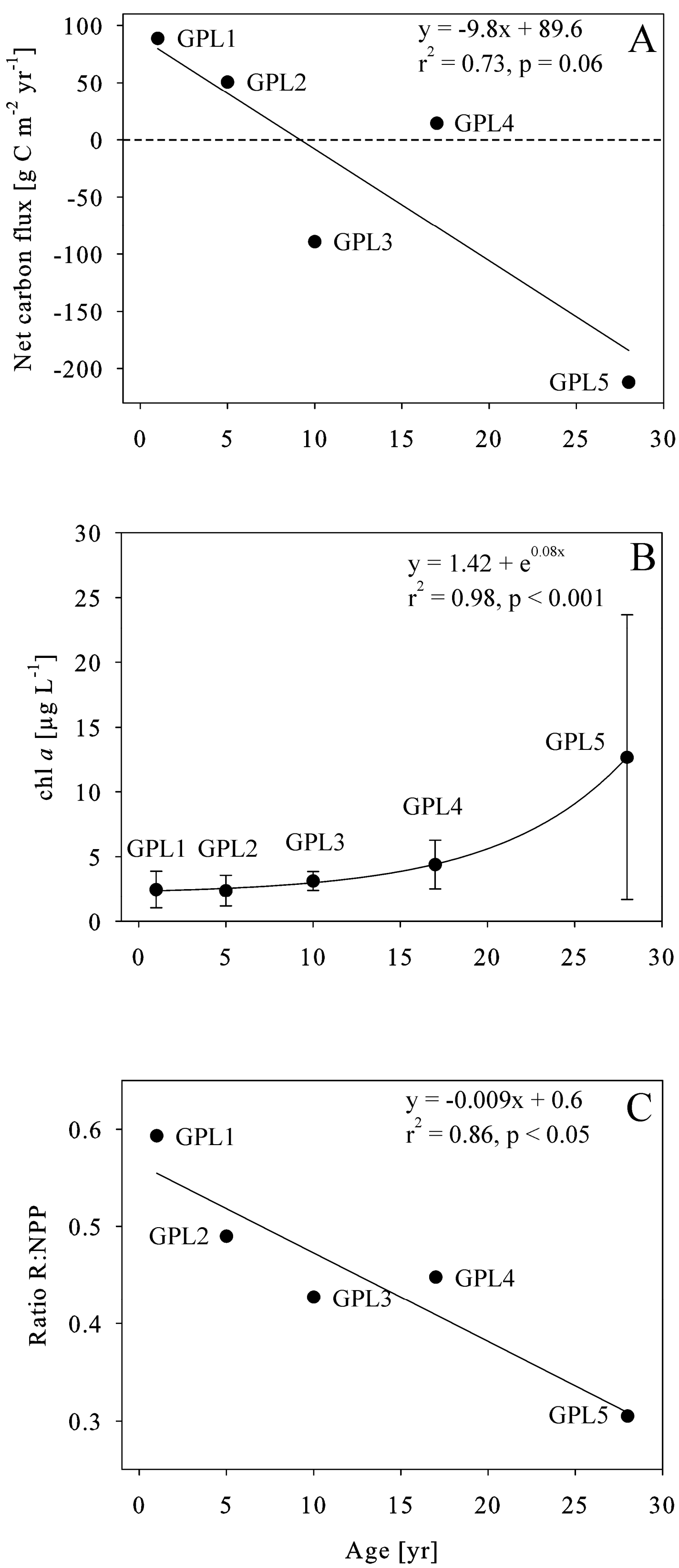


Figure 4: Relationship between net carbon flux pelagic chlorophyll *a* (B), ratio R:NPP (C) and age of the five GPLs. Negative values in panel (A) indicate lower carbon consumption than production, whereas positive values indicate higher carbon consumption than production.

Publication 2:

Positive and negative impacts of five Austrian gravel pit lakes on groundwater quality (published in Science of the Total Environment, 2013)

The second publication points out the significance of GPLs on groundwater quality due to their ability to alter biologic, organic and inorganic parameters in the outflowing groundwater. It is the combination of various lake-biogeochemical processes such as bank filtration and metabolism at the inflow and outflow interfaces as well as processes in the lake water itself that are of major importance for water purification. This study shows hydrogeological characteristics and geographical locations of the five sample GPLs in Austria. Groundwater was sampled from self-installed as well as preinstalled groundwater wells in previously defined areas of groundwater inflow and outflow followed by physico-chemical and microbiological analysis. A groundwater mixing model was established based on stable water isotope analysis ($\delta^{18}O$) and a numeric groundwater flow simulation to calculate lake water residence time of the GPLs.

All GPLs showed well-established density and wind driven mixing of lake water without occurrence of stratification throughout the year. Only GPL1 and GPL4 were stratified during summer months due to colder near bottom groundwater flow. Water temperatures increased significantly in the lake compared to the inflowing groundwater due to atmospheric influence but decreased rapidly to inflowing groundwater values due to water mixing in the outflow. Water temperature is an important parameter for the outflowing groundwater quality as it affects both metabolic activity and survival of microbes and viruses in the adjacent groundwater aquifer.

The authors found that microbial activity at the outflow interfaces depletes the supersaturated lake water from oxygen and may create anaerobic conditions in the outflowing groundwater, also confirmed by decreasing pH values (Figure 5b). The lake interfaces of GPLs are characterized by high microbial activity leading to retention of DOC and nutrients otherwise released into the effluent groundwater. The decrease of both oxygen concentration and pH may be additionally supported by a rapid build-up of organic biomass in the GPLs that leads to sedimentation and subsequent clogging of the lake bottom and interfaces. However, in GPL1, the youngest of the lakes, sufficient sedimentation has yet to occur which decreases the ability to ameliorate the outflowing groundwater water quality. The study indicates that it takes approximately five years for GPLs to accumulate sufficient sediment before release of

DOC in the outflowing groundwater decreases significantly. However, it was clearly shown that all GPLs significantly reduced nitrogen concentrations due to mainly algal and microbial uptake at the interfaces and in the lake water (Figure 5d).

Microbial abundance increased significantly in the outflowing groundwater of all GPLs (Figure 5f). However bank filtration proofed to be a powerful process for microbe removal as shown by a significant decrease of microbial abundance values after a distance of 25 meters from the outflow well-shore line. Hence we suggest that groundwater-feeding wells should be placed within sufficient distance to outflowing groundwater areas of GPLs.

Another positive effect of GPLs was found in their ability of water decalcification (e.g. the precipitation of calcite after an increase in lake water pH due to CO_2 uptake of primary production), enhancing the efficient use of groundwater supplied as drinking water by water providers that otherwise suffer from calcite precipitation in their distribution networks (Figure 5c). Also, we shed light on the importance of monitoring programs, recommended to be put in place after resource exploitation of the lakes, guaranteeing the safety of future groundwater supplies. Not only do resource industries but also human activities at GPLs (mainly fish farming and swimming) pose potential long term environmental risks on groundwater quality due to possible groundwater contamination.

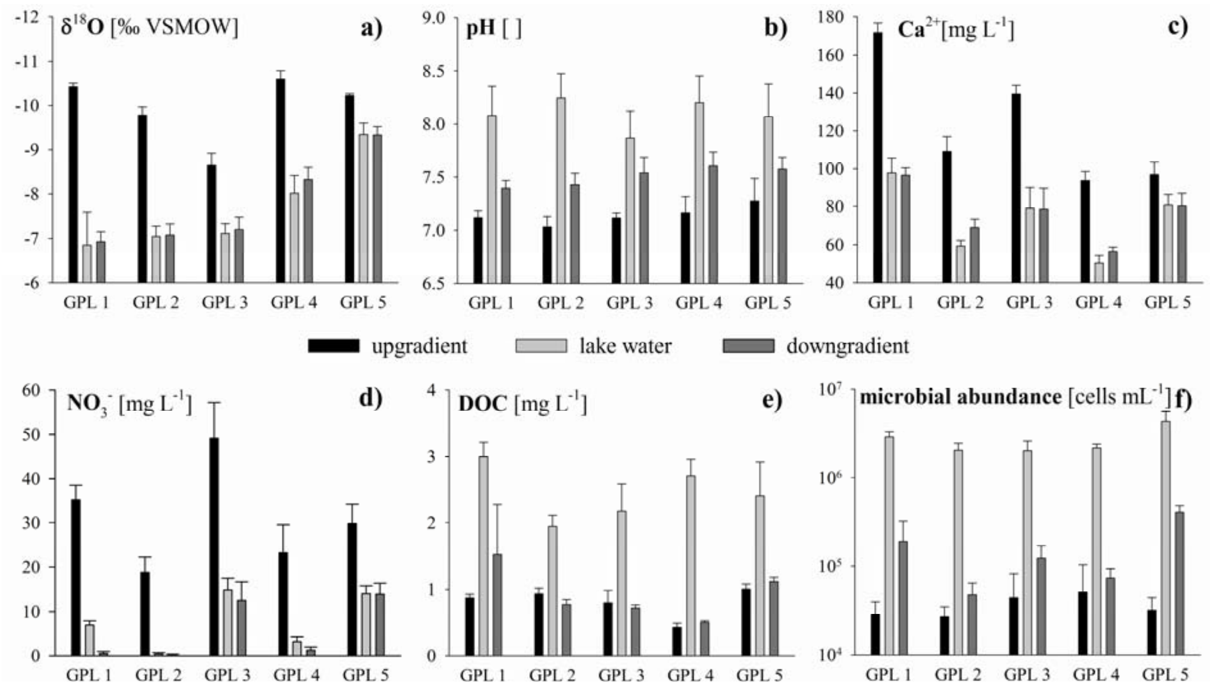


Figure 5: Annual average hydrochemical (pH, Ca^{2+}, NO_3^-, $\delta^{18}O$), and microbial (DOC, microbial abundance) data along the groundwater flow gradient of all GPLs from inflow to lake to outflow.

Publication 3:

Physiological profiles and community metabolism of benthic biofilms in gravel pit lakes (manuscript submitted to Water Research, 2014)

The third publication illuminates the importance of microbial metabolism and carbon cycling at the inflow and outflow interfaces of GPLs where most of these processes occur. After sampling individual stones with biofilm coverage at the according inflow and outflow interfaces of the GPLs, we incubated biofilms in Biolog Ecoplates. Each of the 96 wells of one micro plate yielded a color development due to carbon substrate utilization in the well. The color intensity was read spectrophotometrically and was analyzed using PCA for graphical demonstration of 6 carbon substrate groups. We used multiple regression models to explore possible effects of nutrient concentrations, DOC quantity and quality as well as lake water and interface metabolism on the physiological profiles at the outflow interfaces.

Key findings of this study suggest that GPLs are comparable to natural seepage lakes due to similar connectivity to the adjacent groundwater aquifer and subsequent exposure of lake metabolism to groundwater derived nutrients and DOC that may finally shape the interface physiological profiles. Additionally we found significant differences in carbon quality and aromaticity based on the measurement of FI and $SUVA_{254}$ indices, respectively, suggesting a shift in DOC from a groundwater derived microbial source, also enriched in aromatic compounds, to the *in situ* production of DOC of lower aromaticity. DOC is a key factor for microbial metabolism at the interfaces and in the lake water of GPLs. We suggest that a change in nutrient concentrations as well as carbon quantity and quality may indirectly affect biofilm metabolic activity due to changes in carbon source utilization expressed through the creation of distinct physiological profiles at the interfaces of GPLs. This was confirmed based on PCA analysis (Figure 6) and by comparing changes of carbon substrate group utilization between the interfaces. For instance, utilization of amines was pronounced at the outflow compared to the inflow interfaces whereas polymers had the overall highest utilization in all GPLs and at both interfaces averaged over all seasons. Higher utilization of amines at the outflow interfaces suggests *in situ* production of these carbon substrates in the GPLs or differences in community structure and function of the biofilms at both interfaces. Amines for instance are known to be related to microbial growth and many times they result from enzymatic breakdown of algal precursors supporting our suggestion of *in situ* production of certain carbon substrates.

Based on multiple regression models we found patterns of carbon substrate group utilization with nutrient parameters or carbon quality and quantity at the interfaces of GPLs. Amines for instance were mainly related to carbon quantity and quality parameters whereas carboxylic acids were mainly related to parameters describing lake metabolism as well as nutrient concentrations. Hence we suggest that certain carbon substrates being *in situ* derived are increasingly important to biofilm metabolism at the outflow interfaces. This was shown by a significant relationship of amines with biofilm respiration at the outflow interfaces (Table 1) and chlorophyll *a* concentrations in the lake water of all GPLs. Overall we found clear distinctions but also discrepancies in the physiological profiles of biofilms at the interfaces of GPLs which will hopefully lead to further studies and certain adaptations of the analysis to yield the most respectable results.

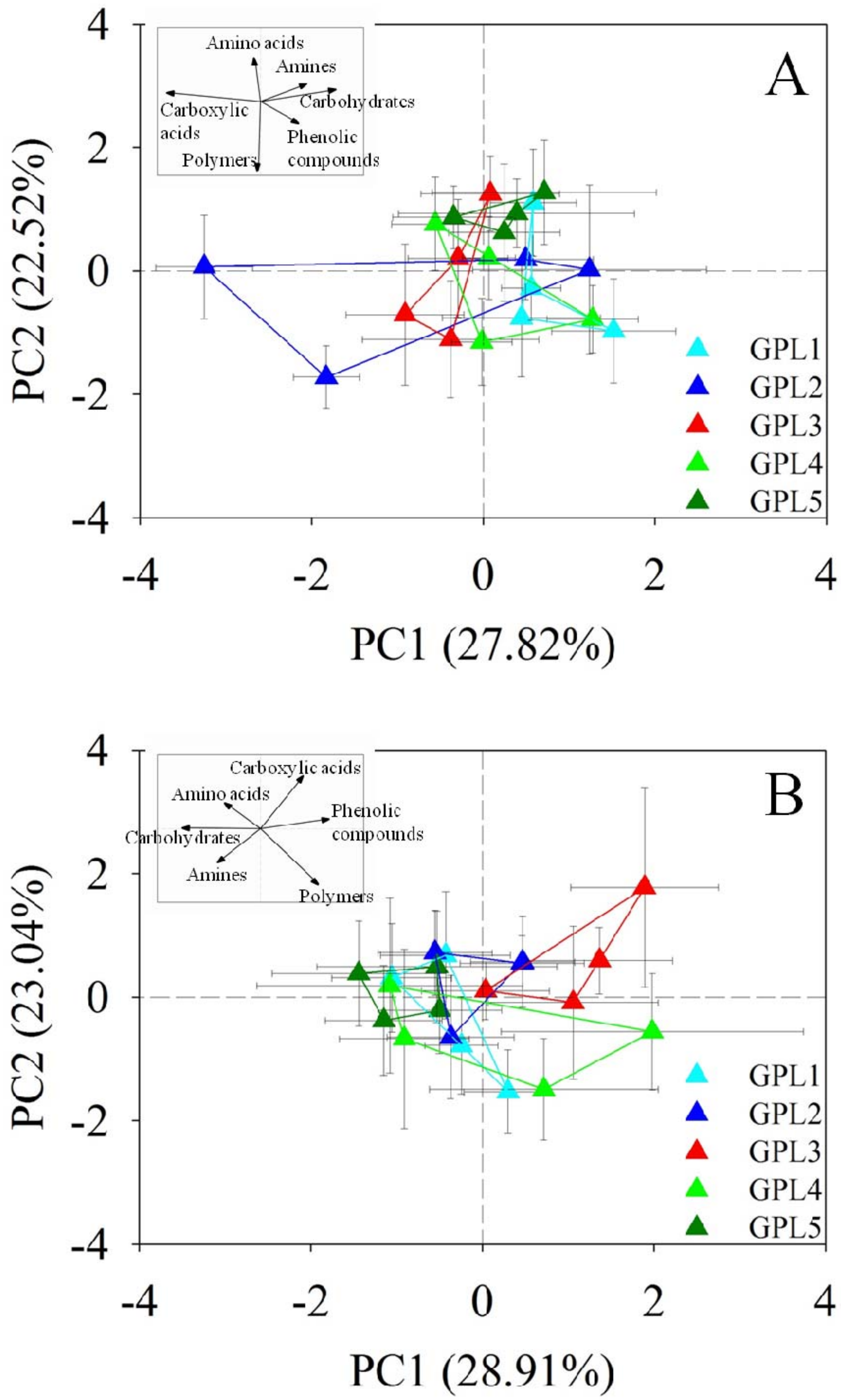


Figure 6: Substrate group utilization at the inflow (A) and outflow (B) interfaces of GPLs 1-5 averaged over all seasons. Vectors show the factor loadings of each substrate group, explaining variations in PC1 and PC2. Distances between symbols of each GPL show the average variance between the seasons. For better graphical representation, we decided to not differentiate between seasons.

Table 1: Multiple regression models for biofilm respiration at the outflow interfaces based on AIC scores.

Rank	Respiration Outflow Habitat Model Covariates				F	AIC	Chi^2	p
1	Carboxylic acids	Amines			2	209.61	11.78	< 0.005
2	Amines				1	210.38	9.01	< 0.005
3	Carboxylic acids	Amines	chl *a*		3	210.79	12.60	< 0.01
4	Carboxylic acids	Amines	Phenolic compounds		3	211.03	12.36	< 0.01
5	Polymers	Carbohydrates	Amines	chl *a*	4	211.14	14.25	< 0.01

Conclusion

Overall this PhD thesis showed that microbial processes significantly contribute to the capacity of GPLs to sequester nutrients from the inflowing groundwater and to turn into long-term sinks for organic carbon after an estimated post-dredging time of five years. These processes are mainly due to immense metabolism at the interfaces and in the lake water of GPLs. Even though GPLs may at first be net sources of carbon for the outflowing groundwater, they immediately contribute to the amelioration of groundwater water quality due to nutrient retention but especially of nitrate and phosphate. Additionally, GPLs serve as recreational areas and represent ecosystems of high biologic diversity in otherwise monotonous agricultural landscapes.

Over time GPLs may completely disconnect from the adjacent groundwater aquifer due to sedimentation processes and subsequent clogging of the lake interfaces thus reducing the risk of potential transfers of in lake contaminants into the outflowing groundwater. However we showed that at no time were compounds such as heavy metals, microbes or BDOC released into the ouflowing groundwater, potentially threatening groundwater quality. GPLs have a variety of positive effects aside from the retention of nutrients and DOC such as the observed increase in pH values and subsequent calcite precipitation due to high primary production in the lake water. This decalcification process serves water providers that are otherwise confronted with the critical problem of calcite precipitation in their water distribution networks.

Similar to natural seepage lakes, groundwater-derived nutrients foster primary production in GPLs and upon degradation, algal cells fuel the DOC pool and contribute to its bioavailability. Although microbial metabolism of biofilms at the GPL interfaces was not directly affected by changes in carbon quality and quantity, we observed clear effects of nutrient concentrations and parameters describing carbon quantity and quality on the functional capacities of microbial communities and their carbon substrate group utilization patterns and *vice versa* effects of certain carbon substrate groups on metabolic activity at the outflow interfaces of GPLs.

Publications forming the basis for this PhD thesis

A. Weilhartner, C. Muellegger, M. Kainz, F. Mathieu, T. Hofmann, T.J. Battin (2012). Gravel pit lake ecosystems reduce nitrate and phosphate concentrations in the outflowing groundwater. Sci. Total Environ. 420:222-228.

C. Muellegger, **A. Weilhartner**, T.J. Battin, T. Hofmann (2013). Positive and negative impacts of five Austrian gravel pit lakes on groundwater quality. Sci. Total Environ. 443:14-23.

A. Weilhartner, G. A. Singer, T. Hofmann, C. Muellegger, T. J. Battin (finished manuscript). Physiological profiles and community metabolism of benthic biofilms in gravel pit lakes.

References

1. Botta, S., Comoglio, C., Quaglino, A. and Torchia, A. (2009) Implementation of Environmental Management Systems in the Extraction of Construction Aggregates from Gravel Pit Lakes. Am. J. Environ. Sci. 5(4), 526-535.

2. Drew, L.J., Langer, W.H. and Sachs, J.S. (2002) Environmentalism and Natural Aggregate Mining. Natural Resources Research 11(1), 19-28.

3. Muellegger, C., Weilhartner, A., Battin, T.J. and Hofmann, T. (2013) Positive and negative impacts of five Austrian gravel pit lakes on groundwater quality. Science of The Total Environment 443(0), 14-23.

