Eberhard Karls Universität Tübingen

Mathematisch-Naturwissenschaftliche Fakultät

Fachbereich Geowissenschaften

Fachbereich Biologie

Master Thesis

in

Geoecology (M.Sc.)

Water quality and sustainability of the water retention landscape at Tamera ecovillage, south Portugal

Sarah Daum

Supervisors:

Prof. Dr. Stefan Haderlein

Prof. Dr. Heinz-R. Köhler

Dr. Christine Laskov

Tübingen, January 22, 2014

Declaration of originality

I hereby declare that this thesis and the work reported herein was composed by and originated entirely from me. Information derived from the work of others has been acknowledged in the text and references are given in the list of sources. Persons who substantially supported me in my work are listed in the acknowledgements. This work has not been previously or concurrently used in parts or as a whole within other exam processes.

Tübingen, January 22, 2014

Sarah Daum

Abstract

Fresh water supply is a major challenge to agriculture in semi-arid zones and deep groundwater pumping for irrigation is applied widely in such regions to span droughts. But climate change and overexploitation of groundwater reservoirs foster instability and qualitative degradation of aquifers, thus adaptation measures to increasing water scarcity such as the construction of fresh water reservoirs from surface runoff were applied during the last decades. Small scale retention basins seem to be ecologically more appropriate in comparison to large dam systems, as construction of large dams causes deforestation and harmful impacts on wildlife. In this context, a water retention landscape with various small artificial lakes was constructed on the area of Tamera ecovillage in south Portugal to enable agricultural irrigation and land regeneration. Additionally, water supply of the village is fed by bank filtrate from one of the artificial lakes. To evaluate water quality and sustainability of the water retention landscape, biogeochemical and hydrological analyses were conducted mainly in the time between November 2012 and April 2013. Isotope analysis of δ ^{18}O and δ ^{2}H values from ground- and surface waters of the study area in conjunction with chloride concentrations and conductivity values were used to investigate interactions between ground- and surface waters. Great seasonal variations of ground- and surface water quality were observed. Although most lakes were observed to be in eutrophic states, the obtained samples from the water supply system did not exceed EU thresholds for drinking water. The artificial lakes were observed to contribute to groundwater recharge, but to conclude for long term trends further monitoring is needed. Therefore suggestions for such monitoring had been made, as the water retention landscape could serve as model project for agricultural regeneration of semi-arid regions.

Zusammenfassung

In semiariden Klimazonen limitiert der Zugang zu Süßwasser die landwirtschaftliche Produktion, weshalb Grundwasser zur Bewässerung in diesen Regionen oft aus großen Tiefen gefördert wird, um Trockenheitsperioden zu überbrücken. Doch Klimawandel und Übernutzung der Aquifere gefährden Qualität und Stabilität der Grundwasserreservoirs, weshalb als Anpassungsmaßnahme an zunehmende Wasserverknappung während der letzten Jahrzehnte Wasserspeicher für Oberflächenabfluss errichtet wurden. Dabei scheinen kleine Wasserreservoirs ökologisch sinnvoller zu sein, da der Bau großer Talsperren Abholzung und Habitatverluste von Wildtieren mit sich zieht. In diesem Zusammenhang wurde eine Wasserretentionslandschaft mit verschiedenen kleinen künstlichen Seen auf dem Gelände des Ökodorfes Tamera in Südportugal angelegt. Dies sollte die Bewässerung von landwirtschaftlichen Flächen sowie eine allgemeine Regeneration der Landschaft ermöglichen. Zudem wird die Trinkwasserversorgung des Dorfs aus Uferfiltrat von einem der künstlichen Seen gespeist. Um Wasserqualität und Nachhaltigkeit der Wasserretentionslandschaft zu evaluieren, wurden im Rahmen dieser Studie biogeochemische und hydrogeologische Messungen hauptsächlich zwischen November 2012 und April 2013 durchgeführt. $\delta\,^{18}O$- und $\delta\,^{2}H$-Werte wurden zusammen mit Chloridkonzentrationen und Leitfähigkeiten der Grund- und Oberflächengewässer auf dem Gelände für die Erforschung von Wechselwirkungen zwischen Grund- und Oberflächengewässern verwendet. Es wurden große saisonale Schwankungen in der Qualität von Grund- und Oberflächengewässern beobachtet. Auch wenn der Großteil der Seen als eutroph eingestuft wurde, lagen die gemessenen Ionenkonzentrationen der Trinkwasserproben unterhalb der EU-Grenzwerte für Trinkwasser. Außerdem wurde aufgezeigt, dass die Seen zur Grundwasserneubildung beitragen, aber um Rückschlüsse auf längerfristige Auswirkungen der Seen auf das Grundwasser ziehen zu können sind weitere Studien nötig. Dazu wurden Methoden für ein längerfristiges Monitoring vorgeschlagen, welches auch im Hinblick auf die Modellfunktion der Wasserretentionslandschaft für die landwirtschaftliche Regeneration semiarider Gebiete interessant ist.

Table of contents

List of figures

List of tables

Abbreviations

cf.	compare
ch.	chapter
cm	centimeter
e.g.	for example
fig.	figure
g	grams
km	kilometers
l	liters
m	meters
mamsl	meters above means sea level
mbgl	meters below ground level
mg	milligrams
µg	micrograms
ml	milliliters
mm	millimeters
µS	microsiemens
n.d.	no data
VISMOV	Vienna Standard Mean Ocean Water
GISP	Greenland Ice Sheet Precipitation
SLAP	Standard Light Antarctic Precipitation

1. Introduction

Water is a critical natural resource and its availability affects social, economic and ecological sustainability. For humans and ecosystems water quality is as important as water quantity (UNESCO 2012).

Many ecosystem services are derived directly from water and agricultural activities especially in semi-arid and arid climate zones depend on the availability of fresh water (UNESCO 2012).

The use of solely groundwater or in conjunction with surface water is of vital importance in these zones in order to alleviate the effects of drought. But aquifer recharge in semi-arid and arid zones is lower than in wet areas, because of low and uneven temporally distributed precipitation (Estrela, Marcuello et al. 1996).

Groundwater abstraction rates for agricultural purposes have tripled worldwide over the past 50 years and withdrawals in many basins are exceeding the recharge rates and thus cannot be considered to be sustainable (UNESCO 2012).

As consequence of groundwater over-exploitation significant losses of habitat and biodiversity were observed as well as impacts on the ecological integrity of streams and wetlands (Ribeiro and daCunha 2010).

Furthermore, climate change causes major threats to global water supply such as instability and degradation of freshwater reservoirs. Adaptation measures to extreme weather events and increasing hydrological variability include surface and groundwater storage in constructed reservoirs, wetlands and soil (UNESCO 2012).

In the case of Portugal, climate change contributes to an increase of water scarcity in the south Portuguese semi-arid regions Alentejo and Algarve (Cunha, Ribeiro et al. 2006). These regions are characterized by irregular water resources and a climate with very hot and dry summers and cold and sometimes rainy winters. Rainfall is concentrated in a short period of time during the wet season from November to February with irregular cycles as periods of drought can last for three or more consecutive years (EEA 2010). Construction of large reservoirs such as the Alqueva dam located in Alentejo region, whose reservoir is considered to be Europe's largest artificial lake, provide fresh water supply for agricultural, urban and industrial areas of the region, even during times of prolonged drought (EEA 2010).

But large dam construction in water deficient areas is often controversial. Apart from providing water storage, economical benefits and renewable energy, the flooding caused by large dams causes disruptions in the local ecosystems (Santos, Pedroso et al. 2008). Among them are deforestation, habitat loss and fragmentation, decline in distribution ranges of wild animal species, lower freshwater flows downstream and thus intrusion of saline waters into previously freshwater locations (Domingues, Sobrino et al. 2007, Santos, Pedroso et al. 2008, Pereira and Figueiredo 2009).

Hence, water storage in soils and wetlands as well as small reservoirs for rainwater harvesting seem to be more appropriate. Rainwater harvesting, which is broadly defined as the collection and storage of surface runoff, has been neglected in agricultural water supply even of a long history in traditional water supply for agricultural purposes (Wisser, Frolking et al. 2010).

Especially the significance of rainwater harvesting in small reservoirs has been underlined by several studies in semi-arid zones (Smith, Renwick et al. 2002, Liebe, van de Giesen et al. 2005, Wisser, Frolking et al. 2010).

Water storage in soils of the Alentejo region seems to be rather low, as soils of the region, derived from schist or granite, are mainly characterised bv scarcity in organic matter, thinness and low water storage capacity (Correia 1993). Additionally, soil erosion as a result of deforestation, agricultural mechanization and often very strong rainfall events, contribute to low water absorption by soils of the region.

Besides the described challenges, land degradation and rural depopulation make sustainable development of Alentejo region difficult, especially with regard to agriculture and land management (Correia 1993). These developments seem to be connected to increasing weather extremes and water scarcity of surface and groundwater during the dry period (Correia 1993, EEA 2010).

To foster land and soil regeneration, various small reservoirs have been built since 2007 on the area of Tamera ecovillage, which is located in southwestern Alentejo. Rainwater harvesting by small reservoirs enables agricultural production and local water supply (Holzer 2012). This so called water retention landscape was assumed to raise groundwater recharge rates by reservoir leakage into aquifers and thus to foster reforestation and land regeneration, as previous attempts of deforestation failed due to poor soils and dryness (Holzer 2012).

Study area

This study was conducted in the area of Tamera ecovillage in southwest Alentejo (cf. fig. 1), measuring 140 km² and located at Monte do Cerro which is part of the parish Reliquias, in the Portuguese municipality of Odemira. GPS data is: 37°42´54" North, 8°30´57" West.

Figure 1: Map of Iberian Peninsula with marked location of the study area. Source: Google maps

The semi-arid climate of the area is characterized by long dry summers, where temperatures often attain 30-4O°C, sometimes over 40°C. Annual precipitation is concentrated in the wet period from September to April and averages about 600 mm, but can reach between 400 and 1200mm. Precipitation during the wet season is irregularly distributed and shows great annual fluctuations (Correia 1993). Very high values of potential evapotranspiration, surpassing 1000 mm, mainly occur during the period from July to September (Chambel and Almeida 1998).

Average groundwater recharge accounts for around 2-5% of annual precipitation (Ribeiro and daCunha 2010).

Geomorphological structures of the region are extensive flat areas with some residual relief. The study area lies between 130 and 200 mamsl in a small valley surrounded by hills of about 200 mamsl height and other valleys (cf. fig. 2), leading into a greater valley with a small stream. The valley of the study site is oriented south-north and opens at the northern end (cf. fig. 2).
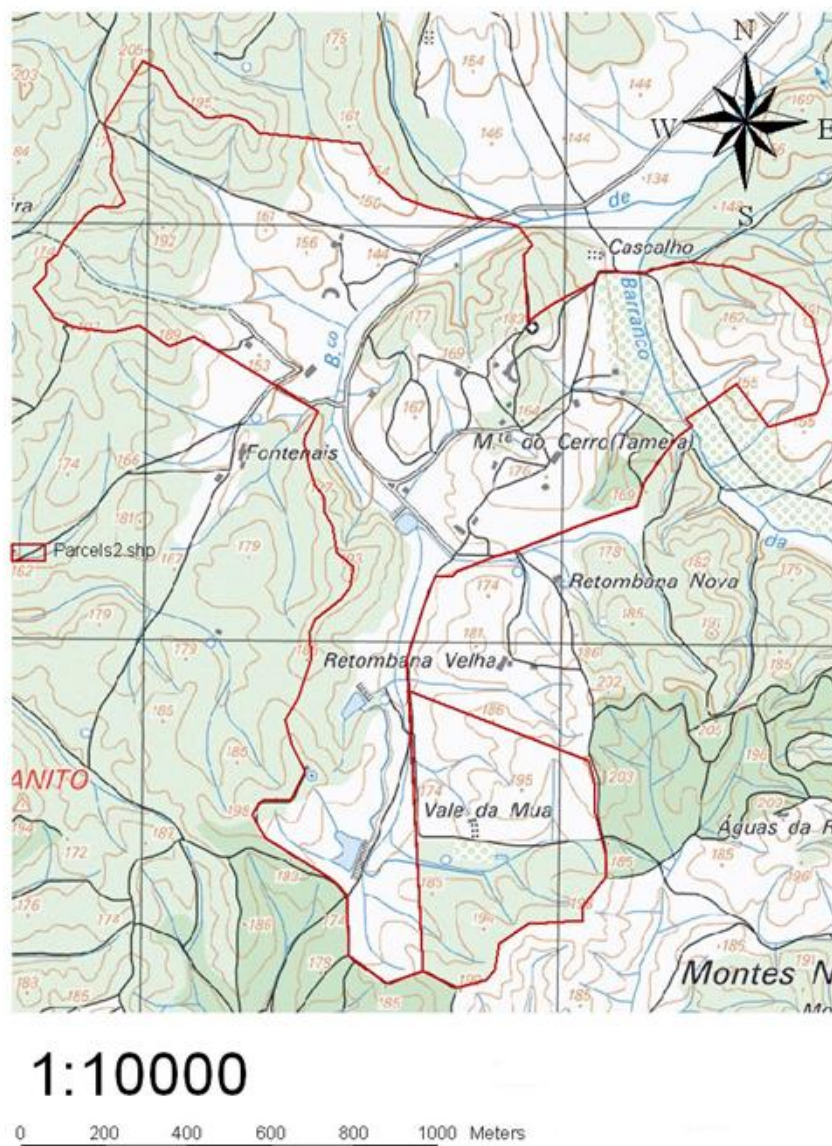
Figure 2: Geomorphology of the study area, the red line marks land boundary of Tamera ecovillage. Source: Instituto Geográfico do Exésito Portugal, Carta Militar N° 545

Rocks of the region are part of the most recent sediments of the South Portuguese Zone, a main geostructural domain of the Iberian Peninsula Precambrian and Paleozoic Shield, derived from sedimentary and volcanic rocks and compressed during the Hercynian Orogeny (Chambel and Almeida 1998). The South Portuguese Zone consists mainly of metamorphic rocks such as shales, schists, phylites, greywackes, quartzites and acid and basic metavolcanic rocks. Rocks are formed by quartz, feldspar (mainly calcium feldspars), micas and clay minerals, particularly caolinite, illite and chlorite. In some parts of the region, carbonates, pyrite and haematite occur in smaller percentages (Pinho, Duarte et al. 2007).

Outcropping shales of the study area are part of the Mira formation, a subdivision of the Baixo Alentejo Flysch Group, which is one of the domains of the South Portuguese Zone, consisting of deepwater turbiditic sediments more than 5 km thick (Fernandes, Orge et al. 2008). Age of Mira formation is late Viséan to early Bashkirian in the Carboniferous respective 345 to 315 million years (Pereira, Matos et al. 2007)

Hard rock aquifers with low permeabilities characterize the hydrogeology of the region, resulting in low aquifer yields, except zones of high fracturing (Chambel 2006). Groundwater in the South Portuguese Zone has a deficient quality with high values of electrical conductivity and sodium-chloride as dominant hydrogeochemical facies (Chambel and Almeida 1998).

For the South Portuguese Zone, three aquifer systems are proposed by Chambel and Almeida (1998): a superficial water table aquifer on a weathered and fractured zone in the first 50 meters, followed by an intermediate aquifer with low permeability but widely spaced vertical fractures which can function as high conductive channels. Finally, a deeper system of highly fractured pyrite masses and rocks in the deepest zones is proposed. However in some places only the first two systems would be present (Chambel and Almeida 1998). Changes of the hydraulic head lead to the interaction of all three systems so that the intermediate system acts as a channel connecting upper and deeper system (Chambel and Almeida 1998).

Soils of the study site are heavy Luvisols in the valleys and Leptosols on the hills with pH around 6.

The cultivated landscape in the Alentejo region is characterized by the traditional agro-silvo-pastoral system, a dispersion of individual trees or groups of trees, associated with animal grazing and cultivation. Occurring trees are *Quercus suber*, *Quercus rotundifolia*, *Quercus pyrenaica, Olea europaea* and *Castanea sativa*. Thereby *Quercus suber* dominates in areas of higher oceanic influence, *Quercus rotundifolia* occurs in the driest areas and *Quercus pyrenaica* grows where average precipitation is relatively high because of the relief (Correia 1993). In addition to the agriculturally cultivated trees, other mediterranean trees like *Quercus coccifera, Quercus lusitanica* grow in the region. The most abundant bushes and grasses include *Arbutus unedo, Cistus, Lavandula stoechas, Rosmarinus officinalis* and *Ulex* (Correia 1993).

With increasing intensification during the 1960s, trees were reduced to a minimum and mechanization as well as fertilization increased. Nowadays many parts of the region are abandoned or overexploited and in some parts of the region trees are dying as a result of droughts, overexploitation, soil erosion and mechanized works affecting their roots (Correia 1993).

River flows of the region are very irregular, with severe droughts contrasting with high flood discharges. Furthermore, deforestation, soil impermeability, urbanization, building on floodplains, the blockage of small creeks or their canalization and the building of walls together with transverse embankments along the small creeks foster flood events during the wet seasons (Ramos and Reis 2002)

Around twenty years ago, Tamera ecovillage was founded on the research area which was a former agro-silvo-pastoral site. Recently, 140 people are living in Tamera ecovillage and yearly several hundreds of visitors and guests stay on the site. Thus, water supply and waste water treatment are an important issue, especially with regard to safe water supply.

Since the construction of the water retention landscape, agricultural practice started on some parts of the area. Mainly vegetables and cereals are grown and some old olive orchards exist on the site. Around the reservoirs, terraces have been built for cultivating fruit trees, vegetables and herbs. Drip irrigation is applied during the dry season. Therefore water is being pumped from the artificial lakes into the fields.

The reservoirs built on the study area since 2007 are spread over the whole area, but mainly are located in the flat areas of the valley. The first reservoir or lake built in the middle of the village in 2007 measures around 3 hectares of water surface and various

smaller lakes were constructed in the following years. In 2011, the biggest water retention space was built further up in the valley, measuring about 5 hectares of area. Over time, the retention spaces of the lakes filled up with rain and surface runoff during the wet seasons.

Water supply was provided by deep wells until November 2012, when the shallow well in the valley was constructed to assure water supply. Water originating from the shallow well is pumped into two different storage tanks from where it flows into households, thereby being filtered by cotton and activated carbon filters before reaching the taps. Grey water from bathrooms and kitchens as well as leak water from compost toilets is lead into a septic tank, from where it flows into a reed bed measuring 200m^2 and planted with *Phragmitis australis, Iris pseudoacorus* and *Mentha aquatica*. Outflows of the reed bed are directed into a small seasonal creek and occasionally into the artificial lake nearby.

Aim of the study

Until now, no studies have been conducted to survey ground-and surface water quality and lake ecology of the reservoirs as well as groundwater recharge of the water retention landscape at Tamera. Generally studies about the influence of consecutive artificially constructed lakes on groundwater are scarce.

The assumed groundwater recharge by leakage of the constructed retention spaces is not proved yet and interactions of ground- and surface waters are not known. Especially with regard to safety of water supply, evaluation of water quality and sustainability of the water retention landscape at Tamera is crucial.

Thus this study focuses on the assessment of water quality in the system, on interactions between water retention basins and surrounding groundwater as well as on lake ecology of the reservoirs. Analysis of groundwater dynamics concerning recharge was conducted. Furthermore, sustainability of water and wastewater management was evaluated and proposals were made for further monitoring of the system.