4. Langer, W.H. (2001) Environmental impacts of mining natural aggregate in Bon, R.L., Riordan, R.F., Tripp, B.T., and Krukowski, S.T., 2001, Proceedings of the 35th forum on the geology of industrial minerals— The Intermountain West Forum 1999. Utah Department of Natural Resources, Utah Geological Survey Miscellaneous Publication 01-2, 127-137.

5. Apaydın, A. (2012) Dual impact on the groundwater aquifer in the Kazan Plain (Ankara, Turkey): sand–gravel mining and over-abstraction. Environmental Earth Sciences 65(1), 241-255.

6. Peckenham, J., Thornton, T. and Whalen, B. (2009) Sand and gravel mining: effects on ground water resources in Hancock county, Maine, USA. Environmental Geology 56(6), 1103-1114.

7. Weilhartner, A., Muellegger, C., Kainz, M., Mathieu, F., Hofmann, T. and Battin, T.J. (2012) Gravel pit lake ecosystems reduce nitrate and phosphate concentrations in the outflowing groundwater. Science of The Total Environment 420, 222-228.

Contributions to publications

Table 2: My personal contributions to the various publications and manuscripts.

	Weilhartner et al., 2012	Muellegger et al., 2013	Weilhartner et al., submitted
Experimental design	75%	35%	100%
Experimental work	100%	45%	100%
Laboratory analysis	80%	35%	100%
Data analysis	95%	35%	70%
Writing of manuscript	90%	25%	90%

Acknowledgements

This research was funded by the Austrian Association for Building Materials and Ceramic Industries, by the Provinces of Lower Austria, Upper Austria, and Styria, and by the Federal Ministry of Agriculture, Forestry, Environment and Water Management.

The work and study was facilitated by the University of Vienna (Department of Environmental Geosciences) and the “WasserCluster Lunz - Biologische Station GmbH” (BERG, LIPTOX), an interuniversity research facility during the years of 2008 to 2014.

This thesis would not have been possible without the help of my many colleagues, friends, family and mentors.

In a group effort Francine Mathieu and Christian Müllegger contributed to field- and laboratory work and subsequent results of this research study. I am also very thankful for technical assistance in the laboratory from Gertraud Stenicka and Christian Preiler as well as statistical help by the invincible Gabriel Singer.

Of course none of this would have been possible without the enduring support of my wife, Heidy, and the love of my daughter, Lilia, who was born during the time of this thesis in the summer of 2012.

Many thanks go to my parents, as they never gave up on me finally finishing my Doctorate. I quote my dad as saying “Aufgebn’ wird nur a Briaf”, and I was more than once at the point of sending Tom a letter of notification. However, persistence is the quality that I find the most important to have absorbed during the last 5 years.

Last but not least, I get to Tom Battin, my supervisor and some awesome fellow that I am very thankful of having gotten to know over the last 8+ years. A great mentor and friend that just wouldn’t let me down and was always full of motivation for my work.

Scientific publications and manuscripts

1. Gravel pit lake ecosystems reduce nitrate and phosphate concentrations in the outflowing groundwater

Andreas Weilhartner [a, b], Christian Muellegger [c], Martin Kainz [b], Francine Mathieu [a, b], Thilo Hofmann [c], Tom J. Battin [a,b] (2012)

[a] Department of Limnology, University of Vienna, Althanstrasse 14, 1090 Vienna, Austria
[b] WasserCluster Lunz – Biologische Station GmbH, Dr. Carl Kupelwieser Promenade 5, 3293 Lunz am See, Austria
[c] Department of Environmental Geosciences, University of Vienna, Althanstrasse 14, 1090 Vienna, Austria

Science of the Total Environment 420: 222-228

Science of the Total Environment 420 (2012) 222–228

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

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

Gravel pit lake ecosystems reduce nitrate and phosphate concentrations in the outflowing groundwater

Andreas Weilhartner [a,b], Christian Muellegger [c], Martin Kainz [b], Francine Mathieu [a,b], Thilo Hofmann [c], Tom J. Battin [a,b,*]

[a] Department of Limnology, University of Vienna, Althanstrasse 14, 1090 Vienna, Austria
[b] WasserCluster Lunz GmbH, Dr. Carl Kupelwieser Promenade 5, 3293 Lunz am See, Austria
[c] Department of Environmental Geosciences, University of Vienna, Althanstrasse 14, 1090 Vienna, Austria

ARTICLE INFO

Article history:
Received 14 October 2011
Received in revised form 12 January 2012
Accepted 13 January 2012
Available online 15 February 2012

Keywords:
Gravel pit lake
Groundwater
Nutrients
Metabolism
Biogeochemistry

ABSTRACT

Gravel excavation often bears conflicts with the use of drinking water as under-water-table mining can directly impact groundwater quality downstream of the open gravel pit lake due to exposure of the groundwater aquifer to the atmosphere and to human activities. To assess this potential impact of GPLs on groundwater, we assessed the mass balance for nitrate (NO_3) and phosphate (PO_4) and whole-ecosystem metabolism of five post-excavation GPLs in Austria. GPLs differed in both age and residence time of lake water. We found that GPLs significantly reduced the concentration of NO_3 and PO_4 as groundwater passes through the lake ecosystem, which in most cases acted as a net sink for these nutrients. Groundwater-derived nutrients enhanced both epilithic and pelagic net primary production in the GPLs, which ultimately leads to biomass accrual. Our data also suggest that this biomass accrual may induce, at least in part, clogging of the GPLs and their successive hydrodynamic isolation from the adjacent groundwater. Despite continuous biomass build-up and elevated concentrations of dissolved organic carbon (DOC) in the lake water compared to the inflowing groundwater, DOC export into the outflowing groundwater remained low. Our data suggest that GPLs could contribute to groundwater amelioration where agricultural land use increases nutrient concentrations in the groundwater given a proper management of these man-made ecosystems.

1. Introduction

Gravel excavation provides the world with one of the most valuable non-fuel mineral resources worldwide (Botta et al., 2009; Drew et al., 2002). Construction industries as well as technical, electrical and health industries rely on the excavation of gravel as raw material and its use in numerous applications for society (Botta et al., 2009; Drew et al., 2002). Applications range from concrete for housing, sewage facilities, water channels and pipes, electric power plants and water dams, and even to ceramic elements in electric devices and tooth fillings. Gravel excavation as one important resource often bears conflicts with the use of drinking water (Botta et al., 2009; Drew et al., 2002). In fact, under-water-table mining can directly impact groundwater quality downstream of the open gravel pit lake (GPL) (Drew et al., 2002; Langer, 2001) due to exposure of the groundwater aquifer to atmospheric exchange and potentially also to human activities, including fish stocking and swimming. Removal of land coverage from the aquifer as well as removal of the gravel itself might interfere with the natural recharge abilities of the aquifer thereby changing groundwater flowpaths (Peckenham et al., 2009). The organic layer on top of the gravel deposit serves as a natural absorbent for solutes and contaminants and its removal may deteriorate the outflowing groundwater quality. This becomes particularly apparent in aquifers where gravel excavation interferes with dedicated groundwater protection programmes. Post-excavation GPLs increasingly affect the landscape in the vicinity of urbanized regions worldwide due to increasing demand in building materials (Garnier and Billen, 1994; Peckenham et al., 2009). During the post-excavation period, GPLs develop as productive (Alvarez Cobelas et al., 1992; Tavernini et al., 2009) man-made lakes that often sustain a high aquatic biodiversity (Hindák and Hindáková, 2003). Post-excavation GPLs are often stocked with fish or serve as recreational areas, and thus require intensive management (Garnier and Billen, 1994). The combination of elevated nutrient loads into GPLs with a typically shallow water column and extensive use often induce hypertrophy of these lakes (Alvarez Cobelas et al., 1992; Tavernini et al., 2009). Biomass accrual may, among other factors, lead to partial clogging and reduce thereby the groundwater – surface water – interaction of older GPLs.

Understanding the multiple interactions between groundwater and surface water is crucial for the management of water resources (Alley et al., 2002). This is particularly true for man-made ecosystems,

* Corresponding author.
E-mail address: tom.battin@univie.ac.at (T.J. Battin).

0048-9697/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.scitotenv.2012.01.032

such as GPLs, which may adversely affect the quality of the outflowing groundwater (Peckenham et al., 2009). However, possible impacts of GPLs on outflowing groundwater remain poorly documented (Alfreider et al., 2001; Kattner et al., 2000; Peckenham et al., 2009). The aim of the present study was to evaluate if GPLs are potential sinks or sources for organic carbon and nutrients, and to elucidate possible underlying processes using a whole-ecosystem approach. We hypothesized that in-lake production and metabolism use much of the influent inorganic nutrients from the inflowing groundwater and that, in turn, GPLs enrich the outflowing groundwater with organic carbon as a result of in-lake carbon production. To test this hypothesis, we constructed mass balances for nitrate, phosphate and dissolved organic carbon (DOC) and estimated whole-ecosystem metabolism of five GPLs differing in size, age and water residence time.

2. Material and methods

All five GPLs were located in landscapes that are dominated by agricultural land use in Austria (Lower Austria, Upper Austria and Styria). Surface areas of the GPLs ranged between 38,000 m² and 164,000 m², and the post-excavation age ranged from 1 to 28 years. GPLs were relatively shallow with mean water depths between 2.3 and 6.4 m, stocked with fish (ca. 150 kg ha^{-1}) and used extensively for recreational purposes. Adjacent aquifers are dominated by quaternary carbonate sand and gravel (see Table 1 for details).

2.1. Groundwater and lake water sampling

For each GPL, we identified zones of inflowing groundwater and outflowing lake water from regional groundwater level contour maps. Based on this information, wells (inner diameter: 0.05 m) were installed down to the aquiclude in representative areas of the inflow and outflow zones around each lake. Groundwater inflow and outflow was furthermore studied using stable isotopes ($\delta^{18}O$, $\delta^{2}H$). Wells to capture the outflowing water from the GPL were installed at a maximum distance of 25 m from the shoreline to prevent mixing with unaffected groundwater. Samples from groundwater were collected with a submersible pump (Grundfos MP1). Wells were pumped at least 3 times the well volume until stabilization of *in situ* parameters (temperature, electrical conductivity, pH, dissolved oxygen) prior to each sampling. Lake water was sampled at 3 sites along the estimated flow path of groundwater in each GPL. Using an YSI probe (6929V2), we first profiled the water column for chlorophyll *a* concentration. Based on this information, we then collected water samples from 0.5 m below surface, at the chlorophyll *a* maximum and at 0.5 m above bottom, at each station of each lake. Samples for inorganic nutrients (N-NH_4, N-NO_2, N-NO_3, P-PO_4), and dissolved organic carbon (DOC) were collected from groundwater wells and lake water as described above and transferred into acid-rinsed polyethylene (PE) bottles. Bottles were kept cool and shipped to the lab within 4 hours. GPL water and both inflowing and outflowing groundwater were sampled once every season ($n=4$).

Table 1
Basic characteristics of the GPLs and their adjacent groundwater.

Lake	Age	Surface area	Mean water depth	Mean lake water residence time	Groundwater inflow
	[yr]	[m²]	[m]	[yr]	[m³ d^{-1}]
GPL1	1	38,000	5.2	1.4	423
GPL2	5	164,000	6.4	1.5	1954
GPL3	10	59,000	2.3	0.2	1500
GPL4	17	60,000	5.6	1.1	790
GPL5	28	86,000	4.2	0.3	3582

2.2. Chemical analysis

Alkalinity and pH, dissolved oxygen, electrical conductivity, and water temperature were measured in the field using WTW probes (pH320, OxiCal-SL, Cond340i); concentrations of N-NH_4, N-NO_2, N-NO_3, P-PO_4 were determined using Continuous Flow Analysis (Alliance instruments). DOC concentration was determined using a Sievers 900 Portable TOC Analyzer (GE Analytical Instruments). Stable isotopes ($\delta^{18}O$, $\delta^{2}H$) for the water mass balance were analyzed using a Picarro L1115-i Isotopic Liquid Water and Water Vapor Analyzer. The precision of $\delta^{18}O$ measurements was ±0.1‰ and ±0.5‰ for $\delta^{2}H$.

2.3. Water and solute mass balance

We established a water balance of all GPLs based on $\delta^{18}O$ and $\delta^{2}H$ as has been previously used (Gat, 2010; Yi et al., 2008). The rate of groundwater inflow (Q_{in}) was calculated from isotope fractionation due to evaporation as

$$Q_{in} * \delta_{in} = Q_{out} * \delta_{out} - Q_n * \delta_n * Q_{Eva} * \delta_{Eva} \quad (1)$$

After substitution of $Q_{out} = Q_{in} + Q_P - Q_{Eva}$, and the assumption that $\delta_{out} = \delta_L$, Eq. (1) was further reduced:

$$Q_{in} = \frac{Q_p * (\delta_L - \delta_P) + Q_{Eva} * (\delta_{Eva} - \delta_L)}{\delta_{in} - \delta_L} \quad (2)$$

where Q_P is precipitation, reported from nearby weather stations, Q_{Eva} is lake water evaporation calculated from meteorological data, δ_{Eva} is the isotopic composition of the evaporated vapor calculated after Craig and Gordon (1965), δ_L is the mean isotopic composition of the lake water, δ_{in} the mean isotopic composition of the inflowing groundwater, and δ_P is the weighted mean isotopic composition of the precipitation (from the Austrian Network of Isotopes in Precipitation, ANIP).

The mean annual residence time (T_R) of the GPLs was calculated as

$$T_R = \frac{V_L}{Q_{in} + P - Eva} \quad (3)$$

where V_L is the GPL volume, P is the precipitation, and Eva is the evaporation.

Based on the groundwater inflow, the outflow from the GPL and the atmospheric deposition, we calculated an average solute mass balance for each GPL according to

$$0 = (Q_{in} * C_{in} + Q_P * C_P) - (Q_{out} * C_{out}) - R \quad (4)$$

where C_{in} and C_{out} are the solute concentrations in the inflow and outflow, respectively, Q_P is the precipitation, and C_P is the solute concentration of the precipitation. Negative residuals, R, indicate net retention of the respective solute within the GPL, which therefore acts as a sink. Positive residuals, R, indicate that the GPL releases a given solute into the outflowing groundwater. Hence, the GPL acts as a source. We used published data of atmospheric deposition of N-NO_3, P-PO_4 and DOC (Fank et al., 2005; Leder, 2008; Willey et al., 2000). Given that groundwater fluxes are annual averages, we calculated solute mass balances with annual average concentrations from all four seasons.

2.4. Community metabolism of epilithic biofilms

In each GPL, we randomly collected 6 rocks (average diameter 10.6±3.7 cm) with epilithic biofilms within those zones that were identified as groundwater inflow and outflow, respectively. We collected rocks from the same water depth (ca. 0.5 m) to make sure that all sites were continuously submerged and exposed to comparable light conditions. This was repeated during each survey to capture the seasonal variability. Samples were immediately transported in lake water from the respective sites (dark, *in situ* temperature) to the laboratory and processed within 6 h. In the laboratory, individual rocks were carefully transferred into respiration chambers containing a stirring mechanism and a planar optode (PreSens Precision Sensing GmbH, Regensburg, Germany) for the measurement of dissolved oxygen concentration. Each respiration chamber was filled with 660 ml sterile-filtered (0.2 μm) water from the respective GPL.

For each rock, community respiration (R) was measured in the dark (12 h), and net primary production (NPP) was measured (4 h) at a light intensity (52 μmol m^{-2} s^{-1}) as it was often measured at 0.5 m depth of the GPLs. We used PHILLIPS TL-D 58/33-640 halogen lamps that have a radiation spectrum similar to sunlight. Metabolism measurements were performed under constant temperature (20 °C). Respiration rates were calculated as

$$R = \frac{\Delta O_2 * V}{A} \tag{5}$$

where ΔO_2 is the decrease of the dissolved oxygen concentration over 12 h in the respiration chamber, *V* is the volume of the water in the respiration chamber, and *A* is the surface area of the rock. NPP was calculated similarly, except that we monitored the increase in O_2 concentration over 4 h. Dissolved oxygen concentrations were measured online at one-minute intervals for a period of 30 min. According to the manufacturer, the detection limit of the planar optodes (PSt6) is 1 μg O_2 L^{-1} and accuracy is ~3%. Oxygen was converted into carbon units using a respiratory quotient of 1 (Smith and Prairie, 2004). Chlorophyll *a* and ash-free dry mass of the epilithic biofilms were measured as described by Hauer and Lamberti (2006).

2.5. Pelagic bacterial secondary production

We estimated pelagic bacterial secondary production (BSP) from the uptake of radiolabelled [3, 4, 5-^{3}H]-1-leucine (Hartmann, 112.6 Ci $mmol^{-1}$). At each sampling date, water samples were collected from all three sites and depths in each GPL. In the laboratory, 10 mL of filtered (GF/F Whatman) samples were transferred into sterile triplicate vials and into duplicate vials that contained formaldehyde (2.5% final concentration) and that served as controls. Each sample was incubated for 1 h (in the dark, 20 °C) with a final concentration of 10 nM [^{3}H]-leucine (previously determined in saturation experiments). Incubation was stopped with 0.5 mL of formaldehyde (37%). Microbial cells were then filtered onto a cellulose nitrate filter (0.2 μm, Millipore HA), which was rinsed twice using ice-cold trichloracetic acid (5%). Filters were then transferred into scintillation vials, dissolved in ethylacetate (1 mL), and added to a scintillation cocktail (8 mL; Ultima Gold, Canberra Packard). Samples were then radioassayed with a liquid scintillation counter (Canberra Packard Tricarb 2000) and bacterial carbon production was calculated as described by Simon and Azam (1989).

2.6. Whole-ecosystem metabolism

To estimate whole-ecosystem metabolism of each GPL, we combined our measurements of epilithic metabolism and of pelagic BSP with published relationships for pelagic and sediment metabolism (Table 2). We used mean values of the *in situ* seasonal measurements of chlorophyll *a* to derive pelagic metabolism. We used GPL bathymetry (Simrad EQ33) and geometry to infer the surface area of the benthic zone where epilithic metabolism was determined. Whole-ecosystem epilithic metabolism was estimated from extrapolation to this surface area using average areal rates from the respiration chamber measurements. We calculated whole-ecosystem metabolism for each GPL estimated from the total carbon production and total carbon consumption according to

Table 2
Relationships used to estimate pelagic and sediment metabolism in the gravel pit lakes. BR is bacterial respiration, BP is bacterial production, PR is pelagic respiration, SR is sediment respiration.

Parameter	Equation	Reference
$R_{pelagic\ heterotrophic}$ (μg C L^{-1} h^{-1})	$BR = 3.42 \times BP^{0.61}$, $r^2 = 0.46$	Del Giorgio and Cole (1998)
$[P]_i$ derived from:	$chl - a(mgm^{-3}) = 0.55\{[P]_i/(1+\sqrt{\tau_w})\}^{0.76}$	Wetzel (2001)
$NPP_{pelagic}$ (g C m^{-2} y^{-1})	$NPP = 7\left\{\frac{\{[P]_i/(1+\sqrt{\tau_w})\}^{0.76}}{0.3+0.011\{[P]_i/(1+\sqrt{\tau_w})\}^{0.76}}\right\}$	Wetzel (2001)
$R_{pelagic\ autotrophic}$ (mmol O_2 L^{-1} h^{-1})	$\log_{10}PR = -0.81 + 0.56\log_{10}$chl-a, $r^2 = 0.71$	Pace and Prairie (2005)
$R_{sediment\ heterotrophic}$ (mmol O_2 L^{-1} h^{-1})	$\log_{10}SR = 0.63 + 0.40\log_{10}$chl-a, $r^2 = 0.83$	Pace and Prairie (2005)

$$Total\ C\ production = \left(NPP_{pelagic} + NPP_{epilithic}\right) \tag{6}$$

and according to

$$Total\ C\ consumption = R_{pelagic\ autotrophic} + R_{pelagic\ heterotrophic} + R_{sediment\ heterotrophic} + R_{epilithic} + BSP) \tag{7}$$

The net carbon flux of each GPL was then calculated as

$$Net\ carbon\ flux = \left(DOC_{outflow} + total\ C\ consumption\right) - \left(DOC_{inflow} + total\ C\ production\right) \tag{8}$$

where DOC inflow and outflow correspond to the fluxes obtained from the mass balance (see above).

3. Statistical analyses

Nonparametric statistical data was analysed using a Wilcoxon matched pairs test for nutrient and solute concentrations, epilithic net primary production and respiration and a Kruskal–Wallis ANOVA with post-hoc comparisons of mean ranks of all pairs of groups (Siegel and Castellan, 1988) for differences in metabolism between GPLs. We performed uncertainty propagation on our metabolism estimates for each season individually with the deviation from replicated measurements (e.g., pelagic chlorophyll *a*, community respiration of rocks) as the error to be propagated.

4. Results

4.1. Water balance and mean residence time of lake water

Based on the stable isotope analyses and the water balance, the mean residence time of the lake water ranged from 0.2 to 1.5 y, with highest values of groundwater inflow in GPL3 and GPL5 (Table 1). This is most likely attributable to the higher hydraulic groundwater gradients in the catchment aquifers of these two GPLs. The atmospheric water balance (precipitation minus evaporation) was positive in all GPLs (mean annual lake water outflow increased between 0.3 and 7.3% compared to mean annual groundwater inflow), except in GPL1, where evaporation exceeded precipitation (evaporation was 5.8% of mean annual groundwater inflow).

4.2. Nutrient and DOC concentrations and fluxes

Average concentration of N-NH_4 was significantly higher ($p<0.01$) in the GPL water (0.07 ± 0.11 mg L^{-1}) than in the inflowing groundwater (0.02 ± 0.02 mg L^{-1}) and was significantly higher in the outflowing groundwater (0.04 ± 0.04 mg L^{-1}) compared to the inflowing groundwater ($p < 0.05$), (Supp. 1, 2). $N\text{-}NO_2$ concentrations were below detection limits in the inflow as well as in the outflow of the GPLs, and were low in the GPL water as well (0.05 ± 0.06 mg L^{-1}). Average $N\text{-}NO_3$ concentration decreased significantly ($p < 0.001$) along the flow path from the inflowing groundwater (7.1 ± 2.8 mg L^{-1}) to the GPL water (1.8 ± 1.4 mg L^{-1}) and outflowing groundwater (1.3 ± 1.5 mg L^{-1}) in all GPLs and seasons. Average concentration of $P\text{-}PO_4$ was significantly lower ($p < 0.001$) in the GPL water (1.4 ± 2.3 μg L^{-1}) than in the inflowing groundwater (28.9 ± 35.5 μg L^{-1}); $P\text{-}PO_4$ concentrations decreased significantly ($p < 0.001$) in the outflowing groundwater (7.6 ± 9.1 μg L^{-1}) compared to the inflowing groundwater. We found the highest $P\text{-}PO_4$ concentrations (maximum 91 μg L^{-1}) in the influent groundwater in GPL5, which decreased below detection limit in the GPL water. Average DOC concentrations were significantly higher ($p < 0.001$) in the GPL water (2.5 ± 0.5 mg L^{-1}) than in the inflowing groundwater (0.8 ± 0.2 mg L^{-1}); inflowing groundwater and outflowing groundwater (0.9 ± 0.5 mg L^{-1}) had comparable average DOC concentrations ($p > 0.05$). Overall, groundwater was the dominant input flux for $N\text{-}NO_3$ and for $P\text{-}PO_4$, except in GPL1 and GPL4 where the atmospheric $P\text{-}PO_4$ deposition exceeded the groundwater flux.

Despite equality of groundwater inflow and outflow, outflow fluxes of $N\text{-}NO_3$ and of $P\text{-}PO_4$ were consistently lower than the respective inflow fluxes in all GPLs. Mass balance results indicate that GPLs were sinks of $N\text{-}NO_3$, with maximal retention rates averaging 2×10^{-2} kg $N\text{-}NO_3$ m^{-2} yr^{-1} in GPL2, and of $P\text{-}PO_4$ with maximal retention rates averaging 1×10^{-3} kg $P\text{-}PO_4$ m^{-2} yr^{-1} in GPL5. Retention efficiencies were as high as 99% in these GPLs.

Patterns of DOC fluxes were not as clear as those for nutrient fluxes. Some of the GPLs retained DOC, while others released DOC to the outflowing groundwater — although outflowing fluxes were lower than those for $N\text{-}NO_3$, for instance (Table 3). Overall, atmospheric deposition was consistently lower than groundwater inflow fluxes for nitrate (0–2% of groundwater inflow flux) and DOC (2–15% of groundwater inflow flux). We found high atmospheric deposition of PO_4 (3–240% of groundwater inflow flux) with highest values in GPL1 (220%) and GPL4 (240%). Nevertheless all lakes were sinks for phosphate with net retention efficiencies as high as 99%.

Table 3
Mass balance results of nitrate ($N\text{-}NO_3$), phosphate ($P\text{-}PO_4$) and dissolved organic carbon (DOC) for all 5 GPLs.

Lake	Groundwater inflow [kg yr^{-1}]	Atmospheric deposition [kg yr^{-1}]	Groundwater outflow [kg yr^{-1}]	Residual[a] [kg m^{-2} yr^{-1}]
N-NO$_3$				
GPL1	1228	13	16	-3×10^{-2}
GPL2	3022	57	33	-2×10^{-2}
GPL3	6077	21	1649	-8×10^{-2}
GPL4	1514	21	85	-2×10^{-2}
GPL5	8803	30	4205	-5×10^{-2}
P-PO$_4$				
GPL1	1	1	0	-3×10^{-5}
GPL2	25	6	12	-1×10^{-4}
GPL3	6	4	2	-1×10^{-4}
GPL4	1	3	0	-7×10^{-5}
GPL5	118	4	19	-1×10^{-3}
DOC				
GPL1	135	6	222	2×10^{-3}
GPL2	669	34	553	-9×10^{-4}
GPL3	438	23	421	-7×10^{-4}
GPL4	124	19	175	5×10^{-4}
GPL5	1307	23	1427	1×10^{-3}

[a] Negative values indicate a sink, positive values indicate a source.

4.3. Epilithic community metabolism

Annual averages of epilithic community NPP and R ranged from 112.9 ± 54.6 g C m^{-2} yr^{-1} to 303.2 ± 66.4 g C m^{-2} yr^{-1}, and from 39.5 ± 20.8 g C m^{-2} yr^{-1} to 74.8 ± 18.9 g C m^{-2} yr^{-1}, respectively, and differed significantly among GPLs (Table 4). Generally, average NPP was up to 4 times higher than R. Community NPP and R did not differ significantly ($p > 0.05$) between inflow and outflow sites.

4.4. Estimation of whole-ecosystem metabolism

Annual averages of pelagic NPP ranged from 88.0 g C m^{-2} yr^{-1} to 290.3 g C m^{-2} yr^{-1} and were lowest in the more recent post-excavation GPLs (GPL1 and GPL2) and highest in GPL5, the oldest GPL of our study. Pelagic autotrophic and heterotrophic R ranged from 68.1 g C m^{-2} yr^{-1} to 186.6 g C m^{-2} yr^{-1} and from 7.3 g C m^{-2} yr^{-1} to 15.4 g C m^{-2} yr^{-1}, respectively. BSP ranged from 6.6 g C m^{-2} yr^{-1} to 22.3 g C m^{-2} yr^{-1} and sediment heterotrophic R from 59.5 g C m^{-2} yr^{-1} to 95.9 g C m^{-2} yr^{-1} (Table 4). In general, pelagic autotrophic NPP contributed up to 18 times more to whole-lake metabolism than pelagic heterotrophic R.

We found a positive although not significant trend between net carbon flux and the age of the GPLs (Fig. 1). Average chlorophyll *a* concentration was positively related to GPL age, whereas the ratio of R to NPP was inversely related to GPL age (Fig. 1). Lake water $N\text{-}NO_3$ concentration was negatively related ($r^2 = 0.82$, $p < 0.05$) with lake water residence time; while $P\text{-}PO_4$ and DOC concentrations were not. We found a significant positive relationship between total carbon production and average $P\text{-}PO_4$ groundwater inflow mass ($r^2 = 0.90$, $p < 0.05$) but not with average $N\text{-}NO_3$ groundwater inflow mass ($r^2 = 0.64$, $p > 0.05$).

5. Discussion

Gravel pit lakes increasingly affect the landscape as demand for gravel resources augments in many parts of the world. The possible impacts of GPLs on the adjacent groundwater initiated a series of studies (Alvarez Cobelas et al., 1990; Garnier and Billen, 1994; Kattner et al., 2000; Labroue et al., 1988; Pinay and Decamps, 1988) that focused to a large extent on the relative change of nutrients in the groundwater adjacent to the GPLs, but not on the ecosystem processes that possibly drive nutrient dynamics. This study provides a first comprehensive ecosystem approach showing that post-excavation GPLs reduce nitrate and phosphate concentrations from the inflowing groundwater, which ultimately fosters both benthic and pelagic primary production. This may lead to considerable accrual of biomass from primary producers, but not to noticeable release of DOC and nutrients into the outflowing groundwater (Table 5).

A major finding of our study is that post-excavation age of the GPLs influences the whole-ecosystem metabolism of the GPLs. Results clearly indicate that these GPLs increasingly become a net sink for organic carbon with increasing age. We also found that whole-ecosystem (benthic and pelagic) NPP increased with post-excavation age, as was also reflected by average pelagic chlorophyll *a* concentration (Fig. 1). Whole-ecosystem R was not associated with post-excavation age due to the outlying GPL2 — the largest GPL in our study (Table 1). Averaging data from all four seasons, we found that GPLs were net autotrophic with ratios of R to NPP ranging from 0.59 to 0.36 decreasing with post-excavation age (Fig. 1). We suggest that benthic biomass contributes to clogging of the GPLs as they age, which leads to their successive disconnection from the adjacent groundwater. Initially the groundwater hydraulic gradient and the hydraulic conductivity in the adjacent aquifer are key controls on groundwater inflow. With increasing GPL age, the sedimentation of dead biomass may induce partial clogging thus reducing the exchange between groundwater and lake water. Ultimately, this

Table 4
Estimates of pelagic and epilithic metabolism [g C m^{-2} yr^{-1}] for each GPL and season. Superscripts indicate significant differences in epilithic metabolism within GPLs according to a Post hoc test after Siegel and Castellan (1988). See methods for details on relationships of pelagic and sediment metabolism.

Lake	$NPP_{epilithic}$	$R_{epilithic}$	$NPP_{pelagic}$	$R_{sediment}$ (heterotrophic)	$R_{pelagic}$ (autotrophic)	BSP	$R_{pelagic}$ (heterotrophic)
GPL1	112.9 ± 54.6[a]	39.5 ± 20.8[a]	88.0	67.8	147.6	14.8	11.9
GPL2	197.1 ± 20.8[b]	64.3 ± 10.2[b]	85.1	63.6	186.6	11.7	10.3
GPL3	168.9 ± 15.2[a]	51.7 ± 11.7[a]	108.5	59.5	68.1	6.6	7.3
GPL4	180.6 ± 12.1[a,b]	53.5 ± 5.2[a,b]	143.5	81.8	179.5	10.8	9.9
GPL5	303.2 ± 66.4[b]	74.8 ± 18.9[b]	290.3	95.9	167.6	22.3	15.4

development will lead to internal recycling of inorganic nutrients increasingly overwhelming nutrient inputs from the inflowing groundwater. At the same time, clogging of the benthic zone in the outflowing parts of the GPLs may reduce the export of nutrients and DOC into the outflowing groundwater.

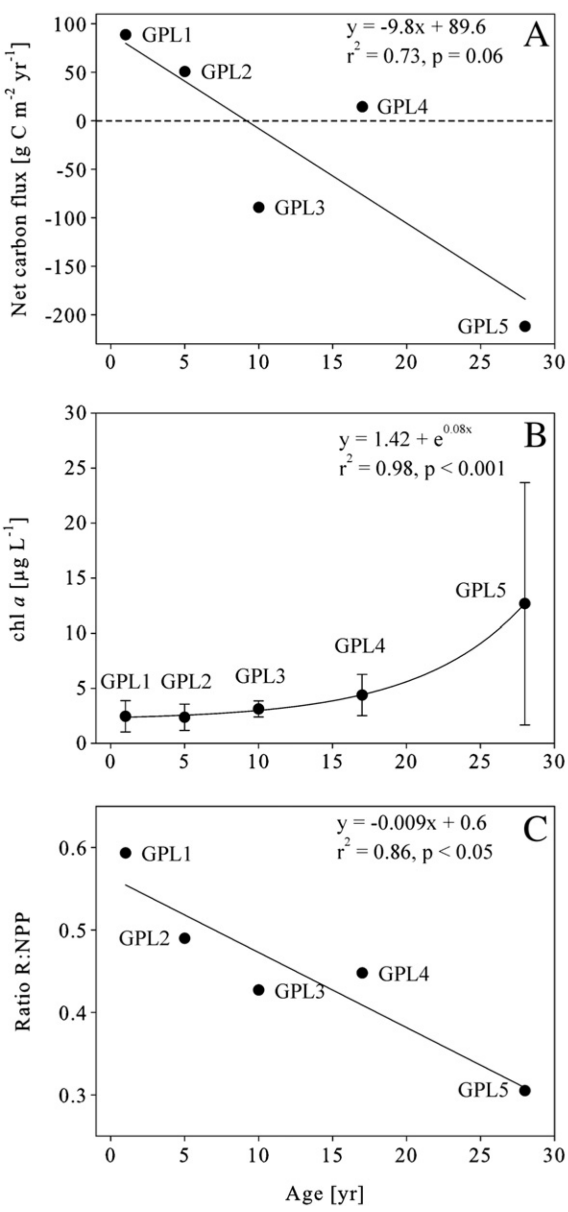


Fig. 1. Relationship between net carbon flux (A), pelagic chlorophyll *a* (B), R:NPP (C) and age of the five gravel pit lakes (GPL1-5). Negative values in panel (A) indicate lower carbon consumption than production, whereas positive values indicate higher carbon consumption than production.

Our estimates of whole-ecosystem metabolism (e.g., NPP of 201 g C m^{-2} yr^{-1} to 594 g C m^{-2} yr^{-1} in GPL1 and GPL5, respectively) as combined from direct measurements and published relationships (Table 2) are reasonably well bracketed by published *in situ* measurements from other GPLs. For instance, Alvarez Cobelas et al. (1992) estimated pelagic NPP at 750 g C m^{-2} y^{-1} in a hypertrophic GPL, where nutrient concentrations were up to 9 times higher than in our study lakes. This provides confidence that our approach was reasonably robust to put GPLs into a comparative ecosystem context.

Various studies have pointed to the changes in nutrient chemistry as water moves from the aquifer into the lake, whether natural or man-made (Alfreider et al., 2001; Hagerthey and Kerfoot, 1998; Vanek, 1987). Such gradients of nutrient concentration and related supply may influence both the composition and biomass of benthic algae as reported from a natural seepage lake (Hagerthey and Kerfoot, 1998). One may therefore expect differences in benthic chlorophyll *a* and possibly also in benthic NPP between the GPL zones with inflowing and outflowing groundwater. However, our data do not fully support this anticipated pattern. This indicates that the GPL water is well mixed, as also suggested by the absence of nutrient gradients across our sample transect in each GPL (Supplementary Information). Nevertheless, we found that inflowing P-PO_4 fluxes into the GPLs affect the pelagic metabolism. This supports earlier findings on the relationship between PO_4 inputs and eutrophication of GPLs (Kattner et al., 2000). These authors showed that PO_4 inputs from the Danube River into fringing GPLs decreased over a series of five consequent GPLs, where the varying PO_4 loads differentially affected pelagic chlorophyll *a* concentration and sedimentation. Kattner et al. (2000) also reported that aging and sedimentation affect sediment permeability of the GPLs and ultimately water residence time in these ecosystems. In our study, we did not find a significant correlation between age and water residence time. In fact, water residence time does not only depend on sediment permeability (decreasing as clogging progresses) but also on the hydraulic gradient across the groundwater-lake interface. High hydraulic gradients in some of our GPLs obviously blurred the relationship between residence time and age.

We found positive relationships between phosphate fluxes into the GPLs and both benthic and pelagic production, but no such relationships for nitrate. This suggests that GPL metabolism is mainly phosphate limited, as is the case for natural lakes. Nevertheless we found that N-NO_3 concentrations decreased significantly in the outflowing groundwater (up to 99%), a gradient that is confirmed by earlier studies on nitrate concentrations in GPLs (Alvarez Cobelas et al., 1990; Labroue et al., 1988; Pinay and Decamps, 1988). For instance, Pinay and Decamps (1988) reported average nitrate concentrations decreasing from 4.3 ± 1.1 mg L^{-1} in the inflowing groundwater to 1.3 ± 0.8 mg L^{-1} in the outflowing groundwater of a GPL. Nizzoli et al. (2010) reported benthic denitrification to account for up to 84 to 97% of total NO_3 reduction in two man-made lakes in Italy. Our data show higher nitrogen retention in GPLs with low water residence time, which agrees with a model by Garnier and Billen (1994) that predicts low water residence time to enhance

Table 5
Estimates of average annual carbon fluxes [g C m^{-2} y^{-1}] for each GPL. Propagation of uncertainty was performed based on the standard deviation of measured chlorophyll *a* and bacterial secondary production.

Lake	DOC inflow	Uncertainty %	Total C production	Uncertainty %	Total C consumption	Uncertainty %	DOC outflow	Uncertainty %	Net carbon fluxes[a]
GPL 1	14.2	7	200.9	38	281.6	38	22.1	57	88.7
GPL 2	17.6	10	282.2	27	336.4	20	14.0	11	50.6
GPL 3	69.8	27	277.4	33	193.1	25	64.7	7	−89.4
GPL 4	11.5	17	324.1	29	335.4	35	14.6	24	14.4
GPL 5	81.7	9	593.6	24	376.0	17	87.8	10	−211.5

[a] Negative values indicate a sink, positive values indicate a source.

nitrate and phosphate sequestration in GPLs. In this study, we did not attempt to elucidate the actual processes of nitrate retention, but denitrification may be an important pathway as reported from other GPLs (Labroue et al., 1988; Nizzoli et al., 2010), for instance.

Our observations show higher total carbon production and lower total carbon consumption in GPLs with low water residence time and *vice versa* in GPLs with high water residence time. Higher carbon production is most likely attributable to higher nutrient fluxes due to a higher groundwater inflow in those GPLs. We assume that high nutrient loading from the inflowing groundwater enhances NPP in the GPLs. This may lead to further clogging and a disconnection from the adjacent aquifer due to the accrual of biomass and sedimentation processes in the lake water. This study reveals that total carbon production is associated with pelagic chlorophyll *a* concentrations and increasing GPL age, which may potentially indicate a shift towards eutrophication. Moreover, atmospheric deposition of P-PO_4 on GPLs appears to add to the P-PO_4 flux from the inflowing groundwater. We found atmospheric deposition of phosphate to be as high as 240% of groundwater inflow flux. We also found a decrease in phosphate concentrations in the outflowing groundwater as high as 99%, indicating substantial removal of phosphate from atmospheric deposition as well as from groundwater inflow. This study is the first to show that GPLs serve as sinks for phosphate as well as nitrate not only from groundwater inflow but also from atmospheric deposition. This seems to be important especially in areas under high agricultural land use and highlights groundwater and atmospheric exchange and nutrient fluxes as important controls on the trophic state of GPLs.

Our findings suggest that GPLs act like natural seepage lakes where groundwater subsidizes the lake metabolism (Hagerthey and Kerfoot, 1998). At the landscape level, our findings strongly suggest that GPLs act as sinks of organic carbon as has recently been reported for agriculturally eutrophic impoundments (Downing et al., 2008). Nutrients from agriculture often accumulate in the groundwater (Alley et al., 2002), which upon arrival in a GPL, can sustain elevated primary production in these man-made lakes. It would thus be primarily autochthonous carbon being retained and, at various degrees, accumulated in GPLs. It is well known that the spatial configuration of gravel bars that differ in size can affect nitrogen sequestration in streams (Dent et al., 2001). Similarly, our data suggest that spatial configuration of GPLs in the landscape could contribute to groundwater amelioration given a proper management of these man-made ecosystems.

6. Conclusion

This study shows that man-made gravel pit lakes significantly sequester nitrate and phosphate from the inflowing groundwater, and therefore serve as natural sinks for these nutrients. Depending on post-excavation age, GPLs serve as either a sink or source for dissolved organic carbon but in any case do not release substantial amounts of DOC into the outflowing groundwater. The retention of nutrients leads to accrual of substantial amounts of biomass within the lake ecosystem that might clog the lake bottom and further increase lake trophic state.