For determination of water quality, ion concentrations of ground- and surface waters as well as waste waters were analyzed. Therefore water sampling took place in November 2013 and April 2013, before and after the wet season. Furthermore conductivity,

temperature, pH and oxygen saturation of ground- and surface waters in the study area were measured.

Stable parameters such as conductivity and chloride concentrations were used to discuss possible interactions between ground- and surface waters. Additionally, δ ^{18}O and δ ^{2}H isotope values of ground- and surface waters from the study site were analyzed from November 2012 and April 2013 samples in order to investigate dynamics of the water cycle in the system. δ ^{18}O and δ ^{2}H isotope values of lakes and surrounding groundwater were analyzed in order to verify possible leakage by the lakes.

Depth profiles of ion concentrations, conductivity, temperature, pH and oxygen saturation from two artificial lakes were taken in order to investigate lake biogeochemistry and stratification. Two more artificial lakes were analyzed for conductivity, temperature, pH and oxygen saturation for comparison of water quality of the different lakes.

Groundwater tables were measured over the time period of one year between October 2012 and November 2013 to monitor trends in groundwater recharge.

Samples from various points in the water supply chain were taken to analyze drinking water quality. Ion concentrations of two storage tanks, a kitchen and a bathroom tap and a water dispenser were analyzed and compared with legal maximum concentrations for drinking water.

Before reaching the reed bed, waste water was sampled before and after treatment in the septic tank. Finally, the outflow of the reed bed was sampled and ion concentrations of all waste water samples were analyzed. Hence, effectiveness of septic tank and reed bed could be analyzed.

2. Material and Methods

2.1 Sampling

Samples were taken from wells, lakes and other surface waters in the area of Tamera ecovillage, such as temporary streams, springs, water holes and rain. Sampling was done before (November 2012) and after the rain season (April 2013). All samples were taken in the 140 km^2 area of Tamera ecovillage, most of the sampling locations were situated

in the watershed of the lakes (cf. fig. 3). The sampling spots are marked in figure 3 and details are listed in table 1.
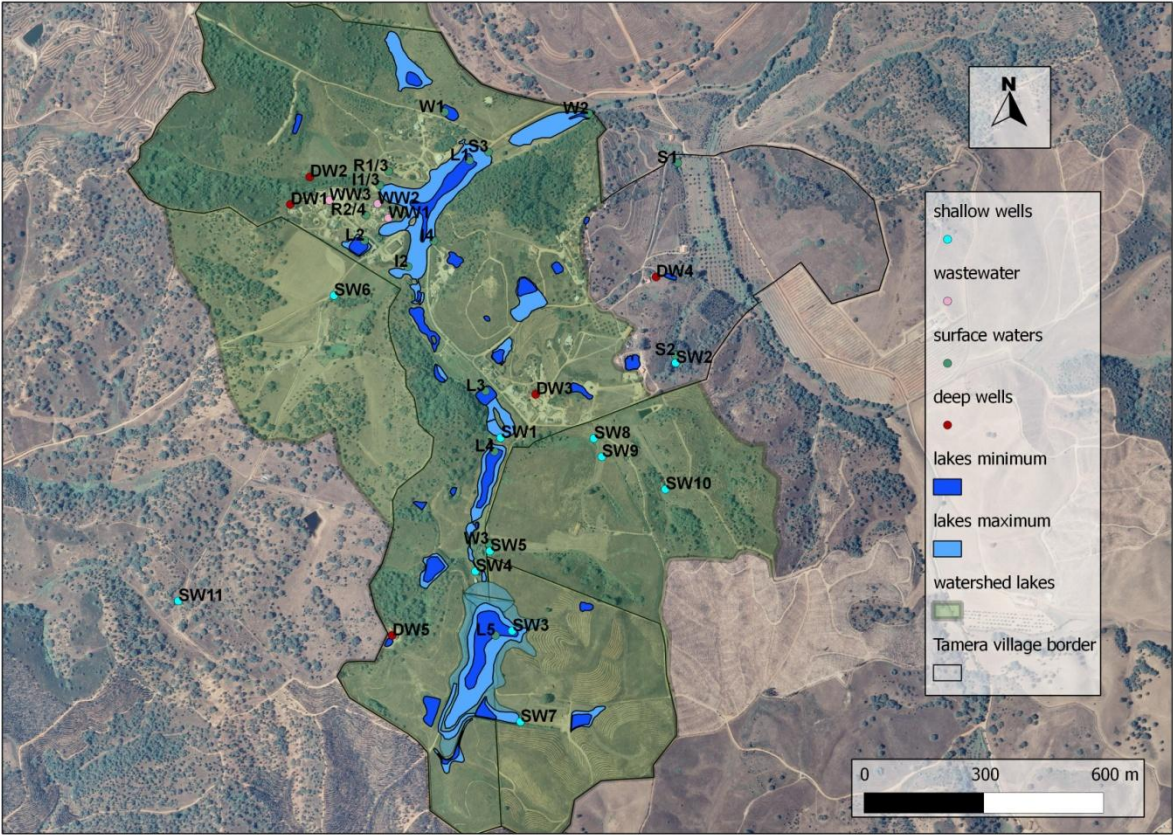
Figure 3: Map of the study site with marked sampling points

Details of sampling points are listed in table 1 on the following sites.

Sample name	Description and use	Sampling dates	Location [mamsl]	Depth of well/lake	Environment
L1	lake ; irrigation	11/11/2012 05/04/2013	145	7-9m below water table	settlement, roads, agricultural terraces
L2	lake	11/11/2012 07/04/2013	145	n.d.	settlement, roads, pasture
L3	lake	07/04/2013	150	n.d.	pasture, road, forest
L4	lake; irrigation	11/11/2012 08/04/2013	155	5m below water table in April 2013	agricultural terraces, road
L5	lake	06/04/2013	165	n.d.	forest, shrubland, roads
DW1	deep well; irrigation	06/11/2012 08/04/2013	161	44 mbgl	settlement, pasture
DW2	deep well	06/11/2012 08/04/2013	156	31.5 mbgl	pasture
DW3	deep well	07/11/2012 11/04/2013	160	n.d.	settlement, garage
DW4	deep well	08/11/2012	150	15 mbgl	pasture
DW5	deep well	11/11/2012 08/04/2013	195	50-60 mbgl	forest
SW1	shallow well; drinking water supply	07/11/2012 08/04/2012	155	6 mbgl	pasture
SW2	shallow well	08/11/2012	160	2.5 mbgl	forest
SW3	shallow well	08/11/2012	168	8.6 mbgl	retention space of L5, shrubland

SW4	shallow well	09/11/2012 06/04/2013	165	5.7 mbgl	stable, shrubland
SW5	shallow well	09/11/2012 06/04/2013	160	2.8 mbgl	shrubland, road
SW6	shallow well	10/11/2012 05/04/2013	168	3.5 mbgl	pasture, road
SW7	shallow well	11/11/2012 06/04/2013	170	5.1 mbgl	pasture, cornfields
SW8	shallow well	11/11/2012 05/04/2013	170	3.1 mbgl	trees, shrubs, road
SW9	shallow well	11/11/2012	170	3.5 mbgl	trees, shrubs, road
SW10	shallow well	06/04/2013	180	3.55 mbgl	forest, pasture
SW11	shallow well	08/04/2013	168	4.8 mbgl	forest
S1	spring; drinking water	08/11/2012	140	-	pasture, orchards
S2	spring, drinking water	08/11/2012	160	-	forest
S3	spring	10/11/2012 05/04/2013	140	-	road, pasture
W1	water hole for animals	07/11/2012	145	-	pasture
W2	water hole for animals	11/11/2012	138	-	pasture
W3	water hole	09/11/2012	160	-	shrubland, road
I1	inflow to L1	04/11/2012	145	-	settlement

I2	inflow to L1	04/11/2012	145	-	settlement, agricultural terraces
I3	inflow to L1	04/11/2012	145	-	settlement
I4	inflow to L1	04/11/2012	145	-	settlement, pasture
R1	rain	04/11/2012	-	-	settlement
R2	rain	07/11/2012	-	-	settlement
R3	rain	07/11/2012	-	-	settlement
R4	rain	11/11/2012	-	-	settlement
WW1	waste water; reed bed outflow	10/11/2012 10/04/2013	148	-	settlement, agricultural terraces
WW2	waste water; reed bed inflow from septic tank	10/04/2013	149	-	settlement, agricultural terraces
WW3	waste water from bathrooms and compost toilet leakage	11/11/2012 10/04/2013	155	-	settlement
D1	water tank	10/04/2013	180	-	-
D2	water tank	08/04/2013	160	-	-
D3	kitchen tap	10/04/2013	-	-	-
D4	water cooler	10/04/2013	-	-	-
D5	bathroom tap	10/04/2013	-	-	-

Table 1: List of sampling points with details about use, sampling dates, location, depth and environment of sampled ground- and surface waters.

Groundwater samples were taken from traditional shallow wells, with depths between around 2 and 8 meters below ground level, and from deep wells (bore holes) with depths between around 15 and 60 meters below ground level (cf. table 1). The shallow wells were constructed during the last centuries with natural stones and thus without

filters, enabling groundwater inflow in all depths of the well. SW1 was constructed in 2012 for drinking water supply of the village and is filtered through its whole depth of 6 meters below ground level by a gravel filter. The deep wells were constructed 10 to 30 years ago by drilling for drinking water supply. They were not used anymore and their water quality had been degrading over the last years because of increasing turbidity. As the deep wells were stabilized by metal pipes, it was assumed that the groundwater was flowing into the deep wells at the bottom of the well. Filters were not known. Sampling was done from the bottom of all wells to prevent mixing with upper water layers. Some deep wells could not be sampled at the bottom, as water was only reachable via a pump installed in the middle of the well connected to a tap above the ground surface.

L1 and L4 were sampled at the deepest point of the lake near to its dam, marked in figure 1. All other lakes were sampled at the lakeside.

Four samples of rainwater were taken in November at the western side of L1 with a beaker during four different rain events (cf. fig. 3 and table 1).

Groundwater and lake profile samples were collected with a groundwater sampler of 60cm length and a water carrying capacity of 200ml. Lake profile samples from November were taken with a plastic limnological sampler of 40 cm length and a water carrying capacity of 1 liter.

Surface water samples were collected by emerging the sampling flask under the water surface and closing the bottle underwater with the cap to fill it completely.

Tap water samples were taken by holding the flasks under the moderate running tap water stream. The samples were filled into different flasks and treated as followed for further analysis. Tap water originating from SW1 was sampled at five different locations: Two storage tanks, one kitchen tap, one bathroom tap and one drinking water container at the guesthouse kitchen.

Samples for titration of alkalinity and for determination of total phosphate were filled to the brim into 100ml amber glass bottles without any treatment. Samples for analysis of ammonium, ortho-phosphate and ferrous iron were filtered with a 0.22 μm syringe filter (Fisher Scientific, Schwerte, Germany) and filled into a 50ml amber glass flask containing 10% hydrochloric acid to prevent oxidation. Samples for ion chromatography were filtered with a 0.22 μm syringe filter (Fisher Scientific, Schwerte, Germany) and

stored in 20ml plastic vials. For isotope analysis ($\delta^{18}O/\delta^2H$) 20 ml glass vials with septum and teflon liner were filled completely without any treatment. All samples were stored at around 4° C until analysis.

2.2 Measurements of groundwater tables

Water tables of the shallow wells were measured by the Ecology Team of Tamera ecovillage in monthly intervals from October 2012 to November 2013. The water tables were measured in reference to the ground level using a mechanical depth gauge. The gauge was fixed on the highest point of the stepping stone and let down until reaching the water surface. Then the height of the stepping stone was subtracted from the measured depth. The ground of the wells was measured likewise, with the gauge reaching the ground of the well. Deep wells were only measured during sampling in November 2012 with a mechanical gauge, in April 2013 with an electric contact gauge.

To compare water tables of lake and surrounding groundwater for researching leakage of lake water, data of groundwater tables around the lakes and water levels of lakes are needed. As water always moves to the side of the lower water table (Hölting and Coldewey 2013), these data could be used for making assumptions about leakage of lakes. But the only groundwater measuring point in a considerable near distance to a lake was SW3. All other wells were located more than 100m away from a lake or were situated in the valley on a lower sea level below a lake. For this reason, qualitative data of lake and groundwaters was used to investigate interactions of ground- and surface waters.

2.3 Measurements with multiparameter probe

In most sampling locations measurements with a multiparameter probe were taken before water samples were collected. The multiparameter sonde 600 QS (YSI, Yellow Springs, USA) connected to the 650 MDS data display and logging system (YSI, Yellow Springs, USA) was used to determine various in-situ parameters. A pressure sensor showed the water depth of the probe. The measured parameters were: temperature [°C],

pH, O2-saturation [% and mg/l] and specific conductivity [μS/cm]. The specific conductivity was normalized to a temperature of 25°C by the probe.

2.4 Sulfide test

For the measurement of sulfide concentrations in the field, the Aquaquant S^{2-} MColortest™ test kit (Merck, Darmstadt, Germany) was used according to the instructions given by the manufacturer. The test allows determining the sulfide concentration in a water sample semi quantitatively by comparing the sample with a color card after the addition of reagents in relation to a blank sample. Under acidic conditions, only dissolved hydrogen sulfide is present. Addition of the reagents dimethyl-p-phenylenediamine and ironIII causes a reaction with the sulfide and a change in color by the formation of methyl blue. The detection limit of this test is 0.02 mg/L S^{2-}, maximum concentration to be measured without dilution is 0.25 mg/L S^{2-}.

2.5. Chemicals

Table 2 shows chemicals used for analysis of ion concentrations as described in the following.

Chemical	Formula	Manufacturer, Place, Country	Order code
Ammonium acetate	NH_4COOCH_3	Acros, Geel, Belgium	21836-0010
Ammonium chloride	NH_4Cl	Fluka, Seelze, Germany	09700
Ammonium molybdate	$(NH_4)_6Mo_7O_{24}\bullet 4H_2O$	Fluka, Seelze, Germany	9878
Ascorbic acid	$L*C_6H_8O_6$	Acros Organics, Geel, Belgium	401471000

Dipicolinic acid	$C_7H_5NO_4$	Fluka, Seelze, Germany	101204302
Ferrozine	$C_{20}H_{13}N_4NaO_6S_2$	Acros, Geel, Belgium	17101
Fe-III standard solution	1000mg/l Fe $Fe(NO_3)_3$ in HNO_3	Merck, Darmstadt, Germany	1197810500
Hydrochloric acid	HCl	Fisher Chemical, Loughborough, UK	10284480
Nitric acid	HNO_3	Merck, Darmstadt, Germany	1004561000
Phosphate standard solution	1000mg/l PO_4^{3-} KH_2PO_4 in H20	Merck, Darmstadt, Germany	1198980500
Potassium antimonyl tartrate	$K(SbO)C_4H_4O_6 \bullet 0.5\ H_2O$	Merck, Darmstadt, Germany	108092
Potassium sodium tartrate	$C_4H_4O_6KNa \bullet 4H_2O$	VWR International, Leuven, Belgium	27068.233
Sodium carbonate	Na_2CO_3	Merck, Darmstadt, Germany	1063921000
Sodium citrate	$C_6H_5O_7Na_3 \bullet 2H_2O$	Sigma-Aldrich, Steinheim, Germany	W302600
Sodium dichloroisocyanurate	$C_3N_3O_3Cl_2Na \bullet 2H_2O$	Sigma-Aldrich, Steinheim, Germany	218928
Sodium hydrogen carbonate	$NaHCO_3$	Merck, Darmstadt, Germany	1063291000
Sodium hydroxide	NaOH	Sigma-Aldrich, Steinheim, Germany	30620

Sodium nitroprusside	$Na_2 [Fe(CN)_5NO] \cdot 2H_2O$	Fluka, Seelze, Germany	71778
Sodium peroxodisulfate	$Na_2S_2O_8$	Sigma- Aldrich, Steinheim, Germany	71890
Sodium salicylate	$C_7H_5NaO_3$	Merck, Darmstadt, Germany	1066010250
Sulfuric acid	H_2SO_4	Fluka, Buchs, Switzerland	84720

Table 2: List of chemicals used for analysis

2.6 Photometric measurements

Photometric measurements were made with a photoLab 6600 UV-Vis spectrophotometer (WTW, Weilheim, Germany), using 1cm disposable polystyrol cuvettes and 5cm glass cuvettes.

2.6.1 Orthophosphate and total phosphate

For the determination of ortho- and total phosphate concentrations of the samples a photometric method based on a modified version of Murphy and Riley (1962) was applied. Briefly, ortho-phosphate and molybdate build up phosphor-molybdate heteropolyacid under acidic conditions, while the following addition of ascorbic acid reduces the molybdate, forming a deep blue complex that is measured with a photometer.

Samples for the measurement of total phosphate underwent an oxidative pretreatment to digest the biomass in the unfiltered samples. Therefore 5 ml of each sample were put in high-pressure testing tubes with an addition of 250 µl of sodium peroxodisulfate (5%). Afterwards, the samples were autoclaved for 2 hours at 121°C.

For the photometric measurement of orthophosphate and total phosphate the following reagents were prepared:

Molybdate sulfuric acid:

For 50 ml, 0.035 g potassium antimonyl tartrate were dissolved in 10ml of millipore water.

Then 1.3g ammonium molybdate were dissolved in another 10 ml of millipore water. 25 ml of a 1:1 diluted sulfuric acid were prepared in a 50 mL flask. In the following the molybdate solution and the tartrate solution were added and then everything was diluted to 50 ml. On the day of the analysis, a 6.25 dilution with millipore water was prepared.

10% ascorbic acid:

1g of ascorbic acid was diluted with 10ml of millipore water. On the day of the analysis, the solution was diluted 25 times with millipore water.

Standard series were prepared with a phosphate (PO_4^{3-}) stock solution (1000mg/l).

2ml of a 1:1 mixture of ascorbic acid (10%) and molybdate sulfuric acid were mixed with 1ml of sample or standard and filled into a 1cm plastic or 5cm glass cuvette, according to the expected concentration. After a reaction time of 30 minutes, the extinction was measured with a wavelength of 710 nm with the photometer. 5 to 8 standards were used to construct a calibration curve of each measurement (R^2 ranged from 0.98 to 0.99).

2.6.2 Ammonium

The measurement of NH4-N was done with a modified method after Krom (1980). The method is based on the substitution reaction of ammonium with sodium

dichloroisocyanurate to chloramines. In presence of sodium nitroprusside, which acts as a catalyst, the chloramines form blue-greenish indophenol complexes.

For the measurement four reagents were prepared:

A) Buffer solution

For 250 ml, 8.25g potassium sodium tartrate were dissolved in 125 ml millipore water, then 6g sodium citrate were added. Finally the solution was diluted with millipore water to 250 ml. The pH was controlled to be 5.2 and was optionally adjusted with 6N HCl.

B) Sodium salicylate solution

2.5 g sodium hydroxide were dissolved in 50 ml millipore water and then 8g of sodium salicylate were added. Then the solution was diluted with millipore water to 100 ml.

C) Sodium nitroprusside solution

0.1 g sodium nitroprusside were dissolved in 100 ml millipore water.

Reagents B and C were mixed in the ratio of 2:1 (v:v) on the day of analysis.

D) Sodium dichlorisocyanurate solution

This solution was prepared freshly on the day of analysis. For 50ml, 0.2 g sodium dichlorisocyanurate were dissolved in 50 ml millipore water.

Standards were prepared with ammonium chloride. For the analysis 1ml of reagent A was given into a 1cm polystyrol cuvette and 600µl of the mixture of B and C were added. Then 1 ml of the sample or standard was added and finally 400 µl of solution D were given into the cuvette.