Acknowledgements

We are grateful to Gertraud Stenicka for her assistance in the laboratory. Financial support came from Forum Mineralische Rohstoffe, the Provinces of Lower Austria, Upper Austria and Styria, and from the Federal Ministry of Agriculture, Forestry, Environment and Water Management.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.scitotenv.2012.01.032.

References

Alfreider A, Loferer-Krössbacher M, Psenner R. Influence of artificial groundwater lakes on the abundance and activity of bacteria in adjacent subsurface systems. Limnologica 2001;31:249–55.
Alley WM, Healy RW, LaBaugh JW, Reilly TE. Flow and storage in groundwater systems. Science 2002;296:1985–90.
Alvarez Cobelas M, Rubio A, Velasco JL. Chemical limnology of a hypertrophic gravel-pit lake. Ann Limnol 1990;26:97-108.
Alvarez Cobelas M, Haering FJ, Velasco JL, Rubio A. The seasonal productivity of phytoplankton in a hypertrophic, gravel-pit lake. J Plankton Res 1992;14:979–96.
Botta S, Comoglio C, Quaglino A, Torchia A. Implementation of environmental management systems in the extraction of construction aggregates from gravel pit lakes. Am J Environ Sci 2009;5:526–35.
Craig H, Gordon LI. Stable isotopes in oceanographic studies and paleotemperatures. Pisa: V. Lishi e F.; 1965.
Del Giorgio PA, Cole JJ. Bacterial growth efficiency in natural aquatic systems. Annu Rev Ecol Syst 1998;29:503–41.
Dent L, Grimm NB, Fisher SG. Multiscale effects of surface–subsurface exchange on stream water nutrient concentrations. J N Am Benthol Soc 2001;20:162–81.
Downing JA, Cole JJ, Middelburg JJ, Striegl RG, Duarte CM, Kortelainen P, et al. Sediment organic carbon burial in agriculturally eutrophic impoundments over the last century. Global Biogeochem Cycles 2008;22:1-10.
Drew LJ, Langer WH, Sachs JS. Environmentalism and natural aggregate mining. Nat Resour Res 2002;11:19–28.
Fank J, Rock G, Partl P, Weisse T. 2005. Erfassung des gegenwärtigen Zustandes und Prognose zukünftiger Entwicklungen der Baggerseen im westlichen Leibnitzer Feld aus hydrologischer, limnologischer und fischereibiologischer Sicht unter Berücksichtigung möglicher nachhaltiger aber auch ökonomischer Nachnutzungsformen. Studie im Auftrag der steiermärkischen Landesregierung; 2005. p. 237.
Garnier J, Billen G. Ecological interactions in a shallow sand-pit lake (Lake Créteil, Parisian Basin, France): a modelling approach. Hydrobiologia 1994;275–276:97-114.
Gat RJ. Isotope hydrology: A study of the water cycle. Ser Envir Sci Manag 2010:6.
Hagerthey SE, Kerfoot WC. Groundwater flow influences the biomass and nutrient ratios of epibenthic algae in a north temperate seepage lake. Limnol Oceanogr 1998;43:1227–42.
Hauer FR, Lamberti GA. Methods in stream ecology. 2nd ed. Academic Press; 2006.
Hindák F, Hindáková A. Diversity of cyanobacteria and algae of urban gravel pit lakes in Bratislava, Slovakia: a survey. Hydrobiologia 2003;506–509:155–62.
Kattner E, Schwarz D, Maier G. Eutrophication of gravel pit lakes which are situated in close vicinity to the river Donau: water and nutrient transport. Limnologica 2000;30:261–70.
Labroue J, Tourenq JN, Mieussens C, Robert J, Donville B. Rôle des lacs de gravières dans la diminution des teneurs en nitrates des aquifères alluviaux de la Garonne Essai de quantification. Ann Limnol 1988;24:31–8.
Langer WH. Environmental impacts of mining natural aggregate. In: Bon RL, Riordan RF, Tripp BT, Krukowski ST, editors. Proc. 35th Forum on the Geology of Industrial

Minerals— The Intermountain West Forum: Utah. Geol Surv Mis Pub; 2001. p. 127–37.
Leder K. Trend und Jahresverlauf der Niederschlagsdaten in Österreich von 1983–2007. Vienna: Technische Universität Wien; 2008.
Nizzoli D, Carraro E, Nigro V, Viaroli P. Effect of organic enrichment and thermal regime on denitrification and dissimilatory nitrate reduction to ammonium (DNRA) in hypolimnetic sediments of two lowland lakes. Water Res 2010;44:2715–24.
Pace ML, Prairie YT. Respiration in lakes. In: Del Giorgio PA, le B. Williams PJ, editors. Respiration in aquatic ecosystems. New York: Oxford University Press Inc.; 2005. p. 103–21.
Peckenham J, Thornton T, Whalen B. Sand and gravel mining: effects on ground water resources in Hancock county, Maine, USA. Environ Geol 2009;56:1103.
Pinay G, Decamps H. The role of riparian woods in regulating nitrogen fluxes between the alluvial aquifer and surface water: a conceptual model. Regul Rivers Res Manage 1988;2:507–16.
Siegel S, Castellan Jr NJ. Nonparametric statistics for the behavioral sciences. 2nd ed. New York: Mcgraw-Hill Book Company; 1988.
Simon M, Azam F. Protein content and protein synthesis rates of planktonic marine bacteria. Mar Ecol Prog Ser 1989;51:201–13.
Smith EM, Prairie YT. Bacterial metabolism and growth efficiency in lakes: the importance of phosphorus availability. Limnol Oceanogr 2004;49:137–47.
Tavernini S, Nizzoli D, Rossetti G, Viaroli P. Trophic state and seasonal dynamics of phytoplankton communities in two sand-pit lakes at different successional stages. J Limnol 2009;68:217–28.
Vanek V. The interaction between lake and groundwater and their ecological significance. Stygologia 1987;3:17–39.
Wetzel RG. Limnology: Lake and river ecosystems. 3rd ed. Academic Press; 2001.
Willey JD, Kieber RJ, Eyman MS, Avery Jr GB. Rainwater dissolved organic carbon: concentrations and global flux. Global Biogeochem Cycles 2000;14:139.
Yi Y, Brock BE, Falcone MD, Wolfe BB, Edwards TWD. A coupled isotope tracer method to characterize input water to lakes. J Hydrol 2008;350:1-13.

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

Christian Muellegger [a], Andreas Weilhartner [b, c], Tom J. Battin [b, c], Thilo Hofmann [a] (2013)

[a] Department of Environmental Geosciences, University of Vienna, Althanstrasse 14, 1090 Vienna, Austria

[b] Department of Limnology, University of Vienna, Althanstrasse 14, 1090 Vienna, Austria

[c] WasserCluster Lunz – Biologische Station GmbH, Dr. Carl Kupelwieser Promenade 5, 3293 Lunz am See, Austria

Science of the Total Environment 443: 14-23

Science of the Total Environment 443 (2013) 14–23

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

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

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

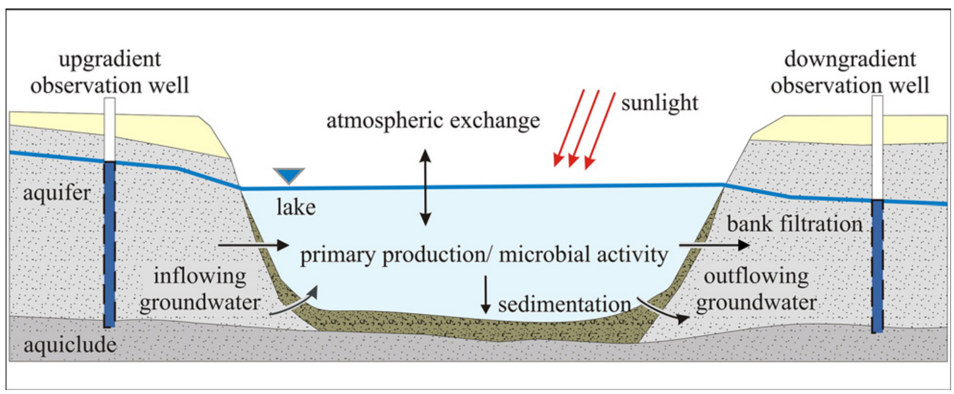
Christian Muellegger [a], Andreas Weilhartner [b,c], Tom J. Battin [b,c], Thilo Hofmann [a,*]

[a] *Department of Environmental Geosciences, University of Vienna, Althanstrasse 14, 1090 Vienna, Austria*
[b] *Department of Limnology, University of Vienna, Althanstrasse 14, 1090 Vienna, Austria*
[c] *WasserCluster Lunz GmbH, Dr. Carl Kupelwieser Promenade 5, 3293 Lunz am See, Austria*

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



ARTICLE INFO

Article history:
Received 14 July 2012
Received in revised form 19 September 2012
Accepted 28 October 2012
Available online xxxx

Keywords:
Gravel pit lakes
Groundwater
Bank filtration
Nitrate removal
Decalcification

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.

* Corresponding author. Tel.: +43 1 4277 53320; fax: +43 1 4277 9533.
E-mail address: thilo.hofmann@univie.ac.at (T. Hofmann).

0048-9697/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.scitotenv.2012.10.097

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,

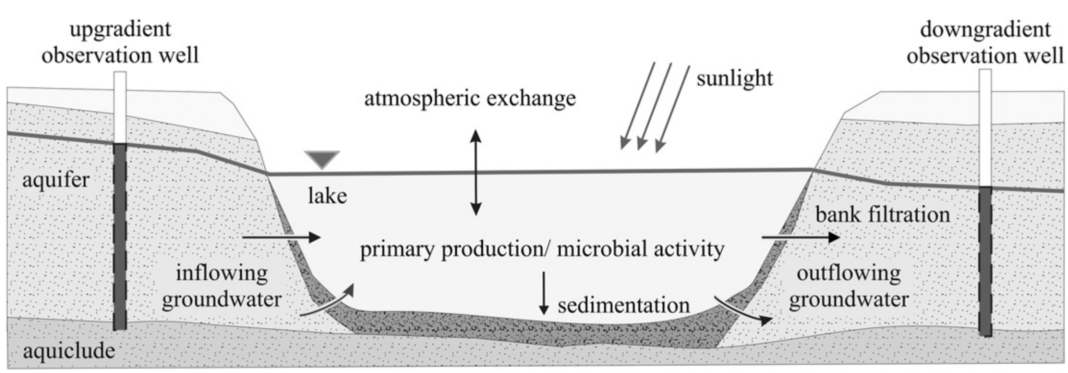


Fig. 1. Schematic cross-section of a groundwater-fed gravel pit lake, and locations of the hydraulically upgradient and downgradient observation wells installed for this study.

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 (≤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^+,

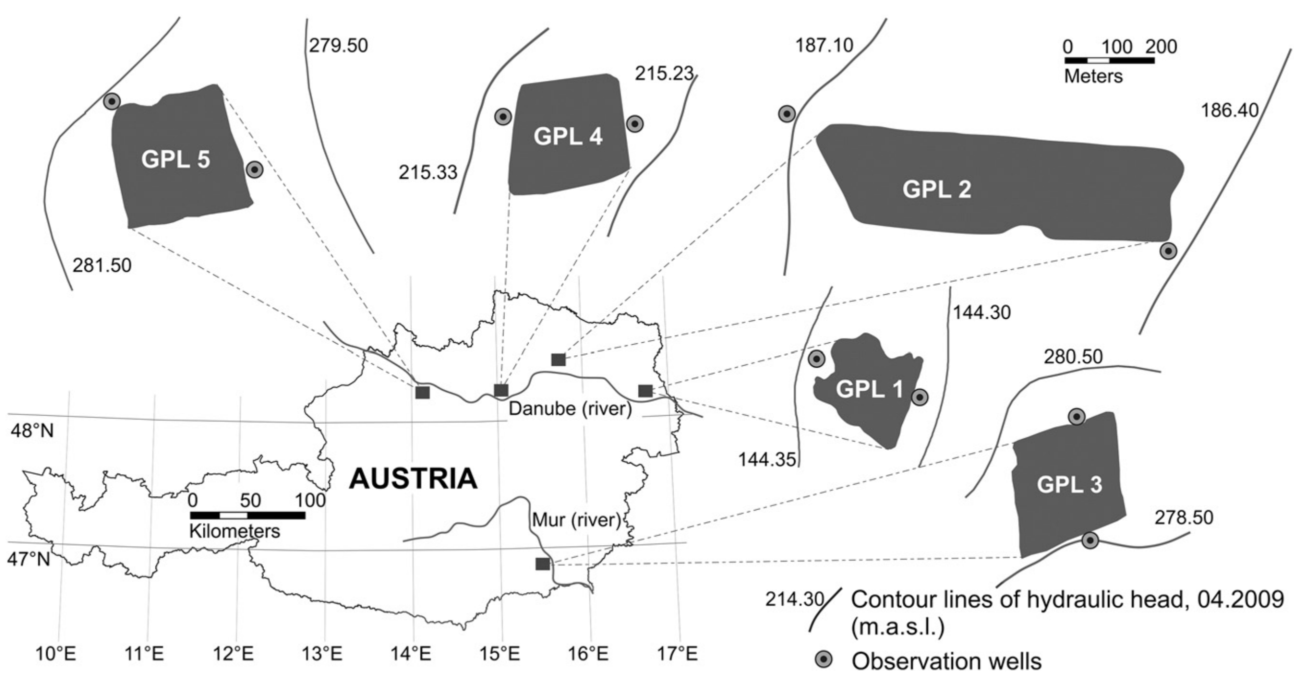


Fig. 2. Locations of the five gravel pit lakes and detailed views of each of the lakes, showing contour lines for the hydraulic heads and the locations of upgradient and downgradient observation wells.

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).

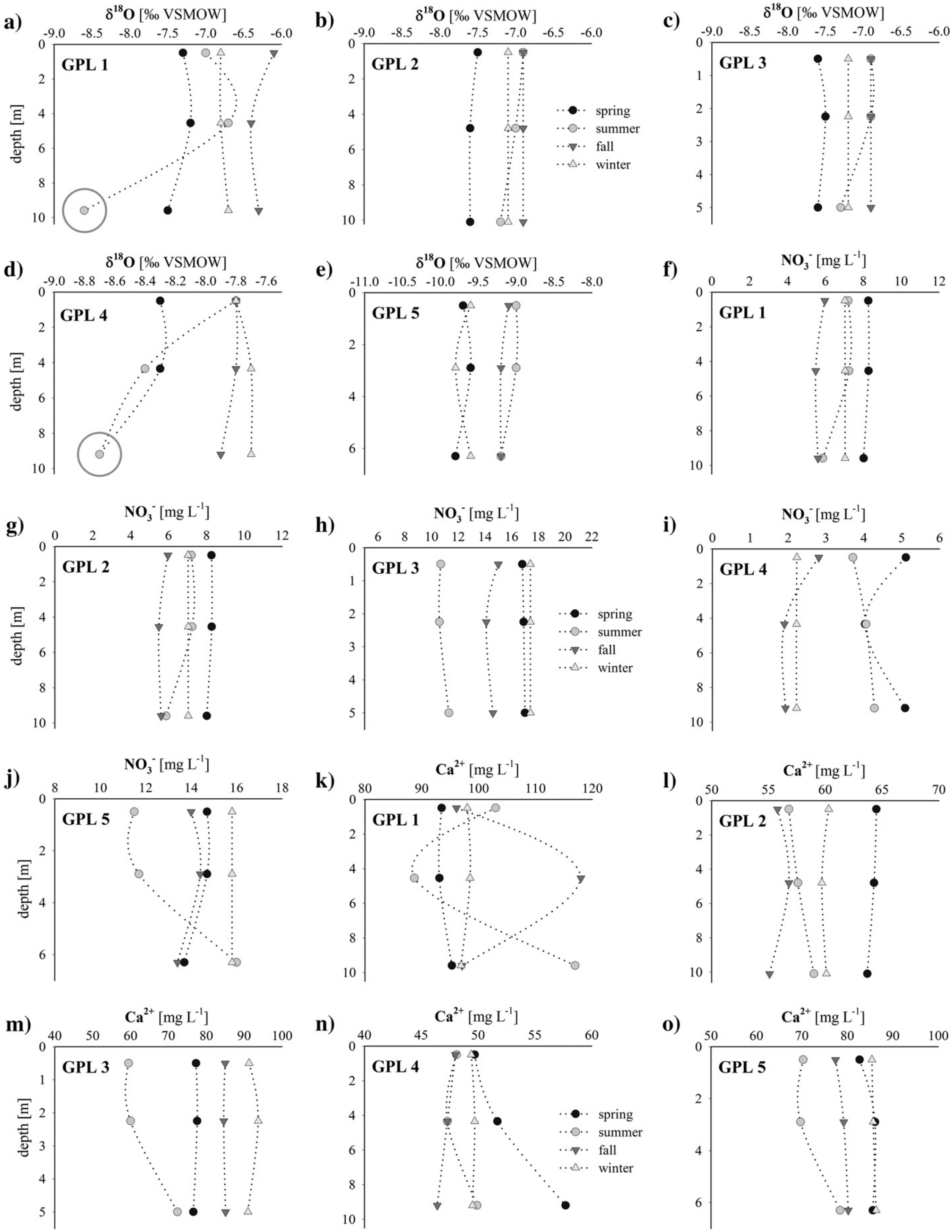


Fig. 3. Vertical lake water profiles for $\delta^{18}O$, NO_3^- and Ca^{2+}, from all five GPLs in all four seasons (from central locations, and showing depth below water surface).

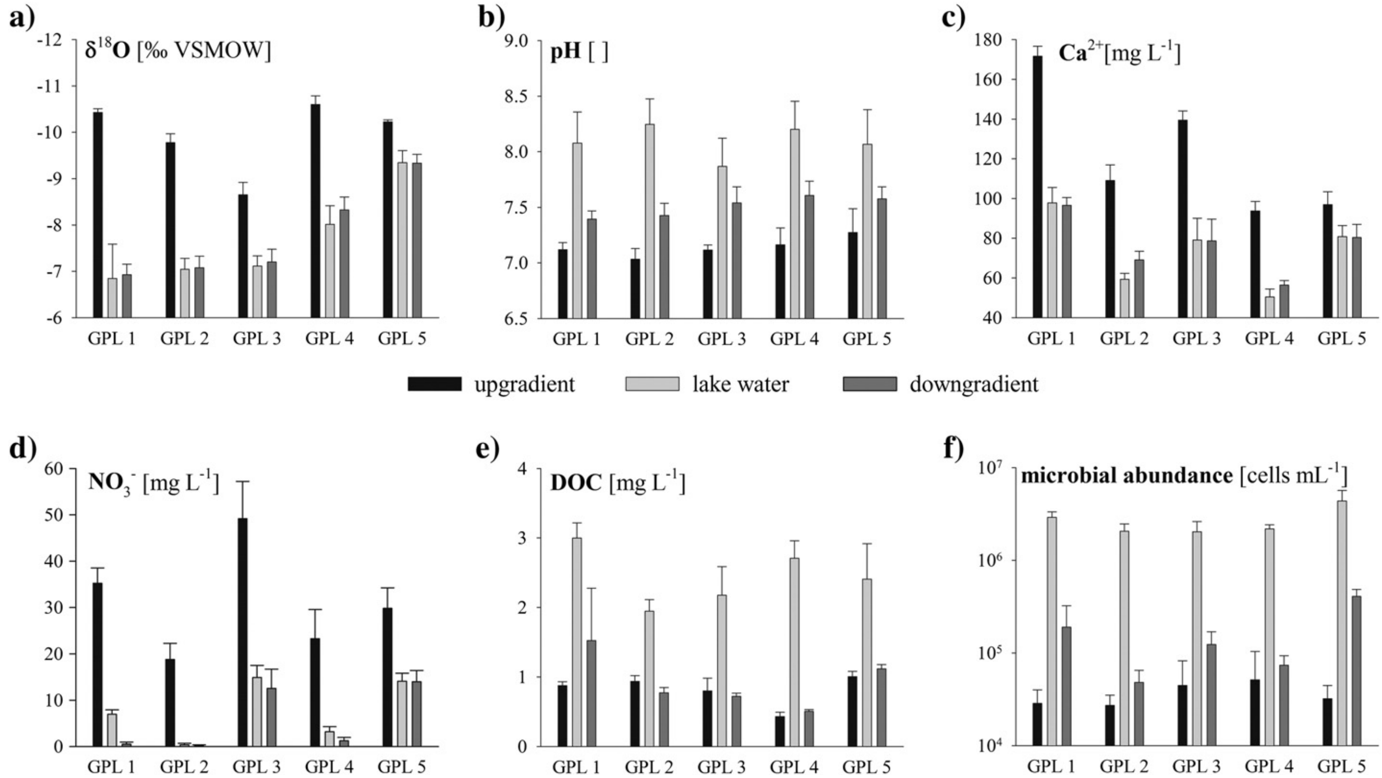


Fig. 4. Annual average hydrochemical (pH, Ca^{2+}, NO_3^-, $\delta^{18}O$), and microbial (DOC, microbial abundance) data along the groundwater flow gradient of all GPLs, with associated standard deviations, for upgradient groundwater (n = 4), downgradient groundwater (n = 4), and lake water (n = 36).

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).

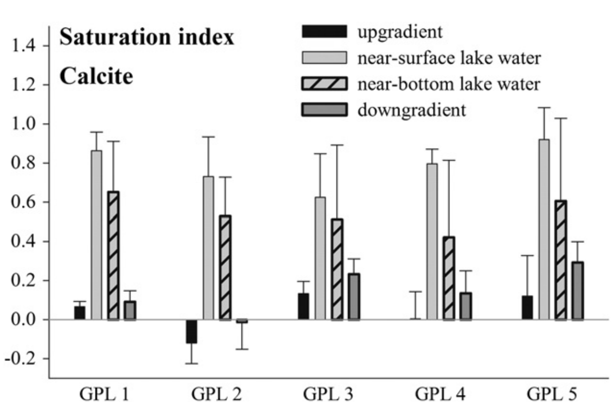


Fig. 5. Annual average calcite saturation indices along the groundwater flow gradient of all GPLs, with associated standard deviations, for upgradient groundwater (n=4), near-surface lake water (n=4), near-bottom lake water (n=4) and downgradient groundwater (n=4).

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 ($+2.7 \pm 1.1 \times 10^6$ cells mL^{-1}, on average). Microbial abundances decreased again rapidly downgradient, but were still high compared to upgradient groundwater abundances ($+1.3 \pm 1.5 \times 10^5$ 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.

Acknowledgments

This work was funded by the Austrian Association for Building Materials and Ceramic Industries, by the Provinces of Lower Austria, Upper Austria, and Styria, and by the Federal Ministry of Agriculture, Forestry, Environment and Water Management. We gratefully acknowledge Bernhard Groiss, Martin Kainz, Francine Mathieu, and Elisabeth Neubauer for their support during field sampling, Mélanie Kah and Ed Mannning for proofreading, Wilfried Körner and Wolfgang Obermaier for laboratory analysis.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2012.10.097.

References

Alfreider A, Loferer-Krössbacher M, Psenner R. Influence of artificial groundwater lakes on the abundance and activity of bacteria in adjacent subsurface systems. Limnologica 2001;31:249–55.
Apaydin A. Dual impact on the groundwater aquifer in the Kazan Plain (Ankara, Turkey): sand-gravel mining and over-abstraction. Environ Earth Sci 2012;65:241–55.
Arbogast BF, Knepper Jr DH, Langer WH. The human factor in mining reclamation. USGS circular; 2000. p. 1191.
Bach M, Huber A, Frede HG. Input pathways and river load of pesticides in Germany — a national scale modeling assessment. Water Sci Technol 2001;43:261–8.
Baker A, Lamont-Biack J. Fluorescence of dissolved organic matter as a natural tracer of ground water. Ground Water 2001;39:745–50.
Battin TJ. Hydrologic flow paths control dissolved organic carbon fluxes and metabolism in an alpine stream hyporheic zone. Water Resour Res 1999;35:3159–69.
Bertleff B, Plum H, Schuff J, Stichler W, Storch DH, Trapp C. Wechselwirkungen zwischen Baggerseen und Grundwasser. Baden-Württemberg: Landesamt für Geologie, Rohstoffe und Bergbau - Baden-Württemberg; 2001.
Botta S, Comoglio C, Quaglino A, Torchia A. Implementation of environmental management systems in the extraction of construction aggregates from gravel pit lakes. Am J Environ Sci 2009;5:525–34.
Brookes JD, Antenucci J, Hipsey M, Burch MD, Ashbolt NJ, Ferguson C. Fate and transport of pathogens in lakes and reservoirs. Environ Int 2004;30:741–59.
Brugger A, Reitner B, Kolar I, Quéric N, Herndl GJ. Seasonal and spatial distribution of dissolved and particulate organic carbon and bacteria in the bank of an impounding reservoir on the Enns River, Austria. Freshwat Biol 2001;46:997-1016.
Couillard Y, Cattaneo A, Gallon C, Courcelles M. Sources and chronology of fifteen elements in the sediments of lakes affected by metal deposition in a mining area. J Paleolimnol 2008;40:97-114.
Drew LJ, Langer WH, Sachs JS. Environmentalism and natural aggregate mining. Nat Resour Res 2002;11:19–28.
DVWK. Ermittlung der Verdunstung von Land- und Wasserflächen - Merkblätter zur Wasserwirtschaft 238. Hamburg — Berlin: Parey; 1996.
Gołdyn R, Podsiadłowski S, Kowalczewska-Madura K, Dondajewska R, Szeląg-Wasielewska E, Budzyńska A, et al. Functioning of the Lake Rusałka ecosystem in Poznań (western Poland). Oceanol Hydrobiol Stud 2010;39:65–80.
Harrison J, Maranger R, Alexander R, Giblin A, Jacinthe P-A, Mayorga E, et al. The regional and global significance of nitrogen removal in lakes and reservoirs. Biogeochemistry 2009;93:143–57.
Hoffmann A, Gunkel G. Bank filtration in the sandy littoral zone of Lake Tegel (Berlin): structure and dynamics of the biological active filter zone and clogging processes. Limnologica 2011;41:10–9.
Johnson MP. Environmental impacts of urban sprawl: a survey of the literature and proposed research agenda. Environ Plann A 2001;33:717–35.
Jürgen J, Laatz W. Statistische Datenanalyse mit SPSS für Windows. 5the ed. Berlin: Springer-Verlag; 2005.
Kedziorek MAM, Geoffriau S, Bourg ACM. Organic matter and modeling redox reactions during river bank filtration in an alluvial aquifer of the Lot River, France. Environ Sci Technol 2008;42:2793–8.
Kinsela AS, Jones AM, Collins RN, Waite TD. The impacts of low-cost treatment options upon scale formation potential in remote communities reliant on hard groundwaters. A case study: Northern Territory, Australia. Sci Total Environ 2012;416:22–31.
Kunkel R, Voigt H-J, Wendland F, Hannappel S. Die natürliche, ubiquitär überprägte Grundwasserbeschaffenheit in Deutschland. Jülich: Forschungszentrum Jülich; 2004.
Lee DG, Kim SJ, Park SJ. Effect of reservoirs on microbiological water qualities in a drinking water distribution system. J Microbiol Biotechnol 2006;16:1060–7.
Leder K. Trend und Jahresverlauf der Niederschlagsdaten in Österreich von 1983–2007. Vienna: Technische Universität Wien; 2008.
Marques ED, Tubbs D, Gomes OVO, Silva-Filho EV. Influence of acid sand pit lakes in surrounding groundwater chemistry, Sepetiba sedimentary basin, Rio de Janeiro, Brazil. J Geochem Explor 2012;112:306–21.
Massmann G, Dünnbier U, Heberer T, Taute T. Behaviour and redox sensitivity of pharmaceutical residues during bank filtration — investigation of residues of phenazone-type analgesics. Chemosphere 2008;71:1476–85.
Nizzoli D, Carraro E, Nigro V, Viaroli P. Effect of organic enrichment and thermal regime on denitrification and dissimilatory nitrate reduction to ammonium (DNRA) in hypolimnetic sediments of two lowland lakes. Water Res 2010;44:2715–24.
Parkhurst DL, Appelo CAJ. User's guide to PHREEQC (version 2) — a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. USGS water-resources investigations report; 1999. p. 99-4259.
Perini M, Camin F, Corradini F, Obertegger U, Flaim G. Use of $\delta^{18}O$ in the interpretation of hydrological dynamics in lakes. J Limnol 2009;68:174–82.
Pitois S, Jackson MH, Wood BJB. Problems associated with the presence of cyanobacteria in recreational and drinking waters. Int J Environ Health Res 2000;10:203–18.
Sampl H. Baggerseen und ihre Wechselbeziehungen zum Grundwasser. Wien: Bundesministerium für Land- und Forstwirtschaft, Österreich; 1995.
Schultze M, Pokrandt KH, Hille W. Pit lakes of the Central German lignite mining district: creation, morphometry and water quality aspects. Limnologica 2010;40: 148–55.

Seebach A, von Rohden C, Ilmberger J, Weise SM, Knöller K. Dating problems with selected mining lakes and the adjacent groundwater body in Lusatia, Germany. Isot Environ Health Stud 2010;46:291–8.
Sharma L, Greskowiak J, Ray C, Eckert P, Prommer H. Elucidating temperature effects on seasonal variations of biogeochemical turnover rates during riverbank filtration. J Hydrol 2012;428–429:104–15.
Sprenger C, Lorenzen G, Hülshoff I, Grützmacher G, Ronghang M, Pekdeger A. Vulnerability of bank filtration systems to climate change. Sci Total Environ 2011;409:655–63.
Stichler W, Maloszewski P, Bertleff B, Watzel R. Use of environmental isotopes to define the capture zone of a drinking water supply situated near a dredge lake. J Hydrol 2008;362:220–33.
Stichler W, Maoszewski P, Moser H. Modelling of river water infiltration using oxygen-18 data. J Hydrol 1986;83:355–65.
Stumm W, Morgan JJ. Aquatic chemistry: chemical equilibria and rates in natural waters. New York: Wiley; 1996.
Tang X, Zhu B, Katou H. A review of rapid transport of pesticides from sloping farmland to surface waters: processes and mitigation strategies. J Environ Sci 2012;24:351–61.
UEPG. Sustainable development in the European aggregates industry — annual review 2010–2011. Brussels: European Aggregates Association; 2012.
Weilhartner A, Muellegger C, Kainz M, Mathieu F, Hofmann T, Battin TJ. Gravel pit lake ecosystems reduce nitrate and phosphate concentrations in the outflowing groundwater. Sci Total Environ 2012;420:222–8.
WHO. Guidelines for drinking-water quality. 4th ed. Geneva: World Health Organization; 2011.
Wiese B, Massmann G, Jekel M, Heberer T, Dünnbier U, Orlikowski D, et al. Removal kinetics of organic compounds and sum parameters under field conditions for managed aquifer recharge. Water Res 2011;45:4939–50.
Yehdegho B, Probst G. Chemical mass budget of two dredged lakes embedded in shallow Quaternary aquifers in southern Austria. Environ Geol 2001;40:809–19.
Zhang H, Zhang Y, Shi Q, Hu J, Chu M, Yu J, et al. Study on transformation of natural organic matter in source water during chlorination and its chlorinated products using ultrahigh resolution mass spectrometry. Environ Sci Technol 2012;46:4396–402.

3. Physiological profiles and community metabolism of benthic biofilms in gravel pit lakes

Andreas Weilhartner [a, b], Gabriel A. Singer [a, b], Thilo Hofmann [c], Christian Muellegger [c], Tom J. Battin [a, b]

[a] Department of Limnology, University of Vienna, Althanstrasse 14, 1090 Vienna, Austria
[b] WasserCluster Lunz – Biologische Station GmbH, Dr. Carl Kupelwieser Promenade 5, 3293 Lunz am See, Austria
[c] Department of Environmental Geosciences, University of Vienna, Althanstrasse 14, 1090 Vienna, Austria

finished manuscript

Physiological profiles and community metabolism of benthic biofilms in gravel pit lakes

Andreas Weilhartner [a, b], Gabriel A. Singer [a, b], Thilo Hofmann [c], Christian Muellegger [c] and Tom J. Battin [a, b*]

[a] Department of Limnology, University of Vienna, Althanstrasse 14, 1090 Vienna, Austria

[b] Wasser Cluster Lunz GmbH, Dr. Carl Kupelwieser Promenade 5, 3293 Lunz am See, Austria

[c] Department of Environmental Geosciences, University of Vienna, Althanstrasse 14, 1090 Vienna, Austria

*Corresponding author: tom.battin@univie.ac.at

Abstract

In gravel pit lakes, benthic microbial biofilms may modulate groundwater-surface water interactions by carbon cycling and nutrient uptake from both the inflowing groundwater and lake water. After bank filtration at the inflow sediment-water interface, DOC and nutrients are subject to a change in quantity and/or quality that may affect biofilm metabolism at the inflow and outflow interfaces of the lakes. We found that biofilm respiration and net primary production was high but did not change significantly between inflow and outflow of 5 gravel pit lakes in Austria. However, we found that due to a change in nutrient concentrations and DOC quantity and quality between lake inflow and outflow, biofilm communities metabolized distinct carbon substrate groups, generating distinct physiological profiles. Our data suggest that a shift in carbon source along the environmental gradient from groundwater to lake water may cause differences in carbon substrate utilization. In groundwater, organic carbon is mainly derived from terrestrial and microbial sources whereas in lake water it is mainly derived from algae. Lake internal processes may lead to high biofilm respiration and production at the inflow and outflow interfaces of gravel pit lakes due to sufficient supply of nutrients and organic carbon.

Keywords: biofilm, physiological profile, gravel pit lake, biogeochemistry, metabolism

1. Introduction

Gravel pit lakes (GPLs) are man-made ecosystems that are formed by excavation of sand or gravel from the groundwater aquifer. They are often characterized by low water residence time due to inflowing groundwater and outflowing lake water, which both may happen across spatially distinct sediment-water interface zones. GPLs are therefore comparable to natural seepage lakes. Due to the hydrological connectivity of GPLs to the groundwater, solutes delivered by groundwater may particularly affect benthic and pelagic microorganisms in these lakes (Hagerthey and Kerfoot, 1998; Hayashi and Rosenberry, 2002; Schneider et al., 2005; Hunt et al., 2006).

Microbial biofilms are attached and matrix-enclosed microbial communities that often dominate life in sedimentary ecosystems (Battin et al., 2003; Plée et al., 2010), including the interface between groundwater and surface water in GPLs. These benthic biofilms include prokaryotes, algae, protozoa, fungi and even small metazoa (Battin et al., 2003; Hall-Stoodley et al., 2004), and regulate key ecosystem processes such as carbon and nutrient cycling (Riding, 2000; Vadeboncoeur et al., 2008; Bartrons et al., 2012). On the lake bottom, biofilms typically occur as microbial mats, whose metabolic effects on the carbonate concentration of lake water often lead to calcium carbonate precipitation (Dittrich et al., 2004; Dupraz et al.; 2009; Plée et al., 2010). This points to carbonate limitation in these environments, and indeed, in seepage lakes for instance, higher benthic algal biomass and diversity of benthic algae was found at sites, where groundwater inflow was elevated compared to sites with reduced groundwater inflow (Hagerthey and Kerfoot, 1998). Also, seepage lakes affected by agricultural land use often receive higher nutrient deliveries from groundwater that may enhance macrophyte growth due to nutrient scavenging (Frandsen et al., 2012).

Recently it was shown that GPLs sequester nutrients from inflowing groundwater without influencing groundwater quality on the outflowing side (Weilhartner et al., 2012; Muellegger et al., 2013). These studies suggest that in-lake primary production constitutes a major sink for groundwater nutrient deliveries. Subsequent biomass build-up in these GPLs is largely degraded and mineralized by microbial heterotrophs or ends up in the lake sediments. Weilhartner et al. (2012) found that benthic biofilms accounted for almost half of the whole-ecosystem metabolism in the studied GPLs, which clearly underscores the functional relevance of these microbial communities. Clearly, this may have major implications especially in agricultural areas where nutrient loads in groundwater can be elevated (Alley et al., 2002; Downing et al., 2008; Frandsen et al., 2012).

To better understand the mechanisms that underlie the sequestration performance of GPLs, it is crucial to study the physiological capacity of the microbial biofilms as the major players in these lakes. In fact, microbial activity and resource use in biofilms may respond to both quantity and quality of nutrients and dissolved organic carbon (DOC) as it passes from the inflowing groundwater into the GPLs and again into the “downstream” groundwater (Weilhartner et al. 2012; Muellegger et al., 2013). It was shown indeed that microbial physiological capacity is related to changing DOC concentration and composition across a range of freshwater ecosystems (Comte and del Giorgio, 2009, 2010). These studies suggest that DOC can regulate the function of microbial communities via differential use of various organic substrates.

The aim of this study was to elucidate the physiologic capacity and response of microbial biofilms in GPLs that differ in size, post-extraction age and residence time. We aimed at understanding possible effects of changing nutrients and DOC along the water flow path on the physiological profiles of the biofilms at the sediment-water interfaces. We also studied whether in turn the differential substrate use affects microbial metabolism at the outflow interfaces of GPLs. We anticipated distinct physiological profiles of microbial biofilms at the inflow compared to the outflow interfaces due to different nutrient and DOC environments. To test this hypothesis, we determined in microbial biofilms substrate utilization using Biolog EcoPlates, community respiration (R) and net primary production (NPP) in five GPLs. Our findings provide important insights into the microbial purification processes as groundwater passes GPLs.

2. Material and Methods

2.1 Site description

All five study GPLs are located in Austria in areas characterized by agricultural land use and thus experience elevated nutrient loading. Adjacent aquifers are dominated by quaternary carbonate sand and gravel. Surface area of the GPLs ranges from 38,000 m^2 to 164,000 m^2, and water depth ranges from 2.3 to 6.4 m. At the time of the study in 2009, Post-sediment extraction age ranged from 1 year (GPL1) to 28 years (GPL5). All GPLs are stocked with fish (ca. 150 kg ha^{-1}) and are extensively used for recreational purposes. We identified GPL inflow and outflow areas using regional groundwater level contour maps and installed groundwater wells (inner diameter: 0.05 m) down to the aquifer (Weilhartner et al., 2012; Muellegger et al., 2013).

2.2 Biofilm sampling

In each lake, we randomly sampled stones (n=6; ca. 10 cm diameter) covered with benthic biofilms in the inflowing and outflowing zone of each GPL once per season. We collected stones from the same water depth (ca. 0.5 m below the water table) to ensure constant submergence of the stones and comparable light conditions among GPLs. Throughout the study period lake water level varied, depending on the season, between 0.3 and 0.9 m. Stones were stored in lake water in the dark and transferred to the lab within 4 hours after sampling. In the laboratory, we removed the biofilm from an area of at least 4 cm^2 yielding enough biomass for the determination of benthic chlorophyll a, ash-free dry mass (AFDM), cell counts and for the Biolog EcoPlate assays.

2.3 Biolog EcoPlate assays

Physiological profiles were derived from carbon source utilization measurements using Biolog EcoPlates. This method assesses a microbial community´s potential ability to metabolize a range of 31 carbon substrates. We used average well color development (AWCD) in the microplates to describe differences in the physiological profiles among communities sampled from various locations (Garland 1996, Weber et al. 2008, Comte and del Giorgio 2010, 2011). Instead of reporting metabolic responses to all 31 substrates in the Biolog EcoPlates individually, we focus on aggregate responses given by polymers, carbohydrates, carboxylic acids, amino acids, amines and phenolic compounds as major functional groups.

Previous work showed that approximately 10^{-5} cells mL^{-1} per microplate well was an adequate density to develop color; this work also showed consistent and reproducible patterns of color development with cells detached from benthic biofilms (data not shown). Therefore, we aimed at using approximately 10^{-5} cells mL^{-1} per well for all Biolog assays. To do so, biofilm slurries were transferred into sterile 50 mL vials and diluted with sterile (30 mL, 0.2-µm-filtered) lake water. Slurries were sonicated (Branson Sonifier W-250D, 15 W at 10% energy input at 20°C, 20 min) to detach microbial cells from debris, algae and various aggregates. The homogenate was centrifuged (4000 rpm, 4 min) and the supernatant containing microbial cells transferred into a separate vial. From this sample we routinely determined microbial cell densities by flow cytometry (BeckmanCoulter Counter) supported by direct counts using epifluorescence microscopy (Zeiss Imager.M1, Jena, Germany) for calibration purposes. Where necessary, cell densities were adjusted to the target density, and each Biolog EcoPlate well was inoculated with 150 µL of cell suspension. Biolog EcoPlates contain 31 different carbon sources in triplicate plus 1 triplicate without carbon source as a control, yielding a total of 96 wells and thus measurements per microplate and measuring occasion. In each well, microbial metabolism reduces a tetrazolium salt yielding a purple coloured compound that is measured spectrophotometrically. Well color development was monitored with a microplate scanner (Molecular Device) every 24 hours for a period of 10-14 days (Garland, 1996; Tam et al., 2003). This period typically included microplate states with an average well color of 0.75. We used one Biolog EcoPlate per replicate stone sampled in the GPL. Overall, 6 replicate stones in each of 2 interface zones (inflow and outflow), 5 lakes, 4 seasons and several days of microplate monitoring yielded a dataset of >250.000 well color measurements constituting 7680 individual well color development profiles.