Furthermore, the cuvette was closed with a lid, shaken shortly and left in the dark. After a reaction time of one hour the extinction was measured with a wavelength of 660 nm. 6 standards were used to construct a calibration curve of each measurement (R^2 was 0.99).

2.6.3 Ferrous iron

The determination method of ferrous iron was based on a modified version of Stookey (1970). It relies on the principle that ferrous iron reacts with ferrozine in a 1:3 ratio: three molecules of ferrozine form a purple, water soluble complex with one Fe^{2+}-ion at pH 4 to 9.

For the quantification the following reagents were prepared:

Ferrozine solution:

250 g (50% w/v) ammonium acetate and 0.5 g (0.1% w/v) ferrozine were dissolved in 500 ml millipore water. The solution was stored in the dark at 4°C.

10% ascorbic acid:

10g of ascorbic acid were dissolved in 100 ml millipore water. This solution was only used for the preparation of the standards.

50% sulfuric acid:

A 1:1 (v/v) dilution of sulfuric acid with millipore water was prepared.

For the preparation of the standards, a Fe-III standard solution (1000 mg/l) was used together with the sulfuric acid and ascorbic acid solutions.
0.5 ml of the prepared sulfuric acid with the respective amount of stock solution were put into a flask, then 1ml of ascorbic acid was added to reduce iron-III to iron-II and finally the solution was diluted with millipore water to a volume of 50ml.

For measuring of ferrous iron concentrations in the samples 1 ml of ferrozine reagent and 1 ml of sample or standard were filled into a 1 cm disposable polystyrol cuvette. The samples were kept dark and after a reaction time of 10 minutes the extinction was

measured with a wavelength of 562 nm. 8 standards were used to construct a calibration curve of each measurement (R^2 was 0.99).

2.7 Titrimetric determination of alkalinity

For the determination of alkalinity, 50 ml of the water sample were titrated with 0.05 N HCl until reaching a pH of 4.2. Meanwhile the sample was mixed continuously with the acid by a magnetic stirrer and the pH was controlled with a pH electrode.
The titrated volume of acid was used to calculate the corresponding alkalinity by using equation 1.

$$Eq. 1 \qquad C_{alk=}\frac{C_{HCL} * V_{HCL}}{V_{sample}} * 1000$$

C_{alk} is the alkalinity in mmol/l, C_{HCl} represents the concentration of the acid in mol/l, V_{HCL} is the volume of the titrated HCL and V_{sample} the volume of the sample, the unit of the volumes is ml.

At a pH of 4.2, HCO_3^- is the most dominant species of the carbonates, so the concentration of HCO_3^- was assumed to equal the alkalinity (Neal 1988).

2.8 Ion Chromatography and calculation of the ion balance

For the determination of various cation and anion concentrations in the water samples the ion chromatograph 883 Basic IC plus (Metrohm, Filderstadt, Germany) was used, connected to an 863 Compact IC Autosampler (Metrohm, Filderstadt, Germany). The columns Metrosept C4-250/4.0 and Supp 4-250/4.0 (Metrohm, Filderstadt, Germany) were used for cation and anion analysis.

For the measurement of the cations magnesium, calcium, potassium and sodium a solution of 1.7 mmol/l nitric acid and 0.7 mmol/l dipicolinic acid was used as an eluent. For the measurement of the anions sulfate, nitrate, nitrite and chloride, the eluent consisted of 1 mmol/l sodium carbonate and 4 mmol/l sodium hydrogen carbonate.

Samples with sulfide content were degassed with nitrogen before measurement. The waste water samples were diluted with millipore water by factors between 10 and 20 for the ion chromatographic analysis.

To estimate the quality of the measured ion concentrations, an ion balance was calculated for every sample. Therefore all measured cation and anion concentrations were transformed into normal concentrations by applying equation 2.

$$Eq.2 \qquad C_{eq} = C \left[\frac{mmol}{l} \right] * charge\ of\ ion$$

Then the normal concentrations were summed up for the ion balance with the use of equation 3.

$$Eq.3 \qquad \Delta I[\%] = \frac{\sum Ceq\ (cations) - \sum Ceq\ (anions)}{\sum Ceq\ (cations) + \sum Ceq\ (anions)} * 100\%$$

Ion balances up to ±5% were regarded as a tolerable quality (Hölting and Coldewey 2013).

2.9 Isotope analysis

2.9.1 Measurement of $\delta^{18}O$ isotopy

10 ml screwcap exetainer vials were filled with a gas mixture of 0.3% CO_2 in helium with a purity of 99.996% and then closed with a membrane cap liner.
In the following approximately 500µl of the sample were injected with a syringe through the membrane into the vial. In order to allow ^{18}O equilibration between CO_2 and H_2O, samples were kept closed for 24 hours. Afterwards, the samples were quantified through injection with a Gas Bench II (Finnigan-Thermo Fisher Scientific, Schwerte, Germany) in a MAT 252 mass spectrometer (Finnigan-Thermo Fisher Scientific, Schwerte, Germany) by using helium as carrier gas and the continuous flow method. Standard deviation of this analysis was about 0.15‰.

2.9.2 Measurement of ^{2}H isotopy

During the analysis the water samples were reduced by chromium to H_2 in an H-Device (Thermo Fisher Scientific, Schwerte, Germany) at 800°C. The H_2 was then quantified in the mass spectrometer MAT 252 (Thermo Fisher Scientific, Schwerte, Germany) with the dual-inlet method without any carrier gas.
The repeatability of this method is about ±1‰.

Calibration was done with the three international standards of VSMOV ($\delta^{18}O=0$‰, $\delta^2H=0$‰), GISP ($\delta^{18}O =-24.75$‰, $\delta^2H =-189.9$‰, relative to VSMOV) and SLAP ($\delta^{18}O =-55.5$‰, $\delta^2H =-428$‰, relative to VSMOV).

3. Results

3.1. Groundwater

3.1.1. Groundwater tables

Figure 4 shows the measured water tables of shallow wells from October 2012 till November 2013. In November 2012, water tables of all shallow wells were more than 2m below ground level and were constantly rising until reaching a maximum water table at heights between 0 and 1m below ground level in the time between December 2012 and May 2013.

All measured shallow wells except SW3 and SW6 stayed at their maximum height for around two months between March and June 2012 and then slowly dropped down to water levels between 0 and 1.5m below ground level in September 2013, before filling up again in November 2013 to heights between 0 and 1 m below ground level (cf. fig. 4).

SW1, which was measured only in November 2012 and April 2013 during sampling, showed a water table of 2m below ground in November and 0m below ground level in April. In April, the grassland area around SW1 was swampy and at some locations around 10cm of water had risen out of the ground on the soil surface.

SW3 showed different results as it had a water level around 8 m below ground level in November 2012, which then rose to 0m in May 2013 and then dropped down again to 4m in October 2013 before filling up again to 3.6m in November 2013 (cf. fig. 4).

SW3 and SW5 had a low water level in November, that was actually only about 60cm above the well ground at SW3 and about 20cm above the well ground at SW5 (cf. fig. 4 and table 1). All other shallow wells had water tables between 1 and 4m above the well ground (cf. fig. 4 and table 1).

SW10 water table continued to drop down from summer 2013 until November 2013, in contrast to the other wells.
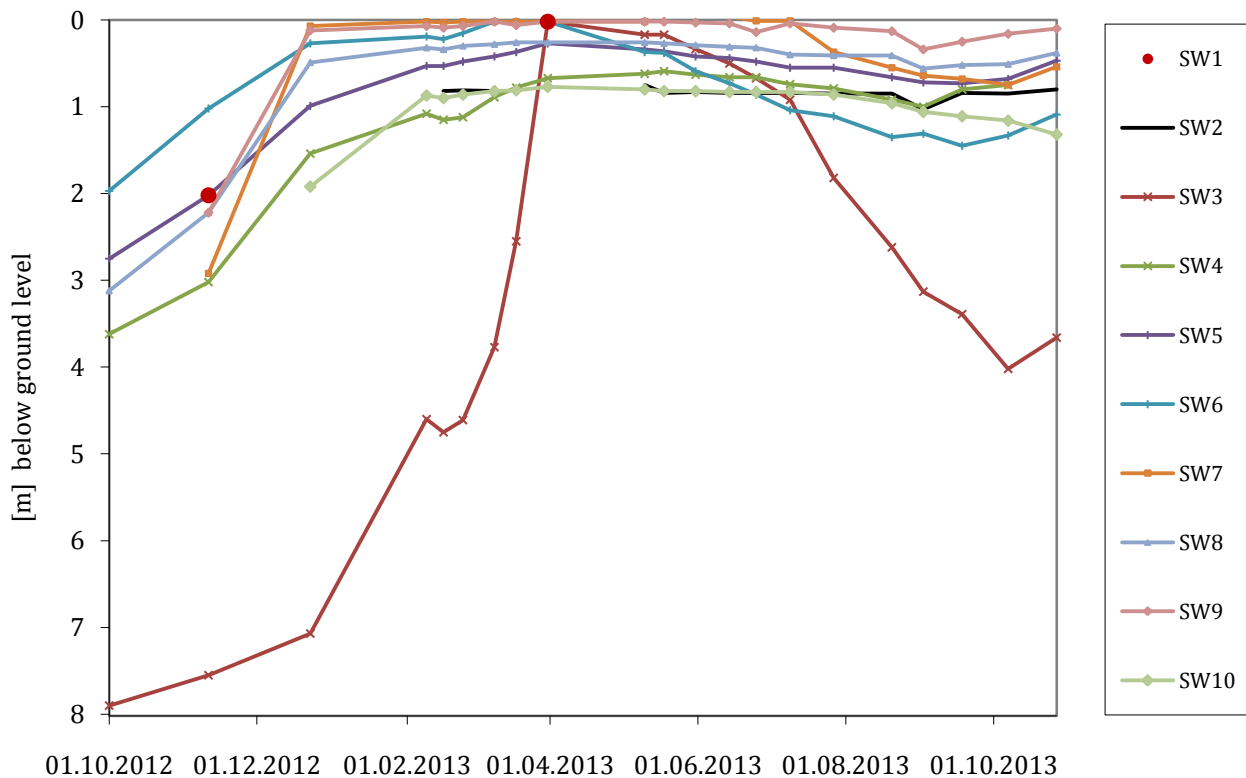
Figure 4: Water tables of shallow wells 1-10 from October 2012 to November 2013. SW1 was only measured in November 2012 and April 2013 during sampling.

Water tables of deep wells DW1, DW2 were measured in November 2012 and April 2013, DW4 was only measured in November 2012. DW3 and DW5 were not accessible. Table 3 shows the measured water tables of the deep wells. The water table of DW1 rose 3m in the time between November 2012 and April 2013, DW2 rose 2,5m (cf. table 3).

	Nov 12	Apr 13
DW1	9,00	6,00
DW2	2,50	0,00
DW4	0,00	no data

Table 3: Water tables of deep wells in November 2012 and April 2013 in meters below ground

3.1.2. Groundwater quality

Water types according to the Piper diagram

All water types found in the research area can be classified as sulfatic/chloridic earth alkali to alkali waters after (Furtak and Langguth 1967).

There were no differences in water type between the samples, but still some slight differences in ion partitions. Overall, there were greater differences in anion than in cation concentrations between the samples (cf. fig. 5).

SW1 differed from the other samples in November by having a relatively high partition of alkalinity. SW1 then changed in partitions of anion concentrations, having a lower partition of alkalinity in April in the range of most other wells.

SW3 and SW5 November anion and cation partitions differed from most other samples with relatively low alkalinity partitions. In April, SW5 cation and anion partitions were in the range of most other samples. SW3 was not analyzed in April, because it was over flooded by L5 (cf. fig. 13).
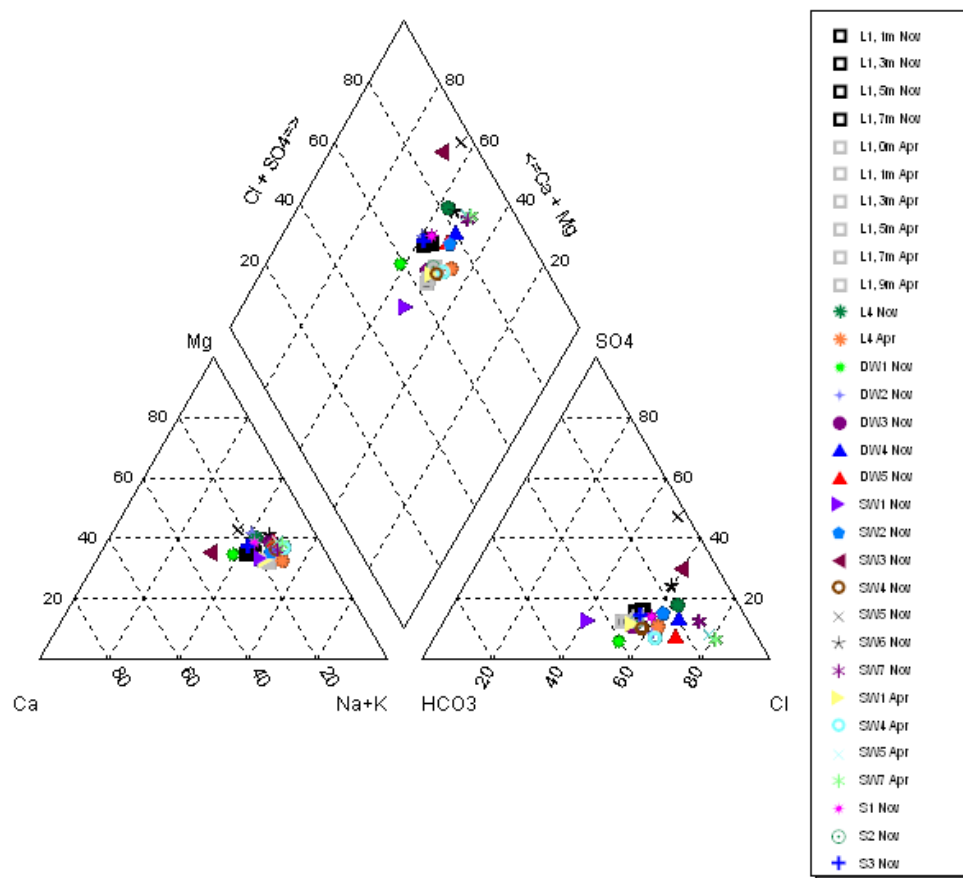
Figure 5: Piper diagram of measured ground- and surface waters of the water retention landscape in November 2012 and April 2013. Surface waters R1-4, I1-4, W1-3 in November and S3 and L5 in April are not shown. SW8 could not be plotted because of missing hydrogen carbonate data.

Conductivity

Figure 6 shows the measured conductivities of deep and shallow wells in November and April. The measured values were between around 84μS/cm minimum and 1500 μS/cm maximum. Some wells and surface waters were only measured in November or April (cf. fig. 6).
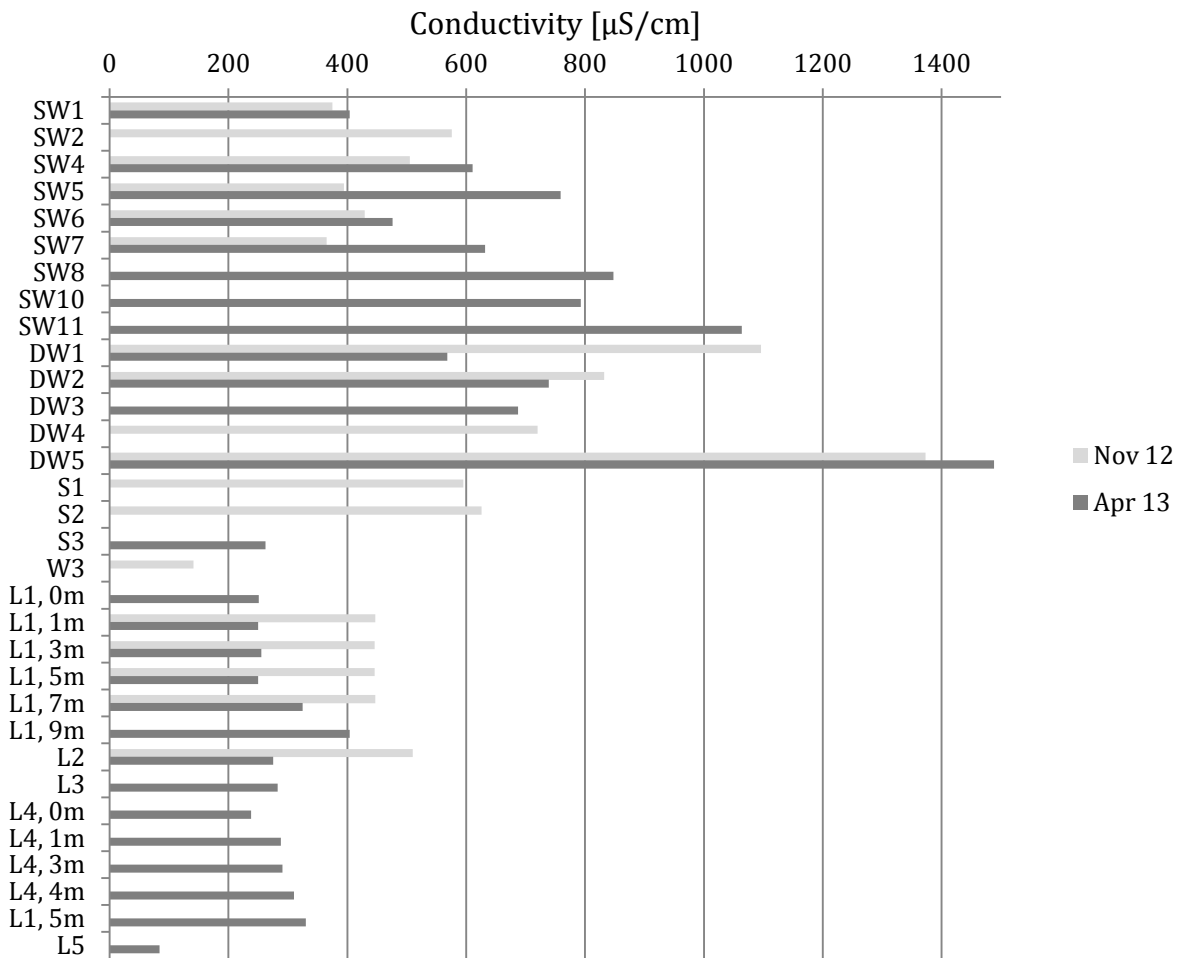
Figure 6: Conductivity of all measured ground- and surface waters in November 2012 and April 2013

In November 2012, the deep wells conductivity was overall higher in comparison to the shallow wells. Thereby the deepest well DW5 had the highest conductivity, being 1373 µS/cm. In contrast, there was no comparable tendency in April, as DW1, DW2 and DW3 had lower values than some shallow wells (cf. fig. 6).

In April, surface waters had overall lower conductivities than wells and springs, but in November the lakes conductivity was very similar to the shallow wells. All measured shallow wells and surface waters had higher conductivities in April in comparison to November, but with regard to the measured deep wells, only DW5 had higher values in April than in November (cf. fig. 6).