2.4 Community metabolism of biofilms

For the measurement of benthic microbial metabolism (respiration, R, and net primary production, NPP) at the GPL interfaces, stones were carefully transferred into respiration chambers containing a stirring mechanism and a planar optode (PreSens Precision Sensing GmbH, Regensburg, Germany) for the measurement of dissolved oxygen concentration. According to the manufacturer the planar optodes (PSt6) have a detection limit of 1 µg O_2 L^{-1} and an accuracy of ~3%. Each respiration chamber was filled with 660 ml sterile-filtered (0.2 µm) water from the respective GPL and received one replicate stone. For each interface, we produced 6 replicate measurements per seasonal sampling occasion. For each stone, R was measured in the dark (12 h) under constant temperature (20 °C). GPP was measured (4 h) at a light intensity of 52 µmol m^{-2} s^{-1}, which compared well with light measurements taken at 0.5 m depth of the GPLs. We used PHILLIPS TL-D 58/33-640 halogen lamps that have a radiation spectrum similar to sunlight. Measurements of dissolved oxygen concentrations were performed online at one-minute intervals multiple times over the 12 and 4 h periods. Oxygen was converted to carbon units using a respiratory quotient of 1 (Smith and Prairie, 2004). To normalize metabolism for biomass, we determined Chlorophyll *a* and ash-free dry mass of scraped biofilms and the biofilm-covered stone area as described in Hauer and Lamberti (2006).

2.5 Lake water bacterial secondary production

Pelagic bacterial secondary production (BSP) in the lake water was determined for all GPLs and seasonal sampling occasions from the uptake of radio-labelled [3, 4, 5-^{3}H]-1-leucine (Hartmann, 112.6 Ci $mmol^{-1}$). At each sampling occasion, water was collected from three sites along a transect corresponding to the estimated flow path from the GPL inflow to the outflow and three water depths (0.5 m below water surface, middle, 0.5 m above lake bottom) of each GPL. In the laboratory, 10 mL aliquots of filtered (GF/F Whatman) sample water were transferred into sterile triplicate vials and into duplicate vials that contained formaldehyde (2.5% final concentration), the latter served as controls. All vials were incubated for 1 h (in the dark, 20°C) with a final concentration of 10 nM [^{3}H]-leucine (previously determined in saturation experiments). Incubation was stopped with 0.5 mL of formaldehyde (37%). Microbial cells were then filtered onto a cellulose nitrate filter (0.2 µm, Millipore, HA), which was rinsed twice using ice-cold trichloracetic acid (5%). Filters were transferred into scintillation vials, dissolved in ethylacetate (1 mL), and mixed with 8 mL scintillation cocktail (Ultima Gold, Canberra Packard). Samples were radio-assayed with a liquid scintillation counter (Canberra Packard Tricarb 2000) and bacterial carbon production calculated as described by Simon and Azam (1989).

2.6 Nutrients and dissolved organic carbon analyses

We sampled lake water at 3 sites along a transect corresponding to the estimated flow path from the GPL inflow to the outflow. At each site, lake water was profiled for chlorophyll *a* concentrations using a YSI probe (6929 V2). Further, we collected samples in the groundwater wells and from all three sites in the lake for the determination of $N\text{-}NH_4$, $N\text{-}NO_2$, $N\text{-}NO_3$, $P\text{-}PO_4$, dissolved organic carbon (DOC) concentration and bioavailable DOC (BDOC). Samples were collected into acid-rinsed polyethylene (PE) bottles that were kept cool and transferred to the lab within 4 hours. Groundwater and lake water samples were used for measurements of aromaticity of DOC ($SUVA_{254}$) at an excitation wavelength of 254 nm (Weishaar et al., 2003) and to estimate the source of DOC based on fluorescence (FI_{370}) at an excitation wavelength of 370 nm (McKnight et al., 2001).

2.7 Data analyses and statistics

In individual wells as well as averaged for a microplate, well color development in Biolog EcoPlates typically follows a sigmoidal curve, with a near-constant lag phase (time until onset of substrate use), a dynamic phase of maximum substrate use and a constant phase characterized by substrate exhaustion. We used a modified Gompertz model:

$$y = A * e^{-e^{\frac{\mu \max * e * (\lambda - t)}{A} + 1}} \quad (1),$$

which is a flexible type of a sigmoidal function where *μmax* is the maximum growth rate, λ is the lag and *A* is the maximum value for *y* (i.e., the well color) modelled as dependent from time *t* (Figure 1). Compared to the classic logistic function, the Gompertz function has a rapidly increasing rate until *μmax* is reached, then the rate decreases slowly when *y* asymptotically reaches *A*. This modified Gompertz model has been successfully used for Biolog well color development curves (Zwietering et al., 1990; Garland et al., 2001; Preston-Mafham et al., 2002).

We fitted the Gompertz model to average well color (AWC) development profiles for each plate and also to WC development profiles of each substrate (using individual data from the 3 replicate wells). Fitting was done on blank-corrected well data (AWC at time point 0 subtracted from all subsequent readings, and AWC from the control well subtracted for all scanning times) with a Levenberg-Marquardt algorithm for non-linear least-squares optimization, thus using the residual sum of squares between model and observed data as minimization fitting criterion. Parameter space was unconstrained during a first fitting run, then the medians of the three fitted parameters were computed for all substrates and plates and used as starting values in a second and final run. From the models fitted to the average well color (AWC) development profiles for each plate, we computed microplate-specific exact times $t_{AWC=0.75}$ for an AWC of 0.75. While $t_{AWC=0.75}$ differs among microplates, several microplates can be expected to have similar average states at these times, potentially freed from differences in growth response and inoculum density. These times t_x were then inserted into the substrate-specific model fits to predict "interpolated" well colors for each of the 31 substrates, which represent metabolic fingerprints or physiological profiles for the microbial communities of individual stones.

To test for significant differences of environmental and microbial variables between GPL inflow and outflow interfaces, we used Student t-tests comparing seasonal averages. We further analysed the effects of season, interface (inflow vs. outflow), lake and their interaction effect using factorial analysis of variance (ANOVA) for data of individual GPLs and data of all GPLs combined. Here we used individual replicates (stones) and treated season and interface as independent treatment factors followed by Fisher LSD *post hoc* pairwise comparisons. To efficiently describe physiological capacities of the microbial communities at the inflow and outflow interfaces of the GPLs we used Principle Component Analysis (PCA) on the metabolic fingerprint data given by interpolated well colors at $t_{AWC=0.75}$ and averaged for six functional substrate groups (Figure 3). PCA was based on a correlation matrix, as the involved variables were dimensionally homogeneous and we wished to keep absolute information on substrate use. Effects of biogeochemical parameters (nutrient concentrations, chl *a*, DOC, BDOC, $SUVA_{254}$, FI_{370}, BSP) on carbon substrate groups were studied based on multiple regression models, which were built based on Akaike's information criterion (AIC). Results for multiple regression models were limited to the 5 models yielding the lowest AIC scores and highest significance.

3 Results

3.1 Nutrients and dissolved organic carbon

We found a significant decrease in N-NO_3 concentrations in the GPL water from the inflowing groundwater to the outflow interface at all study GPLs (Suppl. Table 1). Due to strong seasonal variability P-PO_4 and N-NH4 concentrations only showed a significant decrease in GPL3 and GPL4, and in GPL1, respectively. In contrast, average DOC concentration was significantly elevated at the outflow compared to the groundwater inflow in all GPLs. In parallel, values of FI_{370} as well as of $SUVA_{254}$ were significantly lower at the outflow compared to the groundwater inflow, which indicates a shift in the source and aromaticity of DOC, respectively. BDOC was significantly higher in the GPL water than in the groundwater inflow of all five GPLs. BDOC increased up to 27 fold from the groundwater inflow to the outflow and was highest in GPL5, the oldest GPL of this study.

3.2. Microbial abundance and biomass

When averaged across seasons, microbial abundance did not differ between GPL inflow and outflow interfaces (Suppl. Table 2). Average benthic chlorophyll *a* was lowest at the inflow of GPL1 and highest at the inflow of GPL5. We found significantly lower benthic chlorophyll *a* at the outflow of GPL5 compared to its inflow. Average benthic AFDM was lowest at the inflow of GPL1 and highest at the inflow of GPL4. Overall, across all four seasons, AFDM did not differ between GPL inflow and outflow interfaces. Ratios of chlorophyll *a* / AFDM increased significantly at the outflow of GPL4 compared to the inflow and were highest at the inflow of GPL5. We found a significant positive relationship between P-PO_4 concentrations and benthic chlorophyll *a* at the inflow interface of the GPLs ($r^2 = 0.77$, $p < 0.05$, n=20).

3.3 Biofilm metabolism and bacterial secondary production

Averaged over all four seasons, we found lowest biofilm respiration (R) values at the inflow interfaces of GPL4 and highest values at the inflow interfaces of GPL3 (Figure 2A). Overall, biofilm R did not differ between GPL inflow and outflow interfaces. However we found a significant interaction between interfaces and season ($F = 4.05$, $p < 0.01$) and lake effect ($F = 23.85$, $p < 0.001$). We found lowest values of average biofilm net primary production (NPP) at the inflow interfaces of GPL4 and highest values at the outflow interfaces of GPL5. We did not find significant differences of biofilm NPP between inflow and outflow interfaces. However we found a significant seasonal effect ($F = 14.12$, $p < 0.001$) and interaction between interfaces and season ($F = 4.46$, $p < 0.01$). Bacterial secondary production (BSP) in the GPL water, ranging from 4.96 ± 3.78 mg C L^{-1} d^{-1} to 14.70 ± 7.24 mg C L^{-1} d^{-1}, was lowest in GPL2 and highest in GPL5.

3.4 Physiological profiling

Based on AWCD we found significant effects of season, interface (inflow vs. outflow), and their interaction on the apparent utilization patterns of several substrate groups (Suppl. Table 3). AWCD of substrate groups ranged from 0.17 for amines to 1.25 for polymers at the inflow *versus* 0.06 for phenolic compounds to 1.66 for amines at the outflow interfaces. In general we found that amines were the only substrate group that showed a significant difference in utilization between inflow and outflow interfaces when averaged over all seasons and lakes (One-way ANOVA, $F_{(1, 38)} = 9.11$, $p < 0.005$).

PCA depicted patterns of the physiological profiles of benthic biofilms across all GPLs at the level of functional groups. PCAs for inflow and outflow interfaces are shown to indicate clear separation between the single GPLs (Figure 3A, B).

Vector loadings of carboxylic acids and carbohydrates were highest for PC1 at the inflow explaining 47% and 32% of the variance in the physiological profiles, respectively; polymers explained 62% of the variance in PC2 (Figure 3A). In the outflow of all five GPLs, carbohydrates and phenolic compounds showed the highest vector loadings for PC1 explaining 32% and 25% of the variance, respectively. Polymers and carboxylic acids explained 41% and 35% of the variance in PC2, respectively (Figure 3B). Averaged over all seasons, polymer utilization was highest and explained most of the variance of the physiological profiles at both the inflow and outflow interfaces of all GPLs.

We built multiple regression models to explore whether chlorophyll *a*, nutrients, DOC and lake water BSP may affect substrate group utilization at the GPL outflow (Table 1). To do so, we included a variety of independent variables as predictive variables in the model and removed the less significant variables in a stepwise approach. Based on the indicative AIC score, we found amines, carboxylic acids, phenolic compounds and polymers to yield significant regression models. Carbohydrates and amino acids did not generate significant regression models based on AIC scores. Amines, for instance showed significant relationships ($p < 0.001$) with BSP, chlorophyll *a*, DOC and FI_{370}. Carboxylic acids yielded significant models related to nutrients (NO_3, NH_4, PO_4), DOC and BSP. Phenolic compounds were mainly related to chlorophyll *a*, DOC and NO_3. Polymers yielded models with the lowest significance ($p < 0.05$) compared to the other carbon substrate groups (Table 1).

We further explored the relationship between microbial respiration and substrate group utilization at the GPL outflow (Table 2). Based on the statistical prediction of the AIC score we found the 5 most significant models to yield p-values ranging from 0.005 to 0.01. However, amino acids were the only substrate group that did not generate significant results related to biofilm respiration. Carboxylic acids combined with amines resulted in the most significant model yielding the lowest AIC value. However, the second model including amines only, should be regarded as the most predictive one as the AIC score is only slightly higher and the p-value is in the same range. Hence we find that amines serve as a highly predictive covariate for explaining the relationship of carbon substrate group utilization with biofilm respiration at the outflow interfaces of the GPLs. This was also shown due to significantly higher amine utilization at the outflow compared to the inflow interfaces of the GPLs and a non-stepwise linear regression analysis with positive relationship between amine utilization and biofilm R at the outflow interfaces ($r^2 = 0.29$, $p < 0.05$, n=20). At the inflow interfaces of the GPLs we could not determine a positive relationship of amine utilization with biofilm R ($r^2 = 0.03$, $p = 0.53$, n=20). However, we found a significantly positive relationship between amine utilization at the outflow interfaces with chlorophyll *a* in the lake water ($r^2 = 0.51$, $p < 0.001$, n=20); this suggests *in situ* production of amines in the GPLs.

4. Discussion

Gravel pit lakes increasingly shape landscapes in areas where gravel deposits coincide with urbanization and industrial demand for mineral resources. It has been shown that GPLs can strip nutrients from inflowing groundwater and thereby even improve the quality of groundwater at recharging (outflowing) interfaces (Weilhartner et al., 2012; Muellegger et al., 2013). However, little is known on the potential processes that drive nutrient sequestration and carbon dynamics at the interfaces where most processing occurs (Weilhartner et al., 2012). Our findings illuminate such potential processes at the GPL inflow and outflow interfaces. We did not find any significant change in microbial metabolism and biomass between inflow and outflow interfaces obviously exposed to different solute environments. However, our results suggest differential patterns of substrate utilisation at these interfaces across five GPLs and four seasons. We therefore suggest that changes in nutrient and DOC quantity and/or quality may indirectly affect biofilm metabolic activity due to changes in carbon source utilisation.

Total benthic biomass (as AFDM), microbial cell abundance and chlorophyll *a* did not differ between inflow and outflow interfaces across the GPLs. Benthic biomass, measured in this study, is close to values reported from seepage lakes (Hagerthey and Kerfoot, 1998; Casco et al., 2009; Frandsen et al., 2012). These studies showed higher benthic algal biomass in zones with elevated groundwater seepage, likely due to increased phosphorous loads. Our results cannot confirm this finding based on an inflow vs. outflow comparison in individual GPLs (Suppl. Table 2). This approach, however, is not particularly powerful due to high seasonal variability and a low sample size. On the other hand, our results are consistent with the literature when looking at data across GPLs, as we found a significant relationship between benthic chlorophyll *a* and groundwater $P\text{-}PO_4$ at the inflow interfaces of the GPLs. In general, we observed low seasonal variability of nutrient concentrations in all GPLs except GPL2, where $P\text{-}PO_4$ concentrations in the inflowing groundwater increased 16 times from summer to autumn and winter. This increase in $P\text{-}PO_4$ concentrations may be attributable to fluxes from areas under agricultural use, which constitutes the main land use in the vicinity of these lakes (Muellegger et al., 2013). The rather constant flux of $N\text{-}NO_3$ and $P\text{-}PO_4$ supported biomass accrual and NPP in all GPLs (Weilhartner et al., 2012). We did not observe differences in total biofilm metabolism between inflow and outflow interfaces in the GPLs (Figure 2). This is unexpected given that groundwater fluxes of nutrients into the lakes influence benthic and pelagic algal and microbial biomass (Hayashi and Rosenberry, 2002; Schneider et al., 2005; Hunt et al., 2006). Although we found significant differences in biofilm respiration between lakes, there was no relationship to GPL age. Across all GPLs, DOC concentration was significantly higher in the GPL water than in the inflowing groundwater suggesting noticeable *in situ* production of organic compounds. The decrease of $SUVA_{254}$ and FI along that same flow path suggests a shift in DOC from a microbial source, also enriched in aromatic compounds, to the *in situ* production of DOC of lower aromaticity. In fact, groundwater DOC is largely derived from microbial and terrestrial sources (McKnight et al., 2001; Mladenov et al., 2005; Lapworth et al., 2008).

Because of apparent differences in DOC properties between inflow and outflow interfaces, we anticipated concurrent differences in benthic biofilm metabolism. However, our data failed to prove this assumption. Our findings from the Biolog EcoPlates suggest that microorganisms

in the biofilms had distinct metabolic responses potentially depending on community composition and the substrates prevailing at the inflow and outflow interfaces. Although carbon substrates in the Biolog EcoPlates represent common substrate conditions in aquatic ecosystems, utilization of single substrates within the Biolog EcoPlates may differ from natural conditions as a result of cell-interactions after inoculation in the wells (Preston-Mafham et al., 20002). Hence, comparisons of substrate group utilization patterns between interfaces were expressed at the level of functional groups rather than at the level of individual substrates. However, potential differences in community composition of biofilms at the inflow *versus* outflow interfaces may affect the generation of distinct physiological profiles. Hence, for comparison of different sampling sites and times in the GPLs it is crucial to pay attention to inoculum density and incubation time. However it was found that color development in the Biolog wells is correlated to the density of actively respiring cells rather than total cell density (Garland, 1996).
Differential use of amines between interfaces was most pronounced in GPL1, 2 and 5 with higher utilisation rates at the outflow than at the inflow interfaces. This pattern suggests that amines may originate from *in situ* production in the GPLs, a notion that remains speculative, however, as we did not measure amine concentration in the lake water. However we found a strong positive relationship of amine utilisation at the outflow interfaces with chlorophyll *a* in the GPL water. Average annual concentrations of chlorophyll *a* in the lake water were highest in GPL5, the oldest GPL in this study, and lowest in the younger GPLs 1 and 2 suggesting increasing amine utilisation at the outflow interfaces with increasing GPL age and lake eutrophication. Amines and their derivates, phenyl ethylamine and notably putrescine, are related to microbial growth (e.g., Patel et al., 2006), a relationship that is supported by a weak positive relationship between amine utilisation and biofilm respiration.

Our findings also suggest that phenolic compounds contributed to the observed substrate utilisation patterns. This suggests *in situ* production of phenolics in the GPLs or differences in community structure and function of the biofilms at both interfaces. The phenolics contained in the Biolog EcoPlates (2-hydroxy benzoic and 4-hydroxy benzoic acids) are generally known to inhibit microbial growth lowering the pH of microbial cells and causing disturbance of their metabolic functions (Eklund et al., 1985, Rauha et al., 2000). However, certain bacteria, such as *Pseudomonas putida,* can also use phenolics as carbon substrates (Ley and Schmidt, 2002).

Polymers in aquatic environments range from simple molecules to complex chains of molecules and are often exudates produced by a variety of aquatic organisms (Wotton, 2011). We found that the average seasonal utilisation of polymers was highest among all substrate groups underscoring their potential relevance for the microbial metabolism in the GPL biofilms. This is consistent with findings from Lyons and Dobbs (2012) showing elevated utilisation of polymers expressed as average substrate color development in attached and pelagic microbial communities. These authors suggested that attached microorganisms utilise a wider array of substrates than pelagic microorganisms and therefore had higher metabolism. Algae — abundant in the interfacial biofilms but also in the GPL water — can be major sources of polymers. For instance, green algae can excrete copious amounts of extracellular polymeric substances enhancing the growth of heterotrophic microorganisms (Domozych et al., 2005). Furthermore, it was found that certain lake microorganisms can degrade various polymers including Tween 80 or peptidoglycan (Jørgensen et al., 2010).
Our analyses also revealed carboxylic acids as potentially important substrates for the microbial heterotrophs in the interfacial biofilms. In lakes, carboxylic acids can result for instance from the photodegradation of high-molecular-weight compounds (Bertilsson and Travnik, 2000) and are readily utilised by microbial heterotrophs (Salcher et al., 2013).