Assuming one aquifer system for all wells because of the described similarities of ion partitions shown in the Piper diagram, ions were correlated with conductivity to get an overview of the whole areas hydrogeological situation. Overall, there was a strong correlation with a linear relationship for all wells in November and April between conductivity and chloride concentrations, sodium concentrations and conductivity, as well as for magnesium and conductivity (cf. table 4). Higher ion concentrations correlated with higher conductivities. No clear pattern was found for calcium and hydrogen carbonate concentrations, and no correlation for sulfate concentrations and conductivity.

	Cl^-	Na^+	Mg^{2+}	Ca^{2+}	HCO_3^{3-}	SO_4^{3-}
April 2013	0.94	0.94	0.93	0.07	0.24	0.3
November 2012	0.97	0.97	0.98	0.63	0.6	0

Table 4: Conductivity correlation coefficients (R^2) for linear correlation of the respective cations and anions with conductivity, calculated for November 2012 and April 2013 samples from all measured deep and shallow wells.

Ion concentrations

Figure 7 and 8 show the measured ion concentrations of all ground- and surface waters in November and April. Groundwaters differed from surface waters in both months in ion concentrations. Details are described in the following and can be found in the appendix.

November 2012

Concentration (mg/l)

chloride | nitrate | total phosphate | sulfate
hydrogen carbonate | ammonium | potassium | calcium
magnesium | sodium | ferrous iron

Figure 7: Ion concentrations of all measured ground- and surface waters in November 2012. Because of small sampling volumes, hydrogen carbonate concentrations of I1, SW8 and R1-4 were not measured in November.
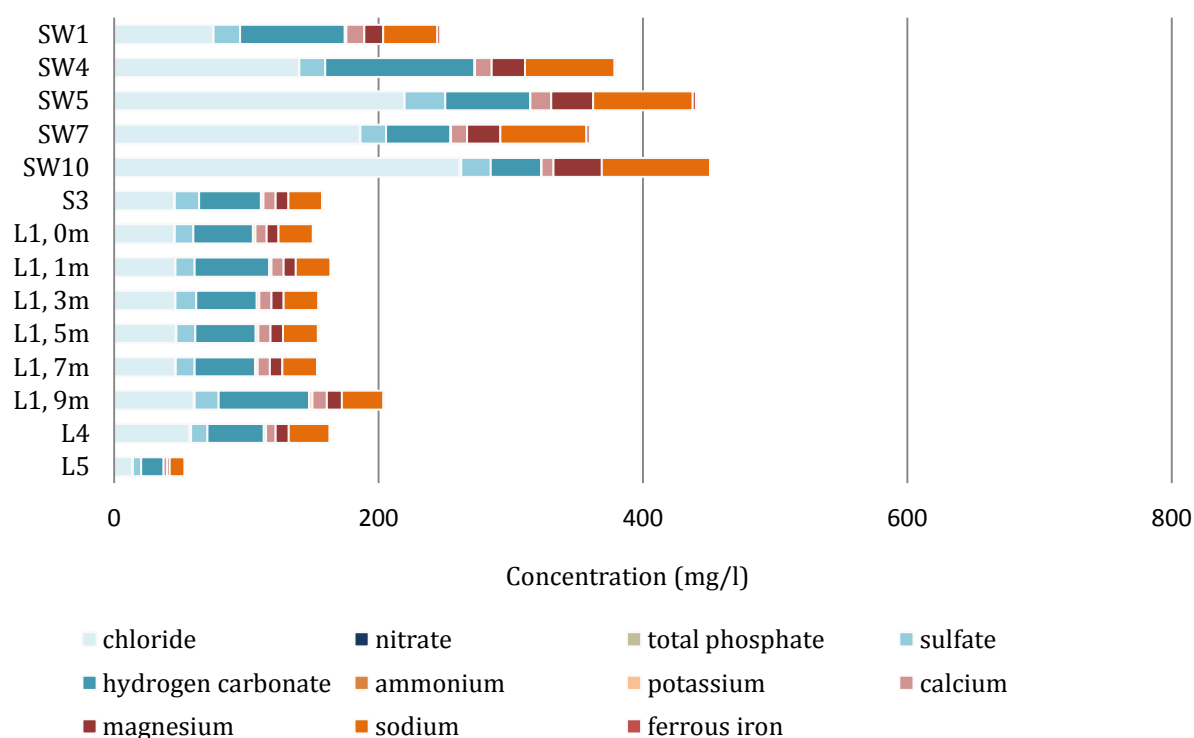
April 2013

Figure 8: Ion concentrations of all measured ground- and surface waters in April 2013

Anions

Anions were analyzed in November from all wells except SW9, SW10 and SW11, and additionally in April from the shallow wells SW1, SW4, SW5, SW7 and SW10.

Chloride

Chloride concentrations varied between 100 and 300 mg/l in November for the deep wells, April values were not measured. The shallow wells had chloride concentrations of 20 to 110 mg/l in November and overall higher concentrations of 75 to 260mg/l in April. Chloride concentrations of the shallow wells increased at SW4 for about 50 %, at SW7 for about 230% and at SW5 with a rate of 410%, SW1 showed a relatively low increase of 10%.

Sulfate

In November, sulfate concentrations ranged between 26 and 40 mg/l for the deep wells and 13 to 69 mg/l for the shallow wells. The shallow wells SW4 and SW7 did not show changes in sulfate concentrations between the seasons, but SW5 and SW1 did: SW5 had decreased from 69 mg/l sulfate in November to 30mg/l in April while the sulfate concentration of SW1 showed a decrease from 27 mg/l in November to 20 mg/l in April.

Nitrate and Nitrite

Nitrate was found in November in DW2 with a concentration of 1.6 mg/l and in SW3-8, thereby the concentrations did not exceed 10mg/l. In April, relatively lower concentrations were found in SW5, SW7 and SW10 with values of 0.2-1.2 mg/l

Nitrite was not found in any samples.

Orthophosphate and total phosphate

Concentrations of orthophosphate in November accounted for 0.03 to 0.7 mg/l for all wells, total phosphate values ranged from 0.01 to 4.5 mg/l. Some samples (SW1, SW3 and SW5) were turbid and showed relatively high total phosphate concentrations, containing sediments from the bottom of the well. In April, there was no detectable orthophosphate in the shallow wells. More details are shown in the appendix.

Sulfide

Sulfide was only found in SW1 with a concentration of 0.09 mg/l at a pH of 6.7 in November and 0.02mg/l at a pH of 6.5 in April. Since the concentrations were so low, they were not further considered.

Alkalinity

The measured alkalinity of the deep wells accounted in November for 78 to 270 mg/l, thereby the deepest two wells DW5 and DW1 showed the highest concentrations of 177 and 273 mg/. DW3, the shallowest deep well, had the lowest concentration of 78 mg/l. The shallow wells alkalinity ranged in November between 5 and 131 mg/l, SW1 having

the highest alkalinity of 131 mg/l. SW3 and SW5 had very low concentrations of 5 and 6 mg/l. In April, the alkalinity concentrations of SW4, SW5 and SW7 were higher in comparison to November, being 113, 64 and 48 mg/l. SW1 showed a lower alkalinity in April of 79 mg/l.

Cations

Cation concentrations of all wells except SW9, SW10 and SW11 were measured in November, in April only SW1, SW4, SW5, SW7 and SW10 were measured.

Sodium

Sodium concentrations of the shallow wells accounted for 8 to 60mg/l in November and 40 to 80 mg/l in April, being overall higher in April. The increase in sodium concentrations was about 4% at SW1, 11% at SW4, 150% at SW7, and 250% at SW5, and thus matching the range of increase in chloride concentrations. The deep wells sodium concentrations were higher than the shallow wells and ranged between 60 to 145 mg/l in November.

Magnesium

All shallow wells had higher magnesium concentrations in April than in November, the concentrations ranged from 4 to 25mg/l in November and from 14 to 36 mg/l in April for the shallow wells. In contrast, SW1 showed a slight decrease in magnesium with concentrations of 16 mg/l in November and 14 mg/l in April. Magnesium concentrations of the deep wells ranged between and 26 and 60 mg/l in November.

Calcium

Calcium concentrations of the shallow wells ranged between 7 and 18 mg/l in April and November, showing no changes bigger than 3 mg/l between the seasons. The deep wells calcium concentrations in November ranged from 15 to 60 mg/l.

Potassium

Potassium concentrations were only found in SW1 (2.8 mg/l), SW3 (0.3 mg/l) and SW6 (2.3 mg/l) in November and in SW1 (0.8 mg/l) in April.

Ammonium

Ammonium was measured from samples of the deep wells n November, and from the shallow wells that were used for drinking water, SW1 and SW2. In April, ammonium concentrations of the shallow wells SW1, SW4, SW5, SW7 and SW10 were measured. In November, ammonium was only found in the deep wells with maximum concentrations of 0.1 mg /l. The ammonium concentrations of the shallow wells measured in April were around 0.3 to 0.4 mg/.

Ferrous Iron

Ferrous iron was measured from samples of the deep wells and SW1 in November. In April, iron concentrations of the shallow wells SW1, SW4, SW5, SW7 and SW10 were measured as well. In November, ferrous iron concentrations of DW2, DW3 and DW4 ranged from 1.8 to 3.3 mg/l, DW1 and DW5 did not show any ferrous iron concentration. SW1 had a concentration of 1.3 mg/l. In April, ferrous iron concentrations of the shallow wells were measured as in the following: SW1: 2.0 mg/l, SW4: 0.3 mg/l, SW5: 2.4 mg/l, SW7: 2.3 mg/l and SW10: 0 mg/l.

Ion Balances

Ion balances calculated for all deep wells did not exceed 5% in November, in April the deep wells were not measured. Ion balances of the shallow wells measured in November ranged from -5 to 8%, thereby SW2, SW4, SW5 and SW6 had ion balances of more than 5%. For the shallow wells measured in April the ion balances accounted for -2 to -9%. Thereby SW5, SW7 and SW10 had values overlapping ±5%.

Ph

Ph values of deep and shallow wells ranged from 6.3 to 6.8 in November and from 6.0 to 7.1 in April, in which the deep wells ph was overall higher than the shallow wells ph.

Temperature

The deep wells temperature reached between 17.3 and 19.1°C in November. In April, the deep wells showed temperatures from 17 to 18.8 °C; thereby DW 5 as the deepest well had the highest temperatures in both seasons. The shallow wells temperatures ranged from 15.1 to 16.9° C in November, where SW1 showed the highest temperature. In April, the shallow wells temperatures ranged from 14.2 to 16.5°C and SW1 had a relatively high temperature of 17.2°C.

Oxygen saturation

Oxygen saturations showed great variations between the different shallow and deep wells. Overall, in April lower oxygen saturations were found in the shallow wells in comparison to November.

The shallow wells oxygen saturation accounted for 5 to 62% in November and for 1 to 44% in April. SW1 and SW7 had with 5% the lowest oxygen saturations in November, in April SW1, SW3 and SW7 had the lowest saturations between 1 and 6.5%.

Oxygen saturation of the deep wells ranged in November from 4% at DW2 to 35% at DW5, in April from 4.5 at DW2 to 39% at DW5 and they did not show changes between the seasons of more than 9%. Oxygen saturation of DW3 and DW5 was measured in a beaker filled from the tap, as there was no access to the well. Thus, the oxygen saturation of both wells might not be identical with the measured values.

3.2. Water supply

Tap water originating from SW1 was sampled at five different locations: Two storage tanks, one kitchen tap, one bathroom tap and one drinking water container at the guesthouse kitchen. The results were as follows.

Ferrous iron was only found in the two storage tanks with concentrations of 0.5 and 0.9 mg/l. As mentioned before, the ferrous iron concentrations of SW1, from where water is being pumped into the tanks, accounted for 2.0 mg/l in April and 1.3 mg/l in November, being much higher than the concentrations of the water in the tanks. The tank water is filtered after leaving the tanks and again before entering the kitchen and bathroom taps.

Furthermore, water quality of the tap waters was analyzed with the methods described above. Sampling took place in April. The results for anions and cations did not exceed threshold limits for drinking water (EU 1998), except ferrous iron concentrations of the two storage tanks. More details are listed in the appendix. Ammonium was found in SW1 in a concentration of 0.37 mg/l. In case of oxidation, this would result in 1.25mg/l of additional nitrate.

Ion balances of the tap waters did not exceed -5%.

Additionally, S1 and S2 were checked for drinking water quality, as they are used for small scale drinking water supply, but not connected to a pipe system. Cation and anion concentrations did not exceed maximum concentrations for drinking water (EU 1998)(cf. appendix). Ion balances of S1 and S2 accounted for respectively 5.3 and -2.4%.

All tap and drinking water samples were not analyzed further for heavy metals, organic pollutants, microorganisms, herbicide and pesticides residues.

3.3. Surface water

3.3.1. Lake 1

L1 was measured in November and April at various depths. The lake had a 3m higher water level in April in comparison to November and showed no stratification of parameters in November, in contrast to April.

Ion concentrations

Anions

Chloride
Chloride concentrations of L1 ranged between 76.6 and 80 mg/l in November and 45 and 60 mg/l in April, thereby increasing with depth in both months. In comparison to the groundwater samples, these concentrations were relatively low in April. In November, they were in the range of the shallow wells chloride concentrations.

Sulfate

Sulfate concentrations accounted for 29.6 to 30.8 mg/l in November and for 14 to 18 mg/l in April, overall increasing with depth. November concentrations were in the range of the groundwater concentrations, April concentrations were slightly lower than groundwater sulfate concentrations.

Sulfide

In November, sulfide was measured at a depth of 7m with a result of 0mg/l. In April, sulfide was not measured in L1.

Alkalinity

The measured alkalinity of L1 accounted for 67 to 79 mg/l for all depths in November, being the highest at a depth of 3m and the lowest at 1m depth. April values ranged from 45 to 69 mg/l, thereby being nearly constant through the depth profile from the surface down to a depth of 7m, with a peak at 1m of depth, and then rising to 69 mg/l at 9m of depth.

Cations

Sodium

November sodium concentrations of L1 were in the range of 41 mg/l at 9m depth to 47 mg/l at 1m depth, showing no clear pattern of stratification through the different depths and being in the range of the shallow wells sodium concentrations. April values reached 26 to 31 mg/l, increasing clearly with depth, and thereby being lower than the shallow wells sodium concentrations.

Magnesium

November magnesium concentrations accounted for 19.5 mg/l for all depths except the deepest measuring point at 7m, where magnesium accounted for 17.9 mg/l. November values were in the range of the shallow wells magnesium concentrations. In April,

magnesium increased constantly with depth, showing concentrations of 8.9 to 11.4 mg/l and being overall lower than the shallow wells magnesium concentrations.

Calcium

Calcium concentrations of L1in November ranged from 19 to 22 mg/l without showing a clear stratification, but having the lowest concentration at the deepest measuring point of 7m depth and being relatively high in comparison to the shallow wells, but lower than most deep wells. In contrast, in April there was a clear stratification of calcium concentrations which started with 8.5 mg/l at 0m depth, increasing to 10.9 mg/l at 9 m depth. April values were relatively low in comparison to the shallow wells.

Potassium

In November, no potassium was found in L1. April potassium concentrations accounted for 1.8 mg/l for all depths except at 9 m, where potassium concentrations reached 2 mg/l.

Nutrients

Phosphate

Total phosphate and orthophosphate concentrations of L1 were overall higher in November than in April (cf. fig. 9). Total phosphate concentrations ranged between 1.4 and 0.3 mg/l in November and decreased constantly with depth. In April, total phosphate concentrations showed a different dynamic: first decreasing from the surface to 1m depth, then increasing to 5m depth and then decreasing again until 9m depth (cf. fig. 9).

Orthophosphate concentrations showed similar trends for November and April by decreasing slightly in the first 3 meters and then increasing until 7m depth. In April, orthophosphate decreased again from 7m on to 0 mg/l at 9m depth. At 3m depth, orthophosphate concentration was also 0 mg/l (cf. fig. 9).
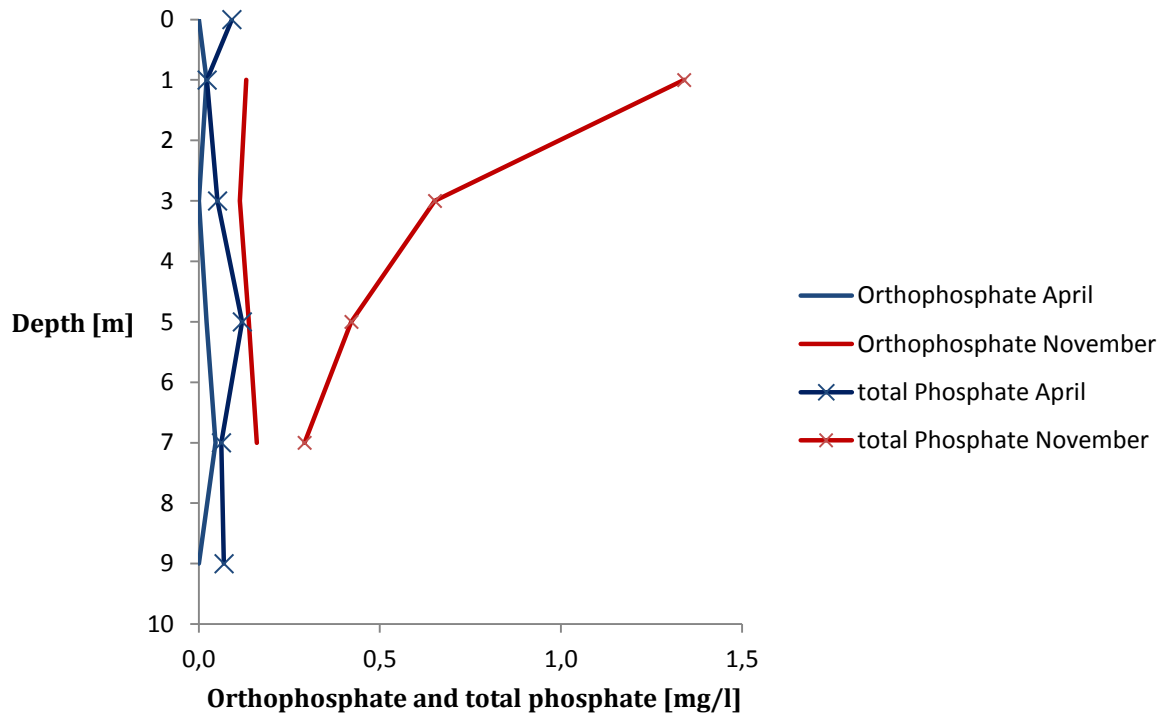
Figure 9: Depth profiles of measured ortho and total phosphate concentrations of L1 in November 2012 and April 2013

Nitrate and Nitrite

Nitrate concentrations accounted for around 2.5 mg/l in November and ranged from 0.3 to 0.7 mg/l in April. They did not show any stratification in November. In April there was a relatively small increase from 7m on to 9m of depth (cf. fig. 10A).