To relate patterns of substrate utilisation to different environmental conditions at the GPL interfaces, we built multiple regression models. We found that DOC concentration and bioavailability, but also parameters potentially relating to its origin, such as chlorophyll *a,* FI and BSP contributed significantly to the models for the outflow interfaces. Amines, for instance, were exclusively associated with parameters describing carbon quantity and quality, whereas other substrates were also related to nutrients (Table 1). We suspect that enhanced utilisation of amines at the outflow interfaces is related to labile DOC from algal exudation. This assumption is in fact supported by observations that notably ammonia and its methylated derivatives (mono-, di- and trimethylamine) are end-products of the microbial turnover of organic matter. Methylamines in many cases result from enzymatic breakdown of algal precursors (e.g., choline, glycine) after zooplankton grazing or viral lysis of phytoplankton cells (Naqvi et al., 2005). Hence a positive relationship between GPL chlorophyll *a* and amine utilization at the outflow interfaces further supports our assumption of amines being produced in the GPLs. We suggest that groundwater derived nutrients enhance primary production in GPLs — and possibly also in natural seepage lakes — and that its breakdown contributes to increased DOC concentration and to a shift in its composition and bioavailability. The availability of this material at the outflow interfaces would ultimately shape the substrate utilisation patterns of the biofilms.

Biolog EcoPlates are now widely applied to unravel patterns of microbial resource use in aquatic ecosystems (e.g., Weber et al., 2007; Comte & Del Giorgio, 2010; Sala et al., 2010). However, this approach also has methodological limitations. For instance, it has been criticized that the implications of any single carbon substrate on the metabolism of a microbial community may be misleading, as single substrates are not representative for the complex mix of naturally occurring substrates (Howard, 1997; Preston-Mafham et al., 2002). We met this criticism by focusing our study on functional substrate groups rather than on the individual compounds as has been done by others (Leon et al., 2012; Dickerson and Williams, 2013).

5. Conclusion

In conclusion, our findings shed light on microbial processes that contribute to the capacity of GPLs to sequester nutrients from the inflowing groundwater and therefore to the water quality downstream of these man-made ecosystems. Groundwater-derived nutrients foster primary production in GPLs and upon degradation, algal cells fuel the DOC pool and contribute to its bioavailability. A shift in DOC composition and bioavailability has repercussions on the microbial community physiology at the outflow interfaces. The overall lacking relationship between resource use patterns (except for amines) and community respiration suggests a certain level of redundancy. Our findings also have consequences for the study of natural seepage lakes, which in several instances are comparable to man-made GPLs.

Acknowledgements

We are grateful for both Gertraud Stenicka and Christian Preiler for their assistance in the laboratory. Financial support was provided by the Provinces of Lower Austria, Upper Austria, and Styria, the Forum Mineralische Rohstoffe and the Federal Ministry of Agriculture, Forestry, Environment and Water Management.

References

1. Alley, W.M., Healy, R.W., LaBaugh, J.W., Reilly, T.E., 2002. Flow and storage in groundwater systems. Science 296(5575), 1985-1990.

2. Bartrons, M., Catalan, J., Casamayor, E., 2012. High bacterial diversity in epilithic biofilms of oligotrophic mountain lakes. Microbial Ecology 64(4), 860-869.

3. Battin, T.J., Kaplan, L.A., Newbold, J.D., Hansen, C.M.E., 2003. Contributions of microbial biofilms to ecosystem processes in stream mesocosms. Nature 426(6965), 439-442.

4. Bertilsson, S., Tranvik, L.J., 2000. Photochemical transformation of dissolved organic matter in lakes. Limnology and Oceanography 45(4), 753-762.

5. Casco, M.A., Mac Donagh, M.E., Cano, M.G., Solari, L.C., Claps, M.C., Gabellone, N.A., 2009. Phytoplankton and epipelon responses to clear and turbid phases in a seepage lake (Buenos Aires, Argentina). International Review of Hydrobiology 94(2), 153-168.

6. Comte, J., del Giorgio, P.A., 2009. Links between resources, C metabolism and the major components of bacterioplankton community structure across a range of freshwater ecosystems. Environmental Microbiology 11(7), 1704-1716.

7. Comte, J., del Giorgio, P.A., 2010. Linking the patterns of change in composition and function in bacterioplankton successions along environmental gradients. Ecology 91(5), 1466-1476.

8. Dickerson, T., Williams, H., 2013. Functional diversity of bacterioplankton in three North Florida freshwater lakes over an annual cycle. Microbial Ecology, 1-11.

9. Dittrich, M., Kurz, P., Wehrli, B., 2004. The role of autotrophic picocyanobacteria in calcite precipitation in an oligotrophic lake. Geomicrobiology Journal 21(1), 45-53.

10. Domozych, D.S., Kort, S., Benton, S., Yu, T., 2005. The extracellular polymeric substance of the green alga *Penium margaritaceum* and its role in biofilm formation. Biofilms 2, 129-144.

11. Downing, J.A., Cole, J.J., Middelburg, J.J., Striegl, R.G., Duarte, C.M., Kortelainen, P., Prairie, Y.T., Laube, K.A., 2008. Sediment organic carbon burial in agriculturally eutrophic impoundments over the last century. Global Biogeochemical Cycles 22, 1-10.

12. Dupraz, C., Reid, R.P., Braissant, O., Decho, A.W., Norman, R.S., Visscher, P.T., 2009. Processes of carbonate precipitation in modern microbial mats. Earth-Science Reviews 96(3), 141-162.

13. Eklund, T., 1985. Inhibition of microbial growth at different pH levels by benzoic and propionic acids and esters of p-hydroxybenzoic acid. International Journal of Food Microbiology 2(3), 159-167.

14. Frandsen, M., Nilsson, B., Engesgaard, P., Pedersen, O.L.E., 2012. Groundwater seepage stimulates the growth of aquatic macrophytes. Freshwater Biology 57(5), 907-921.

15. Garland, J.L., 1996. Analytical approaches to the characterization of samples of microbial communities using patterns of potential C source utilization. Soil Biology and Biochemistry 28(2), 213-221.

16. Garland, J.L., Mills, A.L., Young, J.S., 2001. Relative effectiveness of kinetic analysis vs single point readings for classifying environmental samples based on community-level physiological profiles (CLPP). Soil Biology and Biochemistry 33(7-8), 1059-1066.

17. Hagerthey, S.E., Kerfoot, W.C., 1998. Groundwater flow influences the biomass and nutrient ratios of epibenthic algae in a north temperate seepage lake. Limnology and Oceanography 43(6), 1227-1242.

18. Hall-Stoodley, L., Costerton, J.W., Stoodley, P., 2004. Bacterial biofilms: from the natural environment to infectious diseases. Nature Reviews Microbiology 2(2), 95-108.

19. Hauer, F.R., Lamberti, G.A., 2006. Methods in stream ecology (second edition), Academic Press.

20. Hayashi, M., Rosenberry, D.O., 2002. Effects of Ground Water Exchange on the Hydrology and Ecology of Surface Water. Ground Water 40(3), 309-316.

21. Howard, P.J.A., 1997. Analysis of data from BIOLOG plates: Comments on the method of Garland and Mills. Soil Biology and Biochemistry 29(11–12), 1755-1757.

22. Hunt, R.J., Strand, M., Walker, J.F., 2006. Measuring groundwater–surface water interaction and its effect on wetland stream benthic productivity, Trout Lake watershed, northern Wisconsin, USA. Journal of Hydrology 320(3–4), 370-384.

23. Jørgensen, N.O.G., Brandt, K.K., Nybroe, O., Hansen, M., 2010. Vogesella mureinivorans sp. nov., a peptidoglycan-degrading bacterium from lake water. International Journal of Systematic and Evolutionary Microbiology 60(10), 2467-2472.

24. Lapworth, D.J., Gooddy, D.C., Butcher, A.S., Morris, B.L., 2008. Tracing groundwater flow and sources of organic carbon in sandstone aquifers using fluorescence properties of dissolved organic matter (DOM). Applied Geochemistry 23(12), 3384-3390.

25. Leon, C., Campos, V., Urrutia, R., Mondaca, M.-A., 2012. Metabolic and molecular characterization of bacterial community associated to Patagonian Chilean oligotrophic-lakes of quaternary glacial origin. World Journal of Microbiology and Biotechnology 28(4), 1511-1521.

26. Ley, R.E., Schmidt, S.K., 2002. Fungal and bacterial responses to phenolic compounds and amino acids in high altitude barren soils. Soil Biology and Biochemistry 34(7), 989-995.

27. Lyons, M.M., Dobbs, F.C., 2012. Differential utilization of carbon substrates by aggregate-associated and water-associated heterotrophic bacterial communities. Hydrobiologia 686(1), 181-193.

28. McKnight, D.M., Boyer, E.W., Westernhoff, P.K., Doran, P.T., Kulbe, T., Andersen, D.T., 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. Limnology and Oceanography 46(1), 38-48.

29. Mladenov, N., McKnight, D., Wolski, P., Ramberg, L., 2005. Effects of annual flooding on dissolved organic carbon dynamics within a pristine wetland, the Okavango Delta, Botswana. Wetlands 25(3), 622-638.

30. Muellegger, C., Weilhartner, A., Battin, T.J., Hofmann, T., 2013. Positive and negative impacts of five Austrian gravel pit lakes on groundwater quality. Science of the Total Environment 443, 14-23.

31. Naqvi, S.W.A., Bange, H.W., Gibb, S.W., Goyet, C., Hatton, A.D., Upstill-Goddard, R.C., 2005. Biogeochemical ocean-atmosphere transfers in the Arabian Sea. Progress in Oceanography 65(2–4), 116-144.

32. Patel, C.N., Wortham, B.W., Lines, J.L., Fetherston, J.D., Perry, R.D., Oliveira, M.A., 2006. Polyamines are essential for the formation of plague biofilm. Journal of Bacteriology 188(7), 2355-2363.

33. Plée, K., Pacton, M., Ariztegui, D., 2010. Discriminating the role of photosynthetic and heterotrophic microbes triggering low-Mg calcite precipitation in freshwater biofilms (Lake Geneva, Switzerland). Geomicrobiology Journal 27(5), 391-399.

34. Preston-Mafham, J., Boddy, L., Randerson, P.F., 2002. Analysis of microbial community functional diversity using sole-carbon-source utilisation profiles – a critique. FEMS Microbiology Ecology 42(1), 1-14.

35. Rauha, J.-P., Remes, S., Heinonen, M., Hopia, A., Kähkönen, M., Kujala, T., Pihlaja, K., Vuorela, H., Vuorela, P., 2000. Antimicrobial effects of Finnish plant extracts containing flavonoids and other phenolic compounds. International Journal of Food Microbiology 56(1), 3-12.

36. Riding, R., 2000. Microbial carbonates: the geological record of calcified bacterial–algal mats and biofilms. Sedimentology 47, 179-214.

37. Sala, M., Arrieta, J., Boras, J., Duarte, C., Vaqué, D., 2010. The impact of ice melting on bacterioplankton in the Arctic Ocean. Polar Biology 33(12), 1683-1694.

38. Salcher, M.M., Posch, T., Pernthaler, J., 2013. In situ substrate preferences of abundant bacterioplankton populations in a prealpine freshwater lake. The ISME Journal 7(5), 896-907.

39. Schneider, R.L., Negley, T.L., Wafer, C., 2005. Factors influencing groundwater seepage in a large, mesotrophic lake in New York. Journal of Hydrology 310(1–4), 1-16.

40. Simon, M., Azam, F., 1989. Protein content and protein synthesis rates of planktonic marine bacteria. Marine Ecology Progress Series 51, 201-213.

41. Smith, E.M., Prairie, Y.T., 2004. Bacterial metabolism and growth efficiency in lakes: The importance of phosphorus availability. Limnology and Oceanography 49(1), 137-147.

42. Tam, L., Kevan, P.G., Trevors, J.T., 2003. Viable bacterial biomass and functional diversity in fresh and marine waters in the Canadian Arctic. Polar Biology 26(5), 287-294.

43. Vadeboncoeur, Y., Peterson, G., Vander Zanden, M.J., Kalff, J., 2008. Benthic algal production across lake size gradients: interactions among morphometry, nutrients and light. Ecology 89(9), 2542-2552.

44. Weber, K.P., Gehder, M., Legge, R.L., 2008. Assessment of changes in the microbial community of constructed wetland mesocosms in response to acid mine drainage exposure. Water Research 42(1–2), 180-188.

45. Weilhartner, A., Muellegger, C., Kainz, M., Mathieu, F., Hofmann, T., Battin, T.J., 2012. Gravel pit lake ecosystems reduce nitrate and phosphate concentrations in the outflowing groundwater. Science of the Total Environment 420, 222-228.

46. Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R., Mopper, K., 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environmental Science and Technology 37, 4702-4708.

47. Wotton, R.S., 2011. EPS (Extracellular Polymeric Substances), silk, and chitin: vitally important exudates in aquatic ecosystems. Journal of the North American Benthological Society 30(3), 762-769.

48. Zwietering, M.H., Jongenburger, I., Rombouts, F.M., van 't Riet, K., 1990. Modeling of the bacterial growth curve. Applied and Environmental Microbiology 56(6), 1875-1881.

Table 1 Multiple regression models for carbon substrate groups amines, carboxylic acids, phenolic compounds and polymers based on AIC scores. Carbohydrates and amino acids did not yield significant regression models hence were not included in the table. BSP = bacterial secondary production [µg C L^{-1} d^{-1}], chl *a* = pelagic chlorophyll *a* concentrations [µg L^{-1}], $SUVA_{254}$ = specific UV absorbance in the GPL water (measured photometrically at 254 nm wavelength), FI_{370} = fluorescence index of the GPL water (measured fluorometrically at 370 nm excitation wavelength).

Rank	Amines Model Covariates						F	AIC	Chi²	p
1	chl *a*	DOC					2	-21.82	16.29	< 0.001
2	chl *a*	DOC	FI_{370}				3	-21.55	18.02	< 0.001
3	chl *a*						1	-21.45	13.92	< 0.001
4	BSP	chl *a*	DOC	FI_{370}			4	-20.77	19.23	< 0.001
5	BSP	chl *a*	DOC				3	-20.26	16.73	< 0.001
	Carboxylic Acids Model Covariates									
1	BSP	BDOC	PO_4	NO_3	NH_4		5	-49.08	21.18	< 0.001
2	BSP	DOC	BDOC	PO_4	NO_3		5	-48.36	20.46	< 0.005
3	BSP	PO_4	NO_3	NH_4			4	-48.25	18.36	< 0.005
4	BSP	BDOC	PO_4	NO_3	NH_4	FI_{370}	6	-47.78	21.88	< 0.005
5	BSP	DOC	BDOC	PO_4	NO_3	NH_4	6	-47.56	21.66	< 0.005
	Phenolic Compounds Model Covariates									
1	chl *a*	DOC					2	-39.29	12.10	< 0.005
2	chl *a*	NO_3					2	-39.13	11.94	< 0.005
3	chl *a*						1	-39.11	9.92	< 0.005
4	chl *a*	DOC	NO_3				3	-39.03	13.85	< 0.005
5	chl *a*	DOC	FI_{370}				3	-38.52	13.33	< 0.005
	Polymers Model Covariates									
1	NH_4	$SUVA_{254}$					2	-22.57	8.83	< 0.05
2	chl *a*	NH_4	$SUVA_{254}$				3	-21.75	10.00	< 0.05
3	$SUVA_{254}$						1	-21.53	5.79	< 0.05
4	DOC	$SUVA_{254}$					2	-21.29	7.55	< 0.05
5	chl *a*	$SUVA_{254}$					2	-21.21	7.47	< 0.05

Table 2 Multiple regression models for biofilm respiration at the outflow interfaces based on AIC scores.

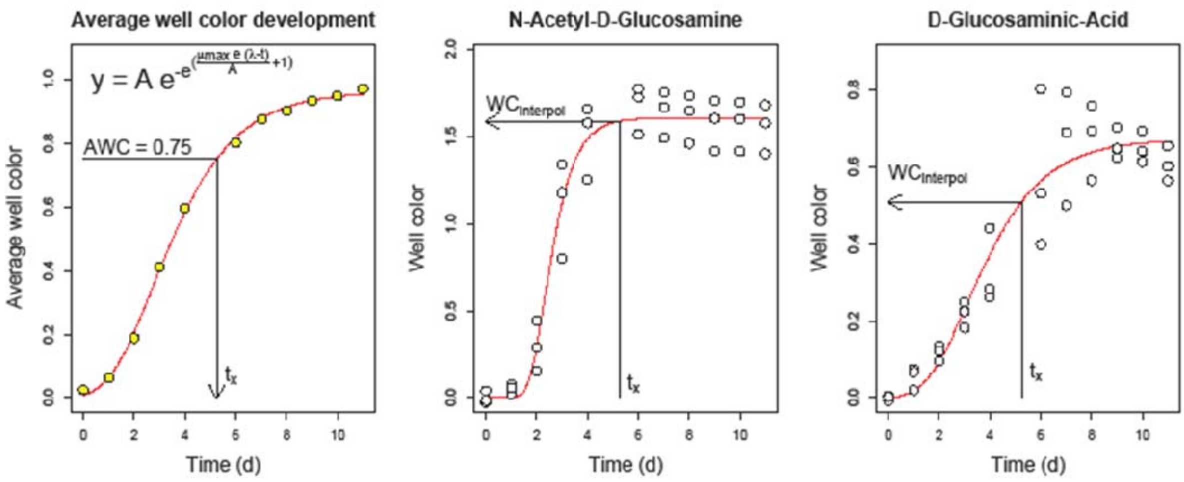
Rank	Biofilm Respiration Outflow Interface Model Covariates				F	AIC	Chi^2	p
1	Carboxylic acids	Amines			2	209.61	11.78	< 0.005
2	Amines				1	210.38	9.01	< 0.005
3	Carboxylic acids	Amines	chl *a*		3	210.79	12.60	< 0.01
4	Carboxylic acids	Amines	Phenolic compounds		3	211.03	12.36	< 0.01
5	Polymers	Carbohydrates	Amines	chl *a*	4	211.14	14.25	< 0.01

Figure legends

Figure 1 Substrate group utilisation curves described by sigmoidal Gompertz model. Graphs show fast and slow utilization curves for two distinct substrates, N-Acetyl-D-Glucosamine and D-Glucosaminic-Acid, respectively.

Figure 2A, B Respiration and net primary production of biofilm communities at the inflow and outflow interfaces of GPL 1-5 (n=6). Standard error of the mean (SEM) was used for representation of variation. Statistics are based on factorial analysis of variance (ANOVA, n=48).

Figure 3A, B Substrate group utilisation at the inflow (A) and outflow (B) interfaces of GPL 1-5 during all seasons. Vectors show the factor loadings of each substrate group, explaining variations in PC1 and PC2. Distances between symbols of each GPL show the average variance between the seasons. For better graphical representation, we decided to not differentiate between seasons.



Average well color development
$y = A\, e^{-e^{\left(\frac{\mu max\, e\, (\lambda - t)}{A} + 1\right)}}$
AWC = 0.75
t_x
Average well color
Time (d)
N-Acetyl-D-Glucosamine
$WC_{Interpol}$
t_x
Well color
Time (d)
D-Glucosaminic-Acid
$WC_{Interpol}$
t_x
Well color
Time (d)

Figure 1

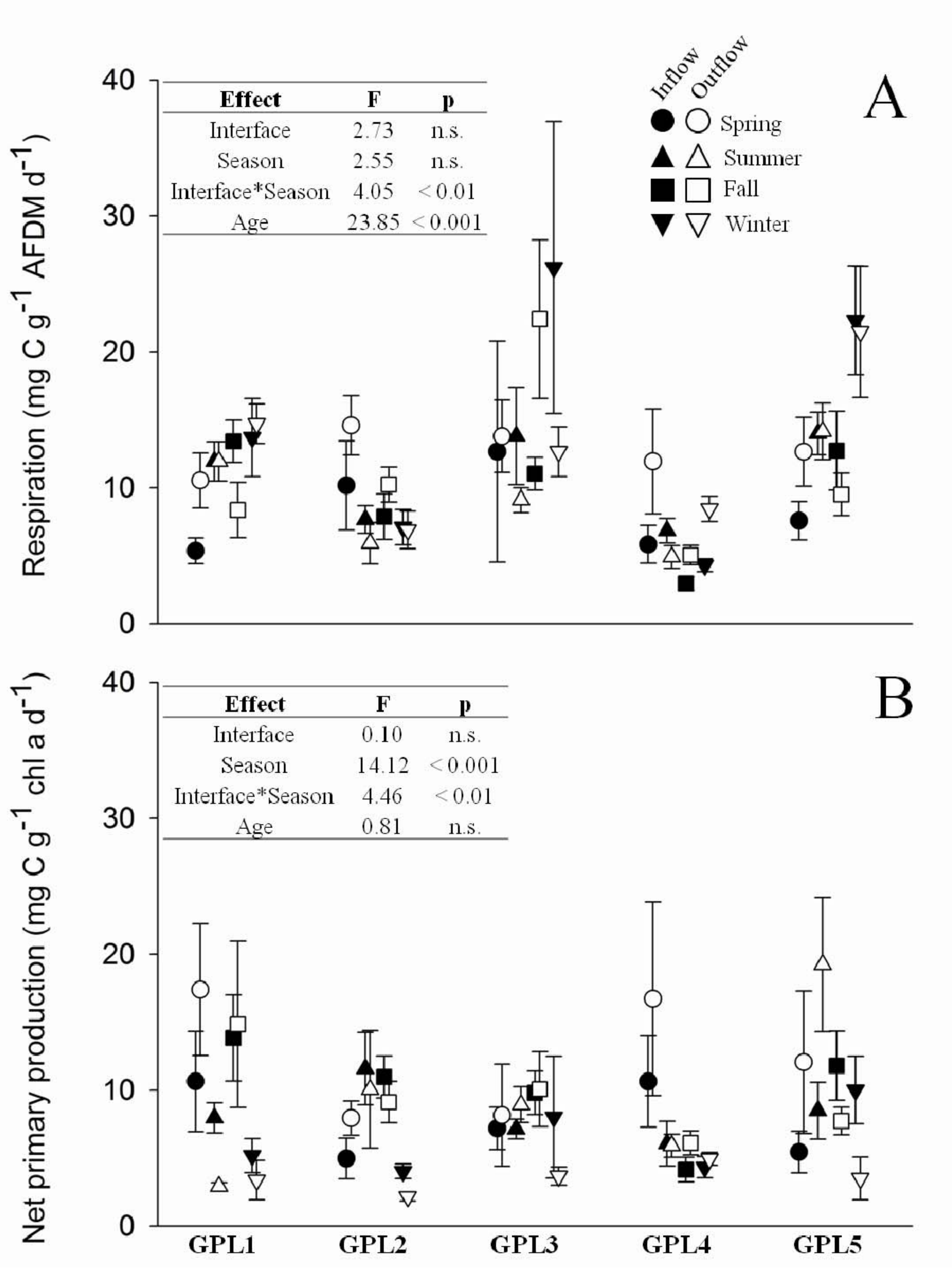

A
Effect F p
Interface 2.73 n.s.
Season 2.55 n.s.
Interface*Season 4.05 < 0.01
Age 23.85 < 0.001
Inflow
Outflow
Spring
Summer
Fall
Winter
Respiration (mg C g-1 AFDM d-1)
B
Effect F p
Interface 0.10 n.s.
Season 14.12 < 0.001
Interface*Season 4.46 < 0.01
Age 0.81 n.s.
Net primary production (mg C g-1 chl a d-1)
0
10
20
30
40
GPL1
GPL2
GPL3
GPL4
GPL5

Figure 2

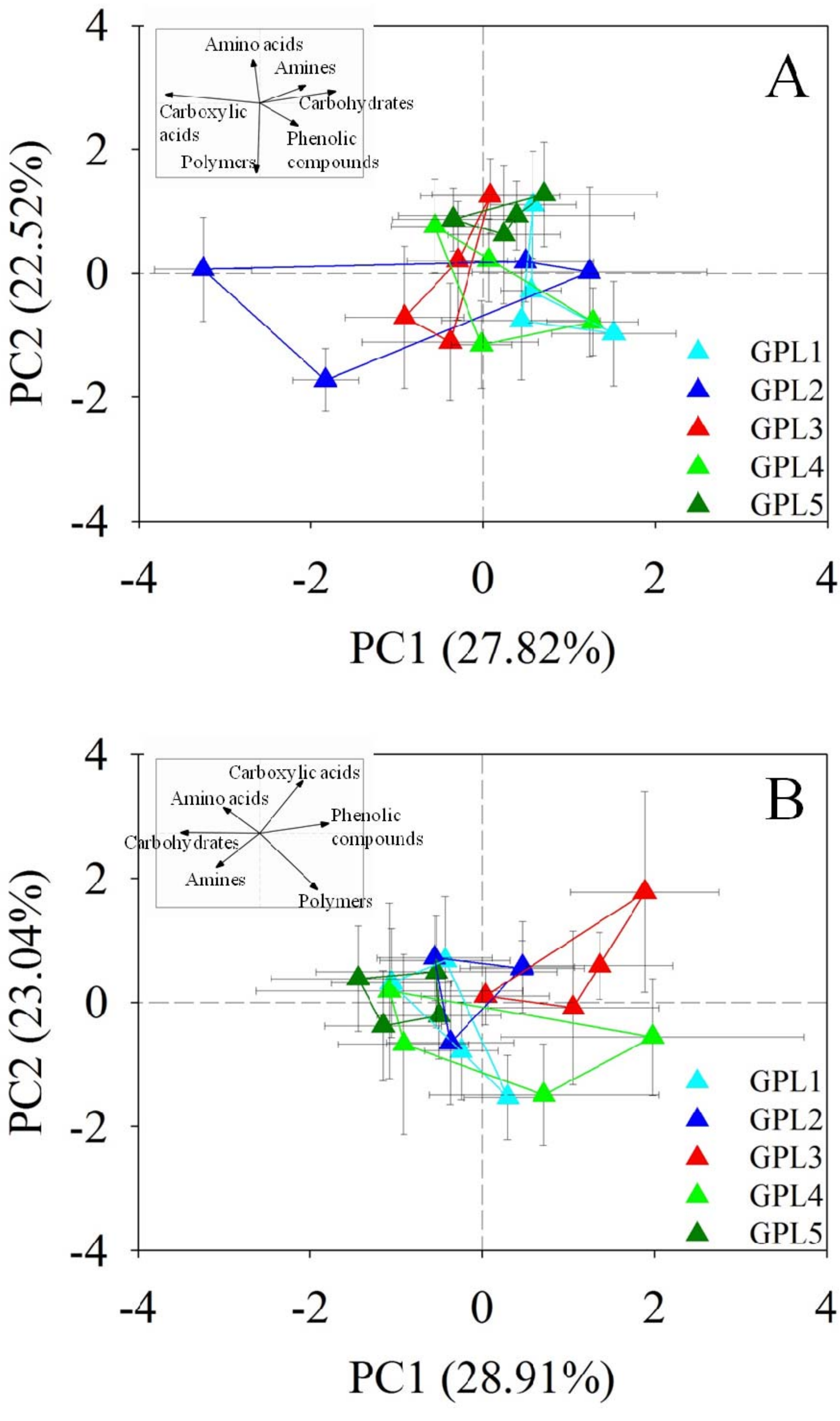

A
Amino acids
Amines
Carbohydrates
Carboxylic acids
Phenolic compounds
Polymers
GPL1
GPL2
GPL3
GPL4
GPL5
PC2 (22.52%)
PC1 (27.82%)
B
Carboxylic acids
Amino acids
Phenolic compounds
Carbohydrates
Amines
Polymers
GPL1
GPL2
GPL3
GPL4
GPL5
PC2 (23.04%)
PC1 (28.91%)

Figure 3

Supplementary tables

Supplementary table 1 Nutrient concentrations and organic carbon parameters in the inflowing groundwater and outflowing lake water of GPL 1-5 (averaged over four seasons ± SD, n=4). Significant differences between inflow and outflow are based on t-test analysis. N-NO_2 concentrations in the groundwater inflow were below detection limit hence could not be determined (n.d.).

Lake	Inflow	Outflow	t	p
		N-NH_4 (mg L^{-1})		
GPL1	0.02 ± 0.02	0.13 ± 0.08	-2.57	n.s.
GPL2	0.01 ± 0.01	0.03 ± 0.02	-1.58	n.s.
GPL3	0.03 ± 0.03	0.05 ± 0.06	-0.71	n.s.
GPL4	0.02 ± 0.01	0.08 ± 0.06	-1.85	n.s.
GPL5	0.01 ± 0.02	0.06 ± 0.04	-1.99	n.s.
		N-NO_2 (mg L^{-1})		
GPL1	n.d.	0.10 ± 0.05		
GPL2	n.d.	0.03 ± 0.02		
GPL3	n.d.	0.05 ± 0.06		
GPL4	n.d.	0.05 ± 0.05		
GPL5	n.d.	0.03 ± 0.03		
		N-NO_3 (mg L^{-1})		
GPL1	7.95 ± 0.86	1.57 ± 0.24	14.23	<0.001
GPL2	4.24 ± 0.91	0.08 ± 0.08	9.08	<0.001
GPL3	11.10 ± 2.09	3.36 ± 0.68	7.03	<0.001
GPL4	5.25 ± 1.64	0.72 ± 0.28	5.45	<0.001
GPL5	6.73 ± 1.15	3.18 ± 0.44	5.77	<0.001
		P-PO_4 (µg L^{-1})		
GPL1	3.43 ± 0.92	1.29 ± 1.26	2.38	n.s.
GPL2	34.43 ± 27.31	1.74 ± 0.44	2.07	n.s.
GPL3	11.67 ± 0.55	2.13 ± 1.67	9.42	<0.001
GPL4	4.40 ± 2.86	0.66 ± 0.82	2.18	n.s.
GPL5	90.53 ± 3.25	1.10 ± 1.47	43.37	<0.001
		DOC (mg L^{-1})		
GPL1	0.88 ± 0.06	3.00 ± 0.25	-16.36	<0.001
GPL2	0.94 ± 0.10	1.95 ± 0.19	-9.42	<0.001
GPL3	0.80 ± 0.21	2.18 ± 0.48	-5.28	<0.001
GPL4	0.43 ± 0.07	2.71 ± 0.29	-15.29	<0.001
GPL5	1.00 ± 0.09	2.41 ± 0.59	-4.72	<0.001
		BDOC (mg L^{-1})		
GPL1	0.03 ± 0.02	0.28 ± 0.22	-2.25	n.s.
GPL2	0.04 ± 0.05	0.29 ± 0.37	-1.32	n.s.
GPL3	0.02 ± 0.01	0.15 ± 0.10	-2.43	n.s.
GPL4	0.01 ± 0.01	0.27 ± 0.14	-3.67	<0.05
GPL5	0.02 ± 0.01	0.33 ± 0.20	-3.09	<0.05
		FI_{370}		
GPL1	2.24 ± 0.05	1.98 ± 0.06	7.40	<0.001

GPL2	2.15 ± 0.04	1.86 ± 0.01	14.83	<0.001
GPL3	2.22 ± 0.07	1.95 ± 0.03	7.47	<0.001
GPL4	2.14 ± 0.06	1.90 ± 0.04	7.36	<0.001
GPL5	2.06 ± 0.09	1.95 ± 0.03	2.42	n.s.
	$SUVA_{254}$			
GPL1	7.80 ± 0.64	3.30 ± 0.31	12.86	<0.001
GPL2	7.62 ± 0.37	4.82 ± 0.35	10.97	<0.001
GPL3	9.05 ± 1.15	4.44 ± 0.76	6.65	<0.001
GPL4	8.33 ± 1.89	3.12 ± 0.35	5.41	<0.001
GPL5	11.22 ± 0.52	6.46 ± 0.65	11.43	<0.001

Supplementary table 2 Microbial abundance, benthic chlorophyll *a*, ash-free dry mass and ratio chlorophyll *a* / ash-free dry mass of biofilm communities at the inflow and outflow interfaces of GPL 1-5 (averaged over four seasons ± SD, n=6). Significant differences between interfaces are based on t-test analysis.

Lake	Inflow	Outflow	t	p
Microbial abundance (x 10^7 cells cm^{-2})				
GPL1	0.37 ± 0.15	0.71 ± 0.37	-1.66	n.s.
GPL2	2.16 ± 1.62	1.72 ± 0.60	0.51	n.s.
GPL3	0.96 ± 0.41	0.96 ± 0.45	-0.02	n.s.
GPL4	2.36 ± 0.70	3.09 ± 2.19	-0.63	n.s.
GPL5	3.86 ± 0.93	3.19 ± 1.42	0.79	n.s.
Benthic chl a (mg m^{-2})				
GPL1	20.86 ± 11.27	65.66 ± 80.83	-1.10	n.s.
GPL2	79.24 ± 46.51	66.57 ± 41.57	0.41	n.s.
GPL3	58.16 ± 14.09	51.56 ± 29.59	0.40	n.s.
GPL4	59.46 ± 15.77	69.09 ± 18.20	-0.80	n.s.
GPL5	108.49 ± 25.48	61.92 ± 14.82	3.16	<0.05
AFDM (g m^{-2})				
GPL1	8.96 ± 3.81	16.98 ± 2.53	-1.32	n.s.
GPL2	28.96 ± 8.74	23.02 ± 6.75	0.88	n.s.
GPL3	12.40 ± 2.11	13.65 ± 6.22	-0.50	n.s.
GPL4	37.29 ± 14.87	23.54 ± 2.86	1.71	n.s.
GPL5	18.44 ± 9.16	17.40 ± 4.06	0.21	n.s.
Ratio chl *a* / AFDM				
GPL1	2.33 ± 1.53	3.87 ± 1.85	-0.52	n.s.
GPL2	2.74 ± 1.31	2.89 ± 0.84	-0.09	n.s.
GPL3	4.69 ± 0.36	3.78 ± 1.24	1.40	n.s.
GPL4	1.59 ± 0.24	2.93 ± 0.29	-6.93	<0.001
GPL5	5.88 ± 3.00	3.56 ± 0.88	2.01	n.s.

Supplementary table 3 Effects of season (spring, summer, fall, winter), interface (inflow, outflow) and the combined effects of both on substrate group utilization at the inflow and outflow interfaces of gravel 1-5 (n=48). Asterisks indicate significant differences of ANOVA results (* = p < 0.05, ** = p < 0.01, *** = p < 0.001).

Carbon source	**Effect**	**GPL1** (F, p)	**GPL2** (F, p)	**GPL3** (F, p)	**GPL4** (F, p)	**GPL5** (F, p)
Polymers	Season	F = 15.85***	F = 2.88*	F = 5.16**	F = 0.48	F = 4.62**
	In-Out	F = 0.16	F = 3.41	F = 0.31	F = 6.67*	F = 0.00
	Season + In-Out	F = 3.79*	F = 3.38*	F = 1.49	F = 14.91***	F = 1.17
Carbohydrates	Season	F = 5.07**	F = 12.81***	F = 2.05	F = 1.11	F = 2.00
	In-Out	F = 1.77	F = 0.32	F = 6.53*	F = 9.79**	F = 5.40*
	Season + In-Out	F = 10.13***	F = 6.72***	F = 1.93	F = 3.62*	F = 1.52
Carboxylic acids	Season	F = 4.15*	F = 39.83***	F = 3.69*	F = 5.97**	F = 11.99***
	In-Out	F = 0.75	F = 10.54**	F = 2.25	F = 1.19	F = 0.04
	Season + In-Out	F = 3.74*	F = 20.95***	F = 5.64**	F = 1.93	F = 6.25**
Amino acids	Season	F = 1.97	F = 8.40***	F = 0.44	F = 2.71	F = 3.00*
	In-Out	F = 0.05	F = 0.39	F = 0.01	F = 1.75	F = 0.73
	Season + In-Out	F = 6.55***	F = 1.04	F = 0.36	F = 5.91**	F = 1.39
Amines	Season	F = 1.67	F = 10.55***	F = 3.16*	F = 2.95*	F = 4.38**
	In-Out	F = 8.68**	F = 35.81***	F = 0.27	F = 5.21*	F = 20.82***
	Season + In-Out	F = 8.70***	F = 1.30	F = 1.54	F = 1.71	F = 2.48
Phenolic compounds	Season	F = 3.80*	F = 0.32	F = 2.30	F = 1.27	F = 2.04
	In-Out	F = 2.85	F = 1.52	F = 17.64***	F = 1.52	F = 0.07
	Season + In-Out	F = 0.61	F = 1.82	F = 0.64	F = 5.58**	F = 2.48

English Abstract

Biogeochemistry and biofilms in gravel pit lakes and effects on the outflowing groundwater quality

Sand and gravel are essential natural resources obtained through various dredging methods but mainly by wet dredging from a groundwater aquifer. Many industries depend on the continuous supply of this non-mineral natural resource for applications such as concrete for housing, sewage facilities, water dams and channels but also ceramic elements for dental practices.

After excavation of the resource, an open water aquifer connects the inflowing groundwater to the atmosphere. Due to exposure of the aquifer to the atmosphere, many biogeochemical as well as anthropogenic effects occur, potentially affecting effluent ground water quality.

However, many gravel pit lakes are close to or within water protection areas that serve for drinking water supply. Hence government authorities see potential threats of gravel pit lakes on the effluent groundwater quality. This study estimated potential effects of gravel pit lakes on the effluent groundwater, measuring nutrient and dissolved organic carbon dynamics in the lake water and groundwater as well as biofilm metabolism at the sedimentary interfaces of the lakes.

The aim of this study was to investigate effects of post-excavation gravel pit lakes (GPLs) on the long-term development of groundwater quality in the effluent areas of the lakes as well as understand key processes involved in shaping this diverse man-made ecosystem. We built models describing nutrient and DOC dynamics using a mass balance approach and further estimated effects of organic contaminants on the groundwater quality via a literature survey of scientific publications.

Deutschsprachige Kurzzusammenfassung

Biogeochemische Prozesse und Biofilme in Baggerseen und deren Auswirkungen auf die abstromige Grundwasserqualität

Sande und Kiese sind unverzichtbare Rohstoffe. Diese werden vorwiegend durch Trocken- und Nassbaggerungen gewonnen. Bei Nassbaggerungen erfolgt ein Eingriff in das Grundwasser, welcher die Wasserqualität in Hinsicht auf biologische, organische und anorganische Parameter verändert. Die Auswirkungen können positiv oder negativ für die Wasserbeschaffenheit sein. Das öffentliche Interesse am Schutz des Grundwassers, im Besonderen für den Schutz der Trinkwasserversorgung, kann in einen Nutzungskonflikt mit dem Interesse, diesen Rohstoff ressourcenschonend durch Nassbaggerungen abzubauen, stehen.

Ziel der Studie war die Untersuchung der Auswirkungen von Nassbaggerungen auf die langfristige Entwicklung der abstromigen Grundwasserqualität, insbesondere welche Stoffe über die Atmosphäre, als Interaktion mit dem Grundwasser an den Unterwasserböschungen der Nassbaggerungen und über die Sohle/das Sediment eingetragen und ausgetragen werden. Des Weiteren wurde untersucht, welche Stoffumsätze im Baggersee selbst zu erwarten sind und anhand von eigenen Messungen und Literaturdaten evaluiert, welche Einflüsse Nassbaggerungen auf die Grundwasserqualität haben. Eine Abschätzung des Verhaltens ausgewählter organischer Schadstoffe wurde auf Basis einer Literaturauswertung vorgenommen.

Curriculum Vitae

Mag. Andreas WEILHARTNER

EDUCATION

2008 – 2014:	PhD in Biology - Ecology with focus on the biogeochemistry and microbial ecology of gravel pit lakes, Department of Limnology, University of Vienna
2007 – 2008:	Diploma thesis with research focus on the toxic effects of nanostructured titanium dioxide (TiO_2) on aquatic microbial biofilms at the University of Vienna and the WasserCluster Lunz – Biologische Station GmbH
2004 – 2005:	ERASMUS Exchange Program at the Universidad Autónoma de Madrid, Spain
2001 – 2008:	Study of Biology/Ecology at the University of Vienna
1996 – 2000:	High school diploma at the Adalbert Stifter Realgynasium, Linz
1991 – 1996:	Realgymnasium Aloisianum, Linz / Hauptschule Leonding
1987 – 1991:	Elementary school, Linz