In April and November, no nitrite was found in L1.
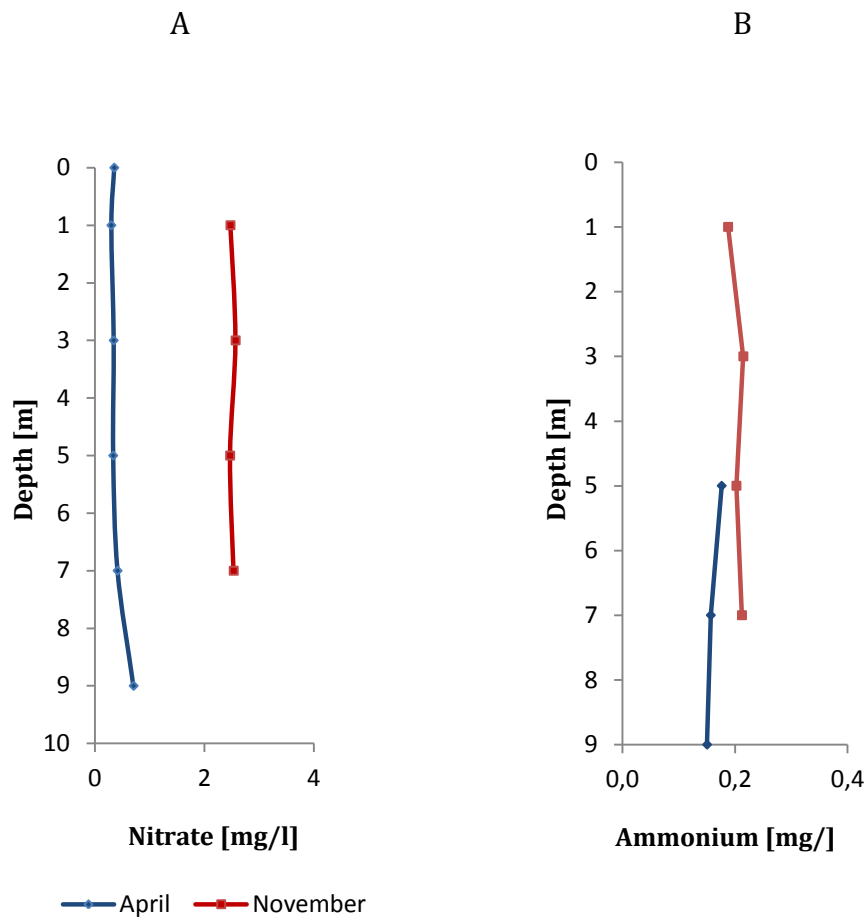
Figure 10: Depth profiles of measured Nitrate and Ammonium concentrations of L1 in November 2012 and April 2013

Ammonium

The measured concentrations for ammonium in L1 accounted for around 0.2 mg/l in November for all depths. In April, only the depths of 5 to 7m were measured and resulted in 0.18, 0.16 and 0.15 mg/l for the respective depths of 5, 7 and 9m, decreasing with depth (cf. fig. 10B).

Ionbalances

Ionbalances of the measured samples from L1 ranged between 1 and 8.5% for November samples. April samples did not exceed ±5%.

Oxygen saturation, conductivity, temperature and pH

Lake 1 had a 3m higher water level in April in comparison to November. In contrast to April, depth profile measurements taken with the multiparameter probe in November showed no stratification in oxygen saturation, conductivity, temperature and pH (cf. fig. 11).
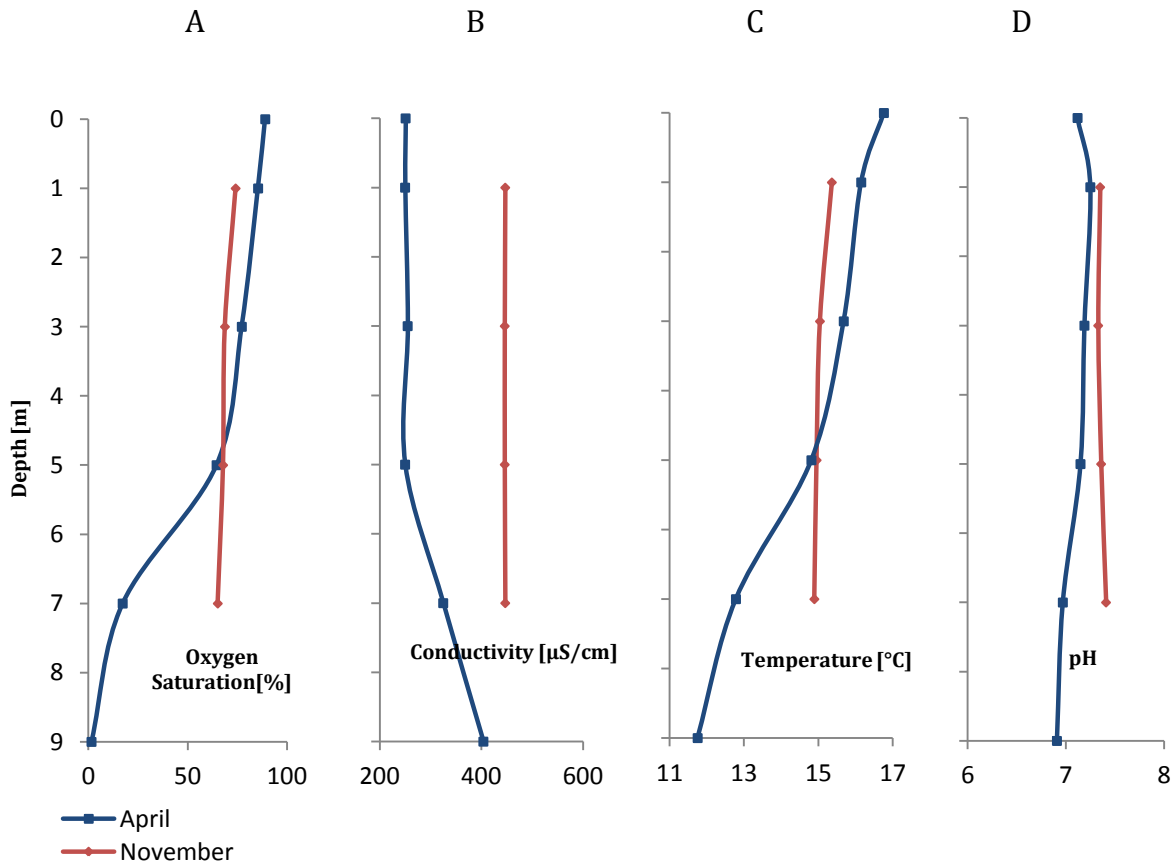
Figure 11: L1 depth profiles of oxygen saturation, specific conductivity, temperature and pH in November 2012 and April 2013

In November, oxygen saturation of the upper 3m was lower in comparison to April, but was much higher in 7m depth than in April. In April, oxygen saturation decreased strongly from 5 m on until reaching 1.5% at 9m depth (cf. fig. 11A).

In April, conductivity increased with depth, starting with 250μS/cm near the surface while maintaining this concentration down to 5m and reaching 400 μS/cm at a depth of 9 m. April conductivity was overall lower in comparison to November (cf. fig. 11B).

The temperature profile in April started with 16.8 °C near the surface, reaching 14.8°C at 5m depth and cooling more down to11.8°C at 9m depth. This was a quite different

profile in comparison to November, where the temperature reached almost constantly values around 15°C for all depths (cf. fig. 11C).

In April, pH values decreased slightly with increasing depth starting at pH 7.1 on the surface and decreasing to pH 6.9 at 9m depth. In November, there was even less dynamic as pH values showed very small fluctuations between 7.3 and 7.4 for all depths, being higher in the deeper layers (cf. fig. 11D).

3.3.2 Lake 1 Inflows

Measured cation and anion concentrations of temporary inflows to L1 in November differed between the four inflows, being mostly lower than the respective highest concentrations of L1 (cf. appendix and fig. 7). But potassium concentrations of the inflows ranged from 1.8 to 3.7 mg/l, in contrast to L1, where no potassium was detected (cf. ch. 3.3.1). Ortho phosphate concentrations of I1, I2 and I4 exceeded ortho phosphate concentrations of L1 (cf. appendix and fig. 9). Nitrate concentrations of the inflows in November accounted for I1: 0 mg/l, I2: 2 mg/l, I3:1.8 mg/l and I4: 2.6mg/l, being not much higher than the nitrate concentrations of L1 with around 2.5 mg/l (cf. fig. 10A). Ammonium concentrations of the inflows were not measured.

Ionbalances of the inflows ranged from 3 to 12%.

3.3.3 Lake 2

L2 was measured at the lakeside at 1.5m of depth in November and April with the multiparameter probe.

In November, the measured values of temperature and pH of L2 were similar to the values measured in L1 (cf. appendix). But conductivity and oxygen saturation accounted for 510 µS/cm and 53%, thus conductivity was higher and oxygen saturation lower than L1 values in November (cf. fig. 11A+B).

In April, L2 had a temperature of 14°C and was around 2°C colder than L1 (cf. fig. 11C). April conductivity of L2 was still higher in comparison with L1, being 275µS/cm (cf. fig.

51

11B), but much lower than in November. Oxygen saturation reached 44% in April, less than L1 in the respective depth (cf. fig. 11A). PH had decreased since November and accounted for 6.6 in April, being much lower than the pH of L1 (cf. fig. 11D). Ion concentrations of L2 were not measured.

3.3.4 Lake 3

L3 was measured in April at the lakeside with the multiparameter probe at a depth of 0.2 m. The measured temperature was 16.8°C, conductivity 283μS/cm, oxygen saturation 93% and ph 6.6 (cf. appendix). Overall, conductivity and pH showed quite similar values in comparison to L2. Oxygen saturation and temperature were relatively higher than the respective values of L2 (cf. appendix). Ion concentrations of L3 were not measured.

3.3.5. Lake 4

L4 was measured in November and April at various depths at the deepest point of the lake. Ion concentrations were measured from the surface water sampled at the lakeside at a depth of 0.2 m.

Ion Concentrations

Anions

Chloride
Chloride concentrations of L4 accounted for 35 mg/l in November, being very low in comparison to L1 and the wells (cf. fig. 7). April chloride concentration of 57mg/l was overall higher than L1 values but lower than the wells (cf. fig. 8).

Sulfate
Sulfate concentration of L4 in November was 12.6 mg/l and in April 12.5 mg/l. In both months, sulfate concentrations were lower than sulfate concentrations of L1 and all wells (cf. fig. 7 and 8).

Nitrate and Nitrite

Nitrate concentrations accounted for 2.9 mg/l in November and 1.2 mg/l in April, exceeding nitrate concentrations of L1 in both months (cf. ch. 3.3.1).

Nitrite was not found in L4.

Orthophosphate and total phosphate

The measured orthophosphate concentrations of L4 were 0.08 mg/l in November and 0 mg/l in April. Total phosphate accounted for 2.9 mg/l in November and 0.06 mg/l in April, thereby being relatively high in November in comparison to L1 and the wells (cf. ch. 3.1.2 and ch. 3.3.1).

Sulfide

Sulfide was not measured in L4.

Alkalinity

The measured alkalinity of L4 was 16.5 mg/l in November and 42.6 mg/l in April, thereby being lower than L1 in both months (cf. ch. 3.3.1).

Cations

Sodium

Sodium concentrations of L4 accounted for 16.5 mg/l in November and 30.6 mg/l in April. In November, the concentration was lower than L1, the April concentration was higher than L1 but lower than the wells (cf. ch. 3.1.2 and ch. 3.3.1).

Magnesium

Magnesium concentration of L4 was measured as 8.5 mg/l in November and 10 mg/l in April, showing no big changes between the seasons. In comparison to L1, L4 magnesium concentrations were lower in November, but higher in April (cf. ch. 3.3.1).

Calcium
L4 calcium concentration accounted for 6.3 mg/l in November and for 7.1 mg/l in April, being lower than L1 calcium values in both months (cf. ch. 3.3.1).

Potassium
Potassium concentrations of L4 resulted in 1.6 mg/l for November and 1.7 mg/l for April measurements, being relatively high in comparison to L1 in November (cf. ch. 3.3.1).

Ammonium
Ammonium was not measured for L4.

Ion balances
Ion balance of L4 was 6.6% in November and -0.5% in April.

Oxygen saturation, conductivity, temperature and pH

Oxygen saturation, conductivity, temperature and pH at L4 were measured with the multiparameter probe in depths of 0, 1, 3, 4m and in the maximum depth of 5m.

In April, L4 showed the same stratification patterns as L1 with oxygen saturation, temperature and pH decreasing with depth as well as conductivity increasing with depth (cf. fig. 11 and 12).

The range of oxygen saturation was from 104 % at the surface to 1.2 % at 5m of depth. Oxygen saturation decreased slightly until 1m of depth and then stronger until reaching 1.4% at 4m of depth (cf. fig. 12A).

Conductivity ranged from 238 µS/cm at the surface to 330 µS/cm at 5m of depth (cf. fig. 12B).

Water temperatures of the depth profile accounted for 19.3°C at the surface to 12.8 °C at the bottom (cf. fig. 12C).

PH values ranged from 7 to 6.7, staying constant until 1m of depth and then decreasing until 4m of depth (cf. fig. 12D).
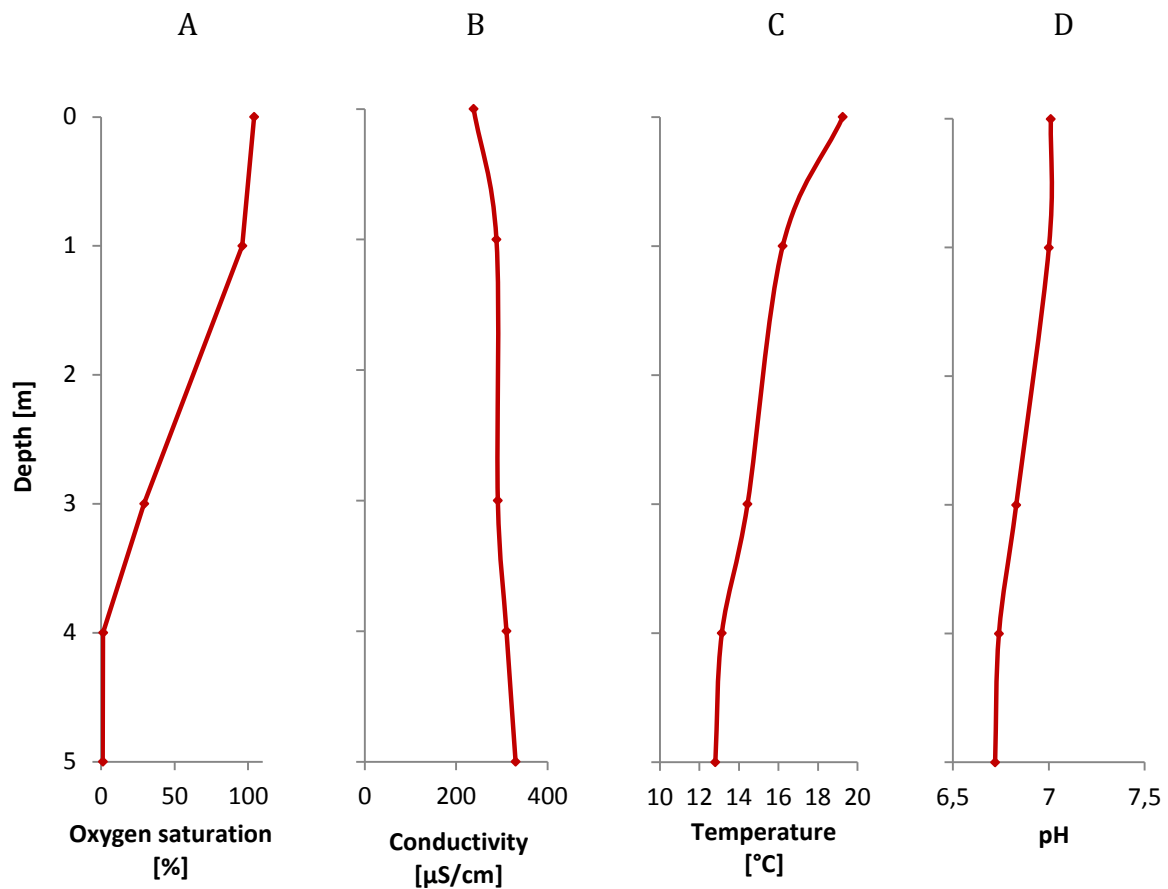
Figure 12: L4 depth profiles of oxygen saturation, specific conductivity, temperature and pH in April 2013

3.3.6 Lake 5

L5 was measured with the multiparameter probe and sampled in April at the lakeside at a depth of 0.2m. In November, L5 was not measured.

In November, L5 had some water holes but was no real lake with a continuous water table. Figure 13 shows the water table of L5 in November and April.

The measured water temperature was 18.4°C and oxygen saturation accounted for 99.2%. Conductivity was very low in comparison to the other lakes, being 84µS/cm. Ph was 7.

Results of the ion chromatography showed relatively low concentrations of cations and anions in L5 in April:

Chloride concentration accounted for 13.5 mg/l, sulfate 6.4 mg/l, sodium 11 mg/l, calcium 2.6 mg/l and magnesium 2.1 mg/l.

Nitrate concentration was 0.5 mg/l, being lower than in L4 but higher than in the upper layers of L1 (cf. ch. 3.3.1 and ch. 3.3.5).

Ortho phosphate concentration was 0.02 and total phosphate accounted for 0.6 mg/l, being higher than in L4 and in the range of L1 phosphate concentrations (cf. ch. 3.3.1 and ch. 3.3.5).

Alkalinity was measured as 16.8 mg/l.

Nitrite and Potassium were not found in L5.

Ion balance of L5 measurements was -0.9%

Figure 13: The left picture shows L5 in November 2012, viewed from the southwestern lakeside, in the back left side of the picture the dam is visible. The right picture shows L5 in April 2013, viewed from the eastwestern lakeside, in the right corner the dam is visible. SW3 is flooded by the lake.

3.4. Rainwater

Chloride concentrations of the rain samples ranged from 12 to 22 mg/l.

Sulfate concentrations resulted in 8 to 20 mg/l.

Nitrate concentrations accounted for 0 to 2.2 mg/l.

Ortho phosphate concentrations accounted for 0.08 to 0.7 mg/l. Total phosphate and alkalinity were not measured.

No cations were found in the rain samples R2-4.

R1 had a relatively high ammonium concentration of 3 mg/l and contained sodium, magnesium and calcium in concentrations of 16, 1.5 and 6 mg/l.

3.5. H and O Isotopy of ground- and surface waters

3.5.1 Local evaporation line

H and O isotopy were measured in November and April from sampled surface- and groundwaters.
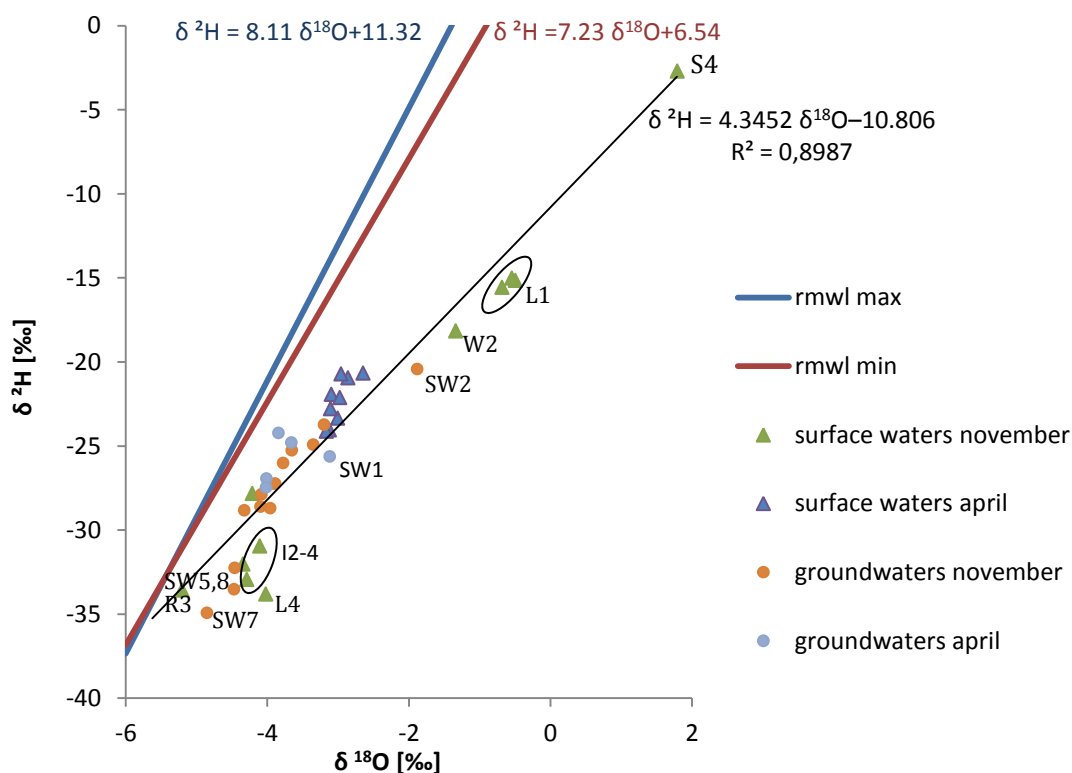
Figure 14: Regional meteoric water line maximum and minimum in blue and red colors, obtained from Carreira, Araujo et al. (2005) from measurements in Beja, South Portugal, by correlating isotope data of monthly weighted mean rainfalls in the years 2002 and 2003 (R²=0.96), and local evaporation line in black color as linear correlation of the measured δ ¹⁸O and δ ²H concentrations of the research area compared to the International Vienna Standard Mean Ocean Water.

Figure 14 shows the local evaporation line in comparison to the regional meteoric water line obtained from Carreira, Araujo et al. (2005), where the deviation of the local evaporation line shows an existing influence of evaporation on the waters in the research area. November surface waters S4, L1 and W2 showed the strongest influence by evaporation, having the heaviest isotopies. In contrast, November samples SW5, 7 and 8 as well as I2-4 and L4 had the lightest isotopies and were therefore the nearest samples to the rainwater isotopie of R3. April samples differed clearly between surface- and ground waters, where ground waters had lighter isotopies than surface waters (cf. fig. 14).

According to Gibson, Edwards et al. (1993) mean annual rain isotopic compositon of the study site was calculated to be -5.877 ‰ $\delta\,^{18}O$ and -36.342 ‰ $\delta\,^{2}H$, marking the intersection of regional meteoric water line and local evaporation line.

3.5.2 Isotopic depth profile of L1

L1 isotopy was heavier in November than in April (cf. fig. 15). November $\delta\,^{18}O$ and $\delta\,^{2}H$ values did not show stratification in lake water isotopy. In April, a clear stratification was detectable, as in depth of 7 and 9m $\delta\,^{18}O$ and $\delta\,^{2}H$ values were significantly heavier in comparison to the upper water layers of L1 (cf. fig. 15).
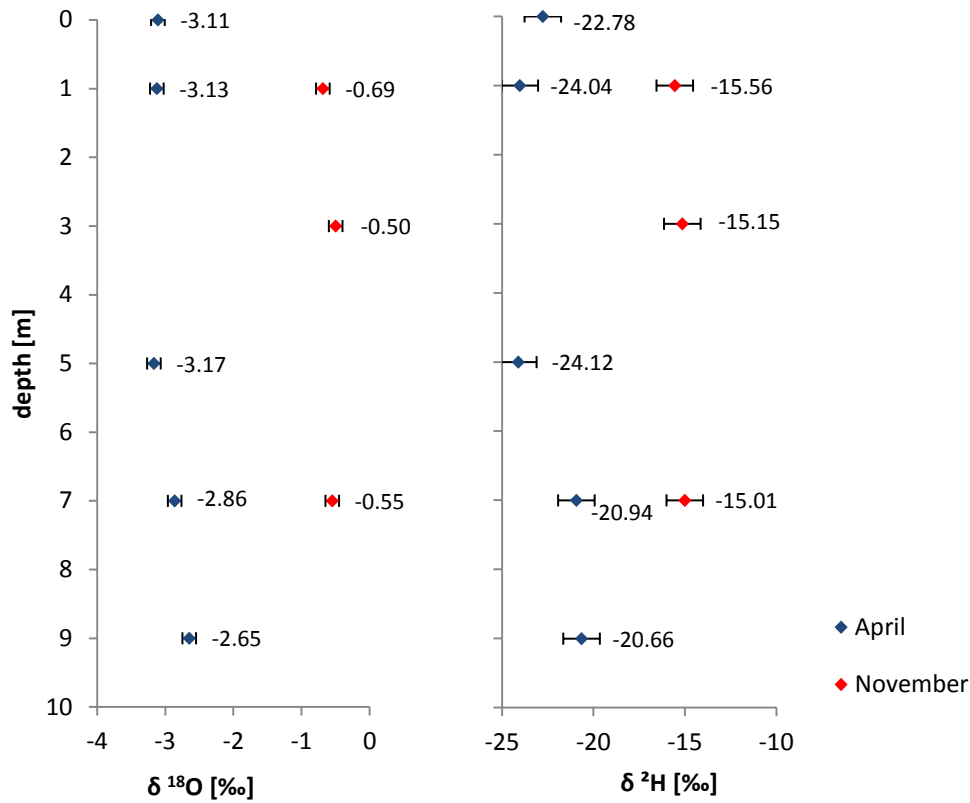
Figure 15: L1 depth profiles of δ ^{18}O and δ ^{2}H values, as compared to International Vienna Standard Mean Ocean Water, measured in November 2012 and April 2013

3.5.3 Isotopy of SW1 and L4

To detect possible influences of L4 on SW1, isotopic data of both waters were measured.

Oxygen and Hydrogen isotopies of SW1 and L4 differed in November with a difference of 0.83‰ for δ ^{18}O and 10.07‰ for δ ^{2}H, where SW1 isotopy was overall heavier than L4 isotopy. In April, the opposite was the case and the differences were relatively small, being 0.14‰ for δ ^{18}O and 3.51‰ for δ ^{2}H (cf. table 5).

	$\delta\ ^{18}O$ [‰]		$\delta\ ^{2}H$ [‰]	
	Nov 2012	**Apr 2013**	**Nov2012**	**Apr 2013**
SW1	-3,20	-3,12	-23,73	-25,62
L4	-4,03	-2,98	-33,80	-22,11

Table 5: SW1 and L4 $\delta\ ^{18}O$ and $\delta\ ^{2}H$ values, as compared to international Vienna Standard Mean Ocean Water, measured in November 2012 and April 2013. Standard deviation of $\delta\ ^{18}O$ analysis is ±0.15‰, standard deviation of $\delta\ ^{2}H$ is ±1‰.

3.6. Wastewaters

WW1 and WW3 were measured in November 2012 and April 2013, WW2 was measured in April only. Figure 16 shows ion concentrations of the wastewaters. WW3 had ion concentrations around ten times higher than WW1 and WW2, with higher concentrations in November than in April. Ion concentrations of WW2 in April were lower than WW1 concentrations. WW1 had almost constant ion concentrations in both months, but less nitrate, total phosphate, ammonium and potassium in April than in November (cf. fig. 16).

Total nitrogen concentrations of WW1 being 15.2 mg/l in November and 8.1 mg/l in April did not exceed EU maximum concentrations for urban waste water in sensitive areas of 15mg/l total nitrogen (EU 1991) in both months. Total phosphorus values exceeded EU maximum concentration for urban waste water of 2mg/l total phosphorus for sensitive areas in both months (EU 1991), being 12.7mg/l in November and 8.5 mg/l in April.
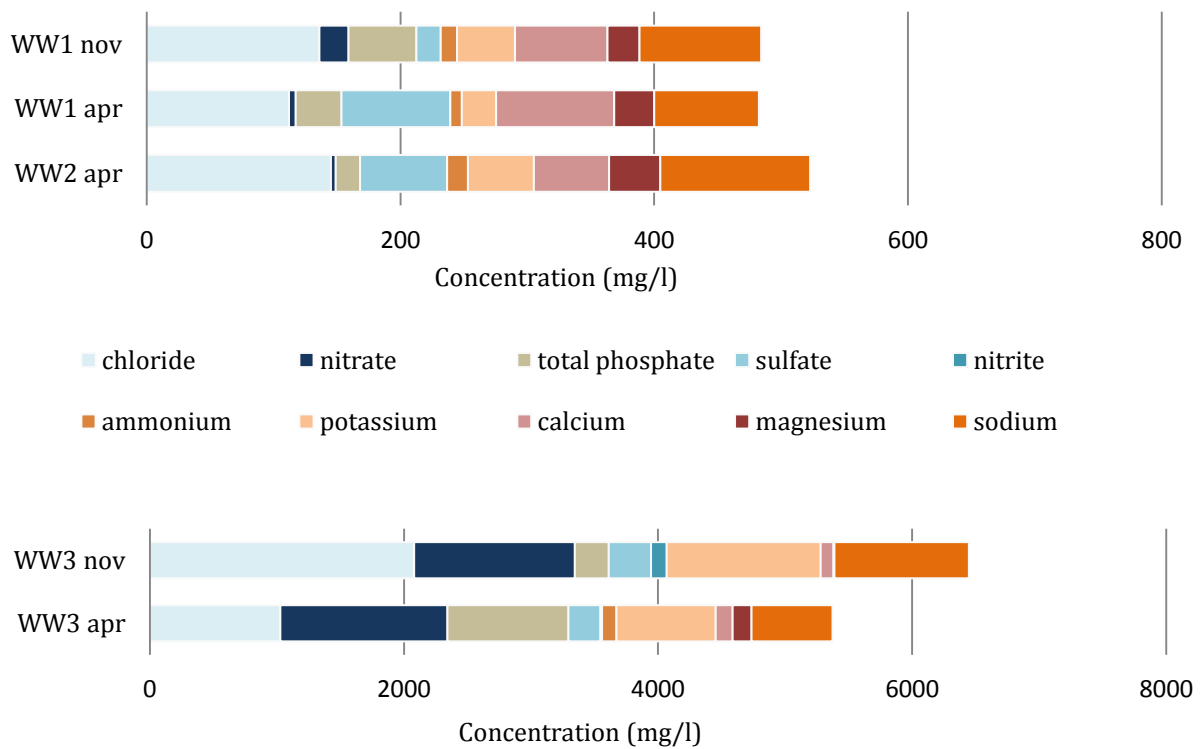
Figure 16: Wastewater ion concentrations measured in November 2012 and April 2013

4. Discussion

4.1. Water quality and water cycle

4.1.1. Groundwater tables

Figure 4 illustrates measured water tables of shallow wells from October 2012 till November 2013. In November 2012, all shallow wells showed water tables more than 2m below ground level and then went on constantly rising until reaching a maximum water table at heights between 0 and 1m below ground level between December 2012 and May 2013. Overall, deep and shallow wells rose between 2.5 and 3m between November 2012 and April 2013 (cf. fig. 4, table 3), resulting in negligible differences between deep and shallow wells in overall increase of water table. This could be a hint of the groundwater system being connected to the same aquifer.

The rise in water tables in November 2012 indicates the beginning of the rainfall period and shows the immediate reaction of the vadose zone to the precipitation. In 2012, the first rain of the season was observed at 3rd of November. On 11th of November, water tables of all shallow wells (SW3, 4, 5, 6, 8) had already risen up for at least 30cm (cf. fig. 4). Thus, the vadose zone is assumed to be highly permeable, which might be due to rock fractionations and quartz veins in the upper weathered and fractured zone of the topmost geologic layer (Chambel and Almeida 1998).

Most wells stayed at their maximum water table for around two months between March and May 2012 and then slowly dropped to a water level between 0 and 1.5m below ground level in September 2013. In November 2013 water tables filled up again reaching 0 to 1 m below ground level (cf. fig. 4). The rise of water tables in November 2013 indicates the beginning of the rainfall period in winter 2013/14. The dropdown in summer may be a result of evaporation and probably underground runoff through the vadose zone. Especially in the swampy areas of the valley evaporation might have had great impact on water tables as well as on salt accumulation in the soil (Chambel and Almeida 1998).

The rising and falling of the shallow wells reflect weather conditions throughout 2013, as water tables reached their minimum and maximum in times with longest dry spell and most rainfalls, August and March, respectively (Weather Station Beja 2013).

This shows that water tables of all shallow wells are reacting almost simultaneously to the weather conditions. However shallow wells differed in maximum water tables as well as in rising and falling velocities of the water tables (cf. fig. 4). This indicates varying hydrogeological situations of the single wells, probably caused by their geographic locations. Furthermore, vegetation covers seem to have great impact on water tables as watersheds of SW3, SW7 and SW6 with no or low tree covers (cf. table 1), showed a faster decline of water tables compared to other shallow wells with vegetation covers like SW8 and SW9 (cf. fig. 4 and table 1). Lower groundwater recharge rates in forested areas have also been reported by Scanlon, Keese et al. (2006).

Water table of SW10 continued to drop down from summer 2013 until November 2013 (cf. fig. 4). This could be a consequence of its location at 180mamsl in a steep

neighboring valley (cf. table. 1), where the first winter rainfalls most probably seep fast through the unsaturated zone into the lower parts of the landscape. Another reason could be the forested area around SW10 preventing substantial groundwater recharge during the beginning of the wet season, as forest cover strongly influences groundwater recharge rates (Scanlon, Keese et al. 2006). SW7 filled up relatively quickly in November 2012 (cf. fig. 4), which underlines the assumption that wells in deforested zones of the research area recharge and discharge more quickly.

Water tables of SW3 strongly differed from other shallow wells, with water levels around 8 m below ground level in November 2012. In May 2013 water level rose till 0m and dropped to 4m in October 2013, before filling up again to 3.6m in November 2013 (cf. fig. 4). As SW3 is located at the edge of the retention space of L5 (cf. table 1, fig. 13), it can be assumed to be highly influenced by water masses accumulating during the rainfall period in the retention area of L5. L5 was built in the year 2011, when very poor rainfalls in winter 2011/12 were reported (Weather Station Beja 2011, Weather Station Beja 2012). L5 filled up with noticeable water masses for the first time during winter 2012/13, during relatively high rainfalls (Weather Station Beja 2013). Therefore time was not sufficient for accumulation of organic and anorganic sediments at the bottom of the lake, which would substantially lower the hydraulic permeability of the retention space (Hölting and Coldewey 2013). As L5 is located in the upper part of the valley, it can be assumed that parts of the water masses which accumulated during the rain period in L5 ran down over time into the valley through the vadose zone. This might have caused water tables to fall more quickly in the area around the lake compared to other areas of the research site. The underground runoff could explain the depression of the SW3 water table curve in February 2013, when low rainfalls probably did not balance underground runoff (cf. fig. 4) (Weather Station Beja 2013). Underground runoff from L5 might percolate into the valley and contribute to runoff at the end of the valley.

In April 2013, water table of L5 did not reach the level of the dam, resulting in no significant above ground outflow of the lake in winter 2012/13 into the valley.

Furthermore, evaporation on the surface of L5 might have had a great impact on the local water tables around the lake and thus on well 3, which might have caused the steep decline of SW3 water tables during summer 2013 (cf. fig. 4).

In November, SW3 ion concentrations were much lower than ion concentrations of other ground- and surface waters and similar to rainwater (cf. fig. 7). Thus no groundwater flow into SW3 in November 2012 is assumed. Instead accumulated old rain water in the well might have caused lower ion concentrations. In the same time L5 was nearly empty, which means there was no possibility of inflowing water from L5 into SW3. With rising ground- and surface water tables in the area, SW3 probably filled up with groundwater throughout winter 2012/13 and was flooded with surface water of L5 at the end of the wet period (cf. fig. 13). Water tables equilibrated at minimum levels of 4m below ground until October 2013 (cf. fig. 4).

The rising and falling of SW3 reflects reported weather conditions much more extremely than the water tables of the other shallow wells. Hence, SW3 seems to be affected much more by weather extremes than the other wells of the area. With prospective rising water tables of L5, this pattern might change in future and could be issue of further research.

4.1.2 Water types

Water types found in the area correspond to data for the South Portuguese Zone of Chambel and Almeida (1998), who defined sodium-chloride to be the dominant hydrogeochemical facies. According to the obtained correlation values, sodium chloride and magnesium concentrations are the main causes for high conductivities of groundwaters in the area (cf. table 4).

Differences in water type of ground- and surface waters were relatively small, with the exception of SW3 and SW5 in November (cf. fig. 5). In November both wells showed low water tables, with 60cm and 20 cm above the well ground for SW3 and SW5, respectively (cf. fig. 4 and table 1). SW3 had very low ion concentrations and SW5 had a very low alkalinity in November (cf. fig. 7 and 8). Therefore both wells might have contained considerable amounts of rainwater at that time, as rain samples had lower ion concentrations compared to wells and there was no possible groundwater inflow into SW5 and SW3 in November. Around 3m away from SW5, water hole W3 is located, which had a very low conductivity and ion concentrations similar to rainwater in

November. The water of W3 can be assumed to be rain water accumulating in the water hole from the road nearby. This water then might have percolated into SW5.

Thus, the analyzed ground- and lake waters might be part of one aquifer system, as the differences in water type are relatively small and differences of SW3 and SW5 are probably caused by high mixing ratios of rain. As DW5 is about 60m deep, it could be part of the intermediate aquifer system proposed by Chambel and Almeida (1998), situated from 50m of depth on. The slightly remote position of DW5 in the Piper diagram could be a hint for this assumption. But as described by Chambel and Almeida (1998), the upper and intermediate aquifer systems can be connected by vertical rock fractures that lead to interaction of both systems. Therefore DW5 can be assumed to be influenced by the upper aquifer.

4.1.3 Conductivity of wells

The pattern of deeper ground waters having higher conductivities (cf. fig. 6) matches with the results of Chambel and Almeida (1998). According to the authors, this would be a consequence of minerals dissolving from the genuine rocks and migration of connate waters due to tectonic stresses, whereby deep mineralized waters would ascend mainly through the highly fractured rocks.

The relatively high conductivities of the shallow wells in April could be a consequence of salts originating from the subsoil and rocks, that are being dissolved by percolating rain water and accumulate in the groundwater (Chambel and Almeida 1998). But the percolating rain water might dilute the conductivity of deeper layers of groundwater, due to their relatively high conductivity (cf. fig. 6). This would explain equilibrating conductivities of deep and shallow wells in April to each other and leads to the assumption of a less stratified aquifer in this time period.

In this context, higher conductivities might indicate lower recharge rates. As conductivity correlates with chloride concentrations (cf. table 4), this also could be assumed for recharge, which accords to the results of deVries, Selaolo et al. (2000). This would mean that the intermediate aquifer zone connected to DW5 has lower recharge rates than the upper zone connected to the shallow wells, DW1 and DW2, which had

overall lower conductivities than DW5. DW5 has a possible intersection with the intermediate aquifer, as discussed already above. As the intermediate aquifer was described to have low permeability (Chambel and Almeida 1998), percolating rain water might not reach DW5 directly and thus may not dilute DW5 ion concentrations. Additionally, Hill and Neal (1997) reported deeper groundwater levels to be controlled by weathering kinetics and residence times rather than by flow mechanisms.

Furthermore, shallow wells seem to have much higher recharge rates than deep wells of the research area, as chloride concentrations in shallow wells showed consistently lower values compared to deep wells (cf. fig. 7). However, recharge rates of the single wells seem to differ, as different increases in chloride concentrations between November 2012 and April 2013 (cf. fig. 7 and 8) were measured.

DW5 was the only deep well with a higher conductivity in April than in November (cf. fig. 6), but DW3 and DW4 were not measured in both months. Therefore only DW1 and DW2 can be compared with DW5 with regard to changes in conductivity. DW5 higher conductivity in April could be influenced by the pumping, as DW5 is the only deep well which is still being pumped for watering and filling a small pond. Pumping might suck mineral particles into the area around the pump and prevent recharge, which then causes higher conductivities. As DW5 can be assumed to be part of the intermediate aquifer, the geochemical processes in the groundwater connected to DW5 might differ from the upper aquifer system. As flow mechanisms in the intermediate and deep aquifer are not known, this remains issue to further research.

Because of high conductivity of DW5, its water should not be used for irrigation, to prevent possible soil salinisation (Sequeira 2010).

4.1.4 Groundwater quality

Chloride, sodium, sulfate, magnesium and calcium in the water cycle

As discussed above, chloride could be used as an indicator for groundwater recharge and thus different increases in chloride measured in the shallow wells between

November and April generally could indicate different recharge rates for the aquifer layers around the different shallow wells.

As a general trend, all shallow wells chloride, sodium and magnesium concentrations in April were higher compared to November (cf. fig. 7 and 8). It seems that chloride, sodium and magnesium concentrations of the shallow wells were increased by percolating winter rainfalls, which probably transported the ions from the subsoil into the aquifer. This matches with the observed correlations between conductivity and chloride, sodium and magnesium concentrations, which can be assumed to be the most dynamic ions of the system and to accumulate in the percolating rain water.

Shallow wells sulfate concentrations did not change between the seasons, except at SW1 and SW5 (cf. fig. 7 and 8). The slight decline of SW1 sulfate concentration could be explained by sulfate reduction to sulfide as a result of anoxic conditions (Miao, Brusseau et al. 2012) caused by over flooding of the area around SW1 in April. Higher sulfate concentrations in November 2012 in SW5 could be caused by evaporation leading to concentration of sulfate. As SW5 had a very low water table in November 2012 (cf. fig. 4), the relation between surface and water volume in the well could trigger sulfate concentration by evaporation. Overall, sulfate concentrations of the wells seemed to be relatively stable throughout the seasons and only to be affected by changes in redox conditions or evaporation.

Calcium did not seem to play a considerable role in the water cycle, as concentrations stayed stable throughout the seasons and were relatively low (cf. fig. 7 and 8).

Thus, the main parameters indicating recharge of the aquifer system in the research area can be characterized to be chloride, sodium and magnesium. Chloride can be assumed to originate partly from the chloride containing rain (cf. fig. 7), furthermore chloride, sodium and magnesium might be dissolved by percolating rain water from the subsoil and vadose zone, where salts accumulate by evaporation through the dry season (Chambel and Almeida 1998).

Nitrate, ammonium, phosphate and potassium

Nitrate, phosphate and potassium concentrations of the wells decreased between November 2012 and April 2013 (cf. ch. 3.1.2). This might be a consequence of dilution by rain water percolating into the aquifer as discussed above.

Most shallow wells contained nitrate in November and April (cf. ch. 3.1.2). Overall, the range of nitrate concentrations in the wells was in the range of drinking water quality (EU 1998) and very low in comparison to nitrate concentrations in agricultural regions of southern Portugal, which can reach up to 50mg/l (Paralta, Carreira et al. 2007, Ribeiro and daCunha 2010). SW1 contained no nitrate in both seasons, but low concentrations of ammonium in April and low potassium concentrations in both seasons were measured (cf. ch. 3.1.2). Ammonium and potassium concentrations were in the range of maximum concentrations for drinking water (EU 1998). Thus influence of agricultural systems on geochemical parameters of SW1 seems to be in an acceptable range. Total phosphate concentrations of some shallow wells were relatively high, reaching up to 4.5 mg/l (cf. ch. 3.1.2). This could be a consequence of the sampling technique, which enabled sediments from the bottom of the well to enter the groundwater sampler. Thus, total phosphate results probably do not correspond to total phosphate concentrations of the wells, which might be much lower. Ortho phosphate concentrations were in the range of drinking water quality (EU 1998).

Overall, agricultural effects on the groundwater concentrations of nitrate, phosphate and potassium in the research area seem to be negligible under the current crop growing methods.

Alkalinity
Higher alkalinities of the shallow wells in April (cf. ch. 3.1.2) could be a result of carbonates being transported by rain percolation from the subsoil and vadose zone into the groundwater. SW1 had a lower alkalinity in April 2013 than in November 2012 (cf. ch. 3.1.2) and might have been influenced by the water quality of L4, as discussed in chapter 4.2.2.

Ferrous iron
Most wells showed relatively high ferrous iron concentrations (cf. ch. 3.1.2), which might be a result of the local geology and the generally low oxygen saturation levels of

the groundwaters. Ferrous iron concentrations of most wells exceeded the limit for drinking water of 0.5 mg/l (EU 1998).

Oxygen saturation
The generally low oxygen saturation levels of the groundwaters (cf. ch. 3.1.2) might be caused by chemical and microbial oxidation of the sulfide containing genuine rocks as well as overall microbial consumption of oxygen (Wunderly, Blowes et al. 1996).

Overall, with the newly implemented use of surface water for irrigation, a shift in groundwater quality could be possible with possibly higher recharge rates (Stigter, Carvalho Dill et al. 2006). This could also affect vegetation of the area.

4.1.5 Lakes

Lake water trophic state

According to Dokulil, Hamm et al. (2001), L1, L4 and L5 can be classified as meso- to eutrophic systems, as their total nitrogen and phosphate concentrations that accounted for maximal 1 mg/l nitrogen and for 20 to >100 mg/m^3 phosphate (cf. ch. 3.3). Nitrogen concentrations of the lakes did not exceed the mesotrophic limit, but total phosphate concentrations of L1 and L4 in November were even above the eutrophic limit of 100mg/m^3 and in the range of hypertrophic systems. High total phosphate concentrations in November might partly be a result of microbial activity (Jansson 1988), possible phosphate release from the sediment (Boström, Andersen et al. 1988) and particle input by surface runoff into the lakes (Sonzogni, Chapra et al. 1982), especially in L1 which was observed to have various inflows. The sediment particles caused yellow-brown colors of the lakes in November and April, and very low visibility depths located very near to the surface of the lakes.

Even that L5 is very young, April phosphate and nitrate concentrations were already in the mesotrophic range (cf. ch. 3.3) and could indicate a possible future meso- to eutrophic lake ecology.

Future monitoring of the lakes trophic state seems to be essential because of already relatively high phosphate concentrations.

Stratification of L1 and L4

Since L1 and L4 ion concentrations and conductivity increased overall with depth (cf. fig. 8, fig. 11B and 12B), density of deeper layers in L1 and L4 can be assumed to be higher in comparison to the upper layers in the water column in April. As November ion concentrations and conductivity of L1 were overall much higher than in April, but similar to April values at 9m of depth, a layer of older salty water at the bottom of L1 in April can be assumed, which remained due to higher density (Boehrer and Schultze 2008). Consequently, it can be assumed that old lake water stayed in the deeper layers as new water originating from rain and surface runoff accumulated on top during winter rainfalls, after the mixing period in autumn. In November, there was no evidence for stratification of L1, as ion concentrations, conductivity, temperature, oxygen saturation and pH did not show any stratification (cf. fig. 8 and 11). This could possibly indicate monomictic behavior of L1, coinciding with the findings of Morais, Serafim et al. (2007). According to the authors, wind and decrease in temperature cause a complete mixing of water bodies in October. Hence, a mixing of the deeper layers with the upper layers in autumn and winter can be assumed, ceasing at the end of the rain season, when stratification occurs. According to Morais, Serafim et al. (2007), this pattern was also observed in a South Portuguese water reservoir, with a mixing period in autumn and winter and a very defined stratification period from May to September.

With regard to the mixing type of L1, it must be considered that the system is very young and dynamic, because of high oscillations in water table and the recent construction of the water retention spaces since 2006. Hence, the observed trend of monomictic behavior of L1 might change over time. Additionally, as this study observed only one year the overall mixing type of the lake might differ from the observed trend on the long run. Therefore, further studies about stratification and lake water quality should be conducted over longer time periods.

Total phosphate concentrations of L1 decreased with depth in November (cf. fig. 9), which could be a result of higher microbial activity in the upper layers of the water

column and sediment particles input into the upper water column by surface runoff (Sonzogni, Chapra et al. 1982, Jansson 1988). In the deeper layers of the water column, ortho and total phosphate almost reached the same levels in November (cf. fig. 9), which is a hint for possibly lower microbial activity in the deeper layers of the water column at that time (Jansson 1988).

At 0, 2 to 5 and 9m of depth in April, when ortho phosphate accounted for around 0mg/l and total phosphate concentrations were relatively high, higher activity of microorganisms can be assumed (Jansson 1988). This might have led to a complete consumption of ortho phosphate at the respective depths (cf. fig. 9). Thus, stratification of microbial activity in April showed an oscillating pattern in the water column, being the highest at the surface, at 5m of depth and at the bottom of the lake, respectively 9m of depth (cf. fig. 9).

This leads to the assumption of three different major microbial communities present in the water column of L1 in April, according to Jansson (1988) and Shade, Kent et al. (2007). At first a photosynthetic community situated at the surface is assumed. Second, another community of hetero- and autotrophic microorganisms might dominate the layers between 1 and 7m of depth. At last a microbial community adapted to low oxygen saturations is most likely to grow in the deepest layer from 7m on. From 5m of depth downwards, a decline in temperature and oxygen was observed, as well as strongly increasing conductivity from 5m on to the bottom of the lake (cf. fig. 11). This could explain the increasing ortho phosphate concentrations from 5m downwards until 7m of depth, as the microbial activity probably was affected by the changing parameters. From 7m on to the bottom of the lake, the lowest microbial community of possibly anoxic microorganisms might be situated, as ortho phosphate decreased again from 7m on, probably because of microbial consumption (Jansson 1988).

Because of the observed zero concentrations of ortho phosphate in L1 water column (cf. fig. 9), it can be assumed that phosphate was the limiting element of the system in April.

No stratification in nitrate concentrations in November and April (cf. fig. 10A) might be a consequence of aerobic conditions throughout the water column impeding denitrification (Keeney 1973).

Slight decrease in ammonium concentrations connected to slightly increasing nitrate concentrations at the bottom of L1 in April (cf. fig. 10B) leads to the assumption of microbial nitrification (Keeney 1973). April and November ammonium concentrations were very similar, in contrast to other ion concentrations. This might be a consequence of constant ammonium inputs by surface runoff, rain and groundwater.

Nitrogen concentrations of L1 did not seem to limit microbial activity, as no zero concentrations in ammonium and nitrate were observed (cf. fig. 10), even that concentrations were low. Thus, constant nitrogen inputs into L1 could be a possible cause, which might lead to nitrogen accumulation over time.

In April, L4 showed stratification in conductivity, oxygen saturation, pH and temperature similar to L1 with a slighter increase in conductivity with depth (cf. fig. 11, 12). As L4 is overall shallower than L1, this might be a possible cause for a less defined stratification in conductivity in April (Boehrer and Schultze 2008).

Lake water quality

L5 ion concentrations were very low (cf. fig. 8), but nitrate and phosphate concentrations were in range of L1 and L4 (cf. ch. 3.3). L5 was built in 2011 and filled for the first time in winter 2012/13 with considerable amounts of rain and surface runoff. The very low ion concentrations reflect the origin of the lake water directly from rain.

Lower ion concentrations and conductivities of L1 in April in comparison to November (cf. fig. 7 and 8) might be caused by dilution from rain and surface runoff accumulating in the lakes, as analyses of surface runoff suggests considerable amounts of anion inputs by rain (cf. fig. 7). As the inflows I1-4 were measured at the beginning of the rainfall period in November 2012, it can be assumed that they transported salts and particles accumulated in the subsoil during the dry season (Chambel and Almeida 1998) to a greater extent in November as at the end of the wet season, where most particles and salts might have been washed out already. Thus, ion concentration input into the lakes by inflowing surface runoff might have been much lower at the end of the wet season (Hill and Neal 1997), which could explain the relatively low ion concentrations of the lakes in April 2012 in relation to the ion concentrations of I1-4 in November.

Furthermore, the positions of L1 November and April samples in the Piper diagram indicate slight dilution of L1, as partitions of ion slightly changed between the seasons, but ion concentrations did change substantially (cf. fig. 5,7,8). Input by surface runoff into L1 might have changed ion composition, which could explain the slight change of L1 position in the Piper diagram between the seasons.

Especially potassium input seemed to be relatively high, as potassium concentrations, in contrast to all other measured ions of L1, were even higher than in November, (cf. ch. 3.3).

Overall low ion concentrations of L4 in November (cf. fig. 7) might indicate low influences of groundwater on the lake during the dry season. But it has to be considered, that only the surface of the lake was analyzed and thus no assumptions can be made for the deeper layers of L4 in November. In April, L4 had overall higher or similar ion concentrations in comparison to November. Especially L4 sodium, chloride and alkalinity concentrations were much elevated in April (cf. ch. 3.3). The change of position in the Piper diagram of L4 between the seasons indicates a change in water composition (cf. fig. 5). This might have been caused by ion inputs from surface runoff, rain and groundwater inflow during the wet season. L4 is shallower and smaller than L1 (cf. table 1 and fig. 3) and thus has a smaller volume, which means that the ion inputs during the wet season could probably raise lake water ion concentrations to a greater extent and much more quickly than in L1.

L4 phosphate and nitrate concentrations did not follow this pattern, as November values were higher than April values (cf. ch. 3.3). This could be a result of phosphate fixation in the sediment during winter (Boström, Andersen et al. 1988, Gächter and Müller 2003) as well as of dilution by rain and inflows. In comparison with L1, April L4 nitrate concentrations were still higher (cf. ch.3.3).

The relatively high nutrient concentrations of L4 in comparison to L1 (cf. ch. 3.3.1 and 3.3.5) might be a result of the location of L4. It is situated below agricultural terraces, from where leaching of nutrients is bound to occur (cf. table 1) (Paralta, Carreira et al. 2007).

Very low oxygen saturation levels in April at the bottom of L1 and L4 indicate possible anoxia in the sediment (cf. fig. 11A and 12A). Upwelling of low oxygen waters from the

deeper layers at the beginning of the mixing period in autumn can cause generally low oxygen concentrations throughout the water column and affect biological communities (Morais, Serafim et al. 2007).

Anoxia in the sediment of L1 and L4 during summer could cause phosphate release from the sediment and might affect the benthic fauna (Boers and van Hese 1988, Boström, Andersen et al. 1988, Karlson, Rosenberg et al. 2002). Hence, phosphate released by the sediment in summer probably mixes into the water column during the mixing period in autumn. This could promote primary production and growth of cyanobacteria (Morais, Serafim et al. 2007) The observed high November ortho and total phosphate concentrations of L1 and L4 underline these assumptions (cf. fig. 9 and chapter 3.3.).

Furthermore, particulate phosphate input from surface runoff might have substantially contributed to the overall high total phosphate concentrations of the lakes. This assumption is strengthened by the observation that the lakes water was very turbid in November. Particulate phosphate from runoff might exhibit low bioavailability (Sonzogni, Chapra et al. 1982) and thus might not be able to contribute to microbial growth in a great extent.

As the sediment layer of L1, L4 and L5 is relatively young and thus probably still thin, processes of phosphate immobilization and release by the sediment might develop over time with more intensity. This could increase the risk of cyanobacteria bloom in summer, when high light and eventually low nitrate availabilities foster cyanobacterial growth (Morais, Serafim et al. 2007). Cyanobacteria can produce metabolites, such as microcystins, which were reported to be toxic to wildlife and livestocks and might cause human fatalities (Mez, Beattie et al. 1997, Jochimsen, Carmichael et al. 1998). Additionally, phosphate can be expected to further accumulate in the lakes, due to the measured high ortho phosphate concentrations of rainfall and phosphate input by temporary inflows (cf. fig. 7). As reported by Price (1999), nutrient leaching from agricultural areas and municipal sources increase the risk of toxic algae bloom that could affect the water supply. Therefore the prevention of anthropogenic and agricultural phosphate inputs into the lakes is crucial for future lake ecology and sustainability of the research area.

Relatively high ion concentrations of L1 and high conductivities of L2 and L3 in November (cf. fig. 6 and 7) could cause increases in soil and groundwater salinity when used for irrigation (Stigter, Carvalho Dill et al. 2006, Sequeira 2010).

Overall, seasonal variations of the water quality observed in the research area covered a wide range, as a result of climate seasonality and particularly rainfall and solar heating (Chapman 1996). Because of this, establishment of seasonal monitoring programmes for estimations of water quality is essential (Simeonov, Stratis et al. 2003, Serafim, Morais et al. 2006). Additionally, monitoring of soil salinity should be applied.

Differences between lakes

Slight to moderate variations in temperature, pH and oxygen saturation between the analyzed lakes of the research area (cf. ch. 3.3) indicate varying ecological situations of the single lakes, reflecting the different geographical locations and lake morphologies as well as environments of the lakes, some of them influenced by agriculture. Overall similarities in conductivity and stratification indicate rather small differences in lake ecology and stratification between the lakes. But differences in nutrient concentrations, probably caused by varying agricultural influences on the single lakes, should be considered for further monitoring.

4.1.6 Rain water

Chlorite, sulfate, phosphate and nitrate inputs by rain seem to contribute substantially to the respective ion concentrations of surface- and groundwaters in the research area (cf. fig. 7 and ch. 3.4). Particularly chloride input by rain has to be considered for further monitoring studies, if chloride mass balances would be applied (Gee, Zhang et al. 2005) . The research site is located at 30km distance to the coast of the Atlantic and thus can be assumed to be influenced by chloridic rains coming from the sea. Ion concentrations of rain seem to oscillate, as rain ion concentrations differed between the samples (cf. fig. 7).

Chlorite, sulfate, phosphate and nitrate concentrations in surface waters of the area seem to be influenced not by rain ion inputs alone, as surface water ion concentrations

were overall higher than rain ion concentrations (cf. fig. 7 and 8). Other possible ion inputs into surface waters might originate from surface runoff and/or groundwater.

Sample R1 showed abnormally high ion concentrations, especially ammonium, which could be a result of oscillations in the atmosphere ion concentrations or contamination during sampling or analysis (cf. fig. 7).

4.1.7 Ion Balances

Some samples had ion balances exceeding ±5%. The maximum deviance was 12% at I4 in November and -9% at SW10 in April. These could be caused by sampling and transport or might be a result of cations bond in chemical complexes that could not be broken up during analysis (Hölting and Coldewey 2013). Most ion balances were in the appropriate range of ±5%, thus the obtained results provide overall reliable informations about water quality in the research area.

4.1.8 Isotopic composition of ground- and surface waters

$\delta\,^{18}O$ and $\delta\,^{2}H$ results indicate a trend of heavier waters in the northern and lower area of the research area (cf. fig. 14). In detail, S1, W2 and L1 that are situated at the northern end of the valley (cf. fig. 3) showed a relatively heavy isotopic signature, while SW5, 7 and 8 and L4, located in the southern and steeper part of the valley, exhibited relatively light isotopic signatures more similar to rain water (cf. fig. 3 and 14).

Thus, the influence of evaporation on the waters during their way down through the valley is reflected on the isotopic data, as evaporation causes enrichment in both heavy isotopes, $\delta\,^{18}O$ and $\delta\,^{2}H$ (Gibson, Edwards et al. 1993). According to the authors, meteoric waters that have undergone evaporation display systematic enrichment in both $\delta\,^{18}O$ and $\delta\,^{2}H$, resulting in a divergence from the meteoric water line along evaporation lines with slopes of less than 8 and often in the range 4 to 6. The obtained evaporation line matches these findings.

Another factor contributing to changes in isotopic water composition could be microbial activity as microorganisms contribute to isotope fractionation by assimilating the lighter isotopes (Knöller, Vogt et al. 2006).

Rain sample R3 showed an influence of evaporation, as its location was closer to the local evaporation line than to the meteoric water line (cf. fig. 14). This might be a result of the sampling procedure in an open beaker for several hours.

The calculated mean annual isotopic signature of rain almost matches the isotopic composition of R3 (cf. ch. 3.5.1). But isotopic compositions of rain in the research area might vary throughout the seasons, because of temperature-dependent effects during condensation of atmospheric vapor and air-mass history. As consequence, variations in the isotopic composition of precipitation result in seasonal shifts along the meteoric water line (Dansgaard 1964).

Isotopic signature of L1 indicates the origin from rain combined with influences of evaporation as $\delta\,^{18}O$ and $\delta\,^{2}H$ values are much heavier than rain values and located near to the evaporation line (cf. fig. 14).

In April, a clear overall difference between ground- and surface water isotopic signatures was observed, most probably due to greater influence by evaporation (cf. fig. 14). In contrast, isotopic signatures in November indicate great variation in evaporation influences on waters of the research area. The influence of evaporation was greater in November than in April (cf. fig. 14). Less variation of April isotopic signatures can be assumed to be caused by dilution of the waters with rain during the wet season. This reflects seasonal climatic variations of dry and hot summers and wet winters as well as the different hydrogeological situations of the single wells and water bodies. Therefore it has to be taken into account that quality of waters in the research area is influenced by varying parameters.

Isotopic stratification of L1 matches the results obtained from ion concentrations and the hypothesis of disposition of old lake water in the deeper layers in April (cf. fig. 15). In November, isotopic signatures showed no stratification of the water column, matching the results of ion concentrations and other parameters (cf. fig. 15).

Isotopic signatures of November indicate elevated influence of evaporation on L1 water compared to April, due to enrichment of heavy isotopes in November. This matches the climatic seasonality of the region.

4.2. Interactions between ground- and surface water

4.2.1 Groundwater leakage into lakes

Groundwater leakage into L1 can be assumed to occur mostly in the deeper layers of the lake, where possible intersections with the groundwater table would be located. But isotopic signatures of L1 indicate no substantial influence of groundwater in the deeper layers. Groundwater leakage into L1 would be reflected on the isotopic results measured in L1, but L1 November isotopic results were much lower than groundwater isotopic results (cf. fig. 14 and 15). Therefore little influence of groundwater leakage on L1 in November can be assumed. A possible groundwater inflow into L1 in April seems to be relatively small, as April isotopic compositions of L1 were clearly enriched by heavy isotopes compared to groundwater, especially in the lower layers of the lake (cf. fig. 14 and 15).

In order to determine annual volumes of eventually inflowing groundwater into L1, lake water and groundwater samples from the area around L1 should be analyzed throughout the year. This would enable to apply stable isotope mass balance with mean annual $\delta\,^{18}$O and $\delta\,^{2}$H values from rain, lake and groundwater (Krabbenhoft, Bowser et al. 1990).

In November, conductivity of L1 and L2 was similar to conductivity of shallow wells, whereas conductivities in April of all measured lakes showed lower values than conductivities of all wells (cf. fig. 6). Similar conductivities of shallow wells, L1 and L2 might indicate a rather high influence of groundwater on the lakes during the dry season. But isotopic signatures revealed no similarities between L1 and the shallow or deep wells in November, which contradicts the assumption of inflowing groundwater in November. The relatively high lake water conductivities in November can be assumed to be a result of evaporation. As isotopic composition of L2 was not measured in November, groundwater inflow into L2 in November is not known.

L4 showed ion concentrations very similar to rain water in November; hence mainly rainwater might have been in the lake.

The relatively low lake water conductivities of all measured lakes in April (L1, L2, L3, L4, L5) could be a hint for a low influence of groundwater on lake water compositions during the wet season (cf. fig. 6). This matches the position of the surface waters in April above the groundwaters on the evaporation line (cf. fig. 14), indicating no similarities between ground- and surface waters, except for SW1.

Conductivity of L5 in April was very low and ion concentrations were similar to rain water (cf.fig. 6, 7 and 8) which underlines the assumption of no remarkable amounts of groundwater in the lake at that time.

Water tables of SW3 could give a rough idea of interactions between SW3 and L5. In comparison to October 2012, SW3 had a much higher water table in October 2013 (cf. fig. 4). As discussed in chapter 4.1.1, SW3 water table seems to be highly influenced by L5. The difference of SW3 water tables in October 2012 and October 2013 was about 4m, which is much more than the difference between October 2012 and 2013 of other shallow wells showing differences of around 2.5m (cf. fig. 4). This could be a result of the construction of L5. But to know the volume of exfiltrating water, data of the leakage coefficients of the lake sediments and lake floors are needed to apply Darcy´s law (Hölting and Coldewey 2013). These values could not be measured and should be analyzed for further research.

To compare yearly mean water tables of SW3 over longer time periods with varying annual precipitations, more research has to be done. Then a possible influence of L5 on the surrounding groundwater tables might be confirmed or rejected.

Hence, SW3 could be useful for monitoring groundwater tables in the water retention space of L5 during summer when water of L5 is not flooding SW3, but probably influences the groundwater tables of the area. If L5 water tables would be monitored as well, it would be possible to detect exfiltration into the groundwater in the area around SW3 by comparing water tables of SW3 and L5 (Hölting and Coldewey 2013).

4.2.2 Lake 4 leakage into SW1

Isotope analysis results of SW1 and L4 show no clear influence of L4 on SW1 in November, but standard deviations of April δ ^{18}O values of SW1 and L4 were overlapping (cf. table 5). This might indicate SW1 to be influenced by L4 in April. Standard deviations of SW1 and L4 δ ^{2}H values did not overlap in April, but values were close to each other (cf. table 5). Additionally, SW1 isotopic values measured in April were located between surface and groundwater isotopic compositions (cf. fig. 14). Furthermore, SW1 April conductivity and ion concentrations were very low in comparison to other shallow wells and similar to L4 (cf. fig. 6, 7 and 8).

Thus, it can be assumed that April SW1 water was leaking water from L4 probably mixed with some groundwater. Especially measured chloride concentrations go in line with this assumption, as April SW1 chloride concentrations were very low in comparison to the other wells and similar to L4 concentrations (cf. fig. 8).

In November, SW1 seemed to be influenced mainly by groundwater, as ion concentrations, conductivity and isotopy were in the range of most other shallow wells (cf. fig. 6, 7, 8, 14 and table 5). However, an influence of L4 on SW1 cannot be excluded for November.

As SW1 seemed to be fed mainly by groundwater in November 2012, possible effects on the local groundwater table by pumping during the dry season might occur. This could eventually lead to consequences for the surrounding vegetation and has to be considered for further monitoring. But as L5 can be expected to fill up over time and to influence the quantity of groundwater in the valley, the groundwater situation in SW1 area might change during the next years.

Furthermore, sodium and chloride concentrations of SW1 and SW4 increased much less between the seasons compared to concentrations of other shallow wells (cf. fig. 7 and 8). As SW1 and SW4 are located in the valley below L5 and L4, both wells can be assumed to be influenced by leaking lake water, showing relatively low sodium and chloride concentrations in April (cf. fig. 8 and ch. 4.1).

Therefore, water quality of the water supply in the village seems to be highly dependent on L4 and probably also L5 water quality. The influence of L5 on SW1 might increase over time.

4.2.3 L1 leakage into S3

Similar ion concentrations in November of S3 and L1 indicate a possible leakage of L1 into S3. However, a strong influence by groundwater on S3 cannot be excluded, as S3 ion concentrations were in the range of groundwater ion concentrations of November (cf. fig. 7). S3 showed the highest enrichment of heavy isotopes compared to all other waters of the research area. Thus, S3 can be assumed to have been highly influenced by evaporation, as S3 water accumulated below the L1 dam in a shallow basin exposed to the sun. Isotopic results did not show similarities between S3 and L1 in November and between S3 and groundwater (cf. fig. 14). Therefore it can be assumed that only small amounts of water came out of the spring at that time.

In April, S3 was flooded by L1 outflow through pipes in the middle of L1 dam, thus April conductivity and ion concentrations of S3 were almost identical with L1 (cf. fig. 6 and 8).

4.3 Water supply

SW1 provides drinking water for the village, which in terms of ion concentrations has good quality (cf. ch. 3.2). If current agricultural practices in the watershed of SW1 do not change the water can be expected to stay safe with regards to these parameters. The implementation of SW1 marks a step towards sustainable water supply compared to the former practice of deep well pumping. This is especially true as the well seems to be fed by the overlying lake L4 (cf. ch. 4.2.2) which was still filled with water in November 2012, after almost two years of very poor rainfall (Weather Station Beja 2011, Weather Station Beja 2012). In fact, nowadays the water supply of the village not only relies on groundwater but to a great extent on the water retention space of L4 and probably the overlying retention spaces of L5 and other smaller lakes. This can be assumed to contribute to the groundwater flow in the valley, where SW1 is located (cf. ch. 4.2.2 and

4.1.1). But it has to be considered, that with future accumulation of sediments in L4 and L5, leakage of the lakes might reduce, because of decreased permeability of sediment layers at the lake bottoms (Hölting and Coldewey 2013).

L4 was assumed to be influenced by nutrient leaching from the surrounding agricultural terraces (cf. ch. 4.1.5). Therefore regular control of SW1 water quality is crucial.

Another important issue connected to lake water nutrient contents is the possible growth of cyanobacteria (Morais, Serafim et al. 2007), which could affect human and animals health (cf. ch. 4.1.5). The growth of blue-green algae during the dry season has been reported e.g. for the water reservoir Alqueva Dam in South Portugal, which was classified as eutrophic system (Morais, Serafim et al. 2007). Since substantial cyanobacteria growth is connected to high water temperatures and high phosphate concentrations (Morais, Serafim et al. 2007), critical formation of blue-green algae in lakes on the research site might occur in summer, when water concentrations of phosphate rise substantially. However, blooms in winter have been reported for South Portuguese waters as well (Galvao, Reis et al. 2008). This could happen, when agricultural and land management practices would change, e.g. by introduction of livestock, waste water disposal into the lakes or higher application of fertilizers in the catchment area.

Without fail, regular seasonal monitoring of the water qualities on the research site is crucial for safe water supply and environmental conservation.

Ion concentrations of the analyzed tap water samples did not exceed threshold limits (cf. ch. 3.2.), except for iron concentrations of the storage tanks. Measured ferrous iron concentrations in the water supply chain leads to the assumption of substantial amounts of iron accumulating in the pipe system connected directly to SW1. As ferrous iron concentrations in the water in the storage tanks was much lower compared to the water of SW1 (cf. ch. 3.2.), absent iron can be assumed to remain in the pipes as a corrosive layer on the pipe walls (Lin, Ellaway et al. 2001) or to accumulate in parts at the bottom of the storage tanks as iron(III).

To prevent possible further corrosion of the pipes and to lower ferrous iron concentration in the water supply, measures that aerate the water directly after leaving the well should be applied. Aeration followed by rapid sand filtration is usually

recommended for oxidizing ferrous iron in waters with high iron concentration, which is cheaper than application of chemicals so that costs for chemicals can be avoided (Wong 1984).

4.4. Waste water management

The effectiveness of the septic tank seems to be quite good, as WW2 nutrient concentration was around ten times lower than WW3 concentrations in April (cf. fig. 16). But as WW1 reed bed phosphorus outputs were exceeding EU limits in both months and differences in nutrient concentrations between WW1 and WW2 were relatively small (cf. fig. 16 and ch. 3.6), the capacity of the reed bed seems not to be appropriate. Therefore the size of the reed bed should be adjusted or waste water treatment should be improved elsewise.

4.5 Monitoring

4.5.1 Water quality and lake ecology

As mentioned above, further monitoring of water quality of the research area in relation to water supply is crucial for safe water supply. Because of high seasonal and interannual climatologic variations, monitoring that provides representative and reliable informations about water qualities is crucial (Simeonov, Stratis et al. 2003, Serafim, Morais et al. 2006).
Especially possible nutrient input by agriculture and eventual municipal discharge as well as cyanobacteria density should be measured regularly (cf. ch.4.1.5 and 4.3).

Monitoring of lake stratifications would help to understand lake ecology and to track possible changes in lake ecology over time, especially with regard to eutrophication (cf. ch. 4.1.5). This could be of special interest in case of further aquaculture application.

The observed variations in lake ecology between the different lakes of the research site might lead to differing effects of possibly changing environmental parameters, such as mean annual temperature, wind velocity, nutrient input and surface runoff. This should be considered for further monitoring.

Additionally, monitoring of waste water nutrient loads is essential for environmental conservation (cf. ch.4.4).

4.5.2 Groundwater recharge

To monitor sustainability of the water supply at Tamera ecovillage quantitatively, recharge rates together with extraction rates should be evaluated regularly. Higher extraction rates than recharge rates over long time periods would lead to overexploitation.

Various direct and indirect methods for monitoring groundwater recharge on the research site could be applied as listed in Paralta and Oliveira (2005) and Scanlon, Healy et al. (2002). Among them are:

-Measurement of piezomteric fluctuations

Monitoring of water tables and precipitation over long time periods with fixed data loggers and measurements of the hydraulic conductivity could be applied for measuring the relationship between groundwater table and recharge rates and thus enable assessment of long term effects of the water retention landscape on groundwater tables. Thereby comparison between groundwater tables of the study site and of neighboring valleys would enable to evaluate effects of the water retention landscape on groundwater dynamics on the study site in comparison to aquifers of non-influenced valleys.

-Water and physical balance studies

By implementation of a local weather station and analysis of weather data, exact precipitation and evapotranspiration values could be obtained for physical balance studies.

Additionally, monitoring of precipitation and water volumes of the area accompanied by constant measurements of outflowing water masses from the research area would enable water balance studies.

4.5.3 Tracer techniques

Application of long term chloride mass balance studies could help to understand groundwater recharge processes of the research area in more detail. Required data include annual precipitation, total chloride input from dry fallout and precipitation, as well as pore water chloride concentrations (Gee, Zhang et al. 2005).

Long term evaluation of lake, groundwater and rain $\delta\ ^{18}O$ and $\delta\ ^{2}H$ values would enable further studies about ground-and lake water interactions by applying the stable isotope mass balance method (Krabbenhoft, Bowser et al. 1990).

Conclusions

Overall great seasonal variations of ground- and surface water quality in the water retention landscape were observed. Consequently seasonal measurements of water quality and groundwater recharge are crucial for further monitoring. Influences of agriculture and evaporation might affect water quality of artificial lakes and aquifer of the water retention landscape over time. But if current agricultural practice is continued and regular monitoring of water quality is applied, water supply seems to be safe in terms of the measured biogeochemical parameters.

The measured high nutrient outputs from the waste water system of the village into the surrounding surface waters lead to the conclusion that a change in waste water management of the village is needed. The reed bed should be adjusted to the discharge rates of the settlement and monitoring of nutrient outflows into surface waters from the reed bed should be applied regularly in order to prevent further eutrophication of the lakes.

L4 and L1 seemed to leak into the aquifer system at the beginning of the wet season and leakage of L5 during the wet season was assumed. No substantial groundwater inflow into the lakes was found. However, it is not sure whether lakes of the water retention landscape exfiltrate into the aquifer constantly.

Finally it can be concluded that the water supply at Tamera ecovillage by the artificial lakes of the water retention landscape secures sustainable water supply from surface runoff and rain, thus being much more sustainable than the former deep well pumping in the area. This could be a model for agricultural and land regeneration of semi-arid regions.

Acknowledgements

References

Boehrer, B. and M. Schultze (2008). "Stratification of lakes." Reviews of Geophysics **46**(2): RG2005.

Boers, P. C. M. and O. van Hese (1988). "Phosphorus release from the peaty sediments of the Loosdrecht Lakes (The Netherlands)." Water Research **22**(3): 355-363.

Boström, B., et al. (1988). Exchange of Phosphorus Across the Sediment-Water Interface. Phosphorus in Freshwater Ecosystems. G. Persson and M. Jansson, Springer Netherlands. **48:** 229-244.

Carreira, P. M. M., et al. (2005). Isotopic composition of rain and water vapour samples from Lisbon region: a characterization of monthly and daily events. Isotopic composition of precipitation in the Mediterranean Basin in relation to air circulation patterns and climate. Vienna, Austria, Isotope Hydrology Section, International Atomic Energy Agency.

Chambel, A. (2006). Groundwater in semi-arid mediterranean areas. Groundwater and Ecosystems-NATO science series: Earth and environmental sciences. A. Baba, F. W. F. Howard and O. Gunduz, Springer.

Chambel, A. and C. Almeida (1998). Origin of highly mineralised waters in a semi-aridarea of the South Portugueses Zone (Portugal). XXVIII Congress of the International Association of Hydrogeologists and the annual meeting of the American Institute of Hydrologists. B. e. al. Las Vegas, Nevada, USA.

Chapman, D. (1996). Water Quality Assessments - A Guide to Use of Biota, Sediments and Water in Environmental Monitoring-Second Edition Cambridge , GB, Chapman & Hall.

Correia, T. P. (1993). "Threatened landscape in Alentejo, Portugal: the 'montado' and other 'agro-silvo-pastoral' systems." Landscape and Urban Planning **24**(1–4): 43-48.

Cunha, L. V., et al. (2006). Alterações Climáticas em Portugal: Cenários, Impactos e Medidas de Adaptação, projecto SIAM II. Lisbon, Portugal.

Dansgaard, W. (1964). "Stable isotopes in precipitation." Tellus **16**(4): 436-468.

deVries, J. J., et al. (2000). "Groundwater recharge in the Kalahari, with reference to paleo-hydrologic conditions." Journal of Hydrology **238**: 110–123.

Dokulil, M., et al. (2001). Ökologie und Schutz von Seen. Stuttgart, UTB.

Domingues, R. B., et al. (2007). "Impact of reservoir filling on phytoplankton succession and cyanobacteria blooms in a temperate estuary." Estuarine, Coastal and Shelf Science **74**(1–2): 31-43.

EEA (2010). Freshwater - National Responses (Portugal) The European environment – state and outlook 2010. Copenhagen, Denmark, European Environment Agency.

Estrela, T., et al. (1996). Water resources problems in southern Europe - An overview report. Copenhagen, Denmark, European Environment Agency.

EU (1991). Directive 91/271/EEC concerning urban waste-water treatment COM/89/0518 E. Council. Brussels, Belgium.

EU (1998). Directive on the quality of water intended for human consumption. C. o. Europe, Official Journal of the European Communities **330:** 32-54.

Fernandes, P., et al. (2008). Geochemistry of the Baixo Alentejo Flysch Group, South Portuguese Zone: Implications for provenance and palaeoweathering <u>Goldschmidt</u>. Vancouver, Canada.

Furtak, H. and H. R. Langguth (1967). Zur hydrochemischen Kennzeichnung von Grundwässern und Grundwassertypen mittels Kennzahlen. <u>IAH-Congress</u>. Hannover, Germany. **7:** 86-96.

Gächter, R. and B. Müller (2003). Why the phosphorus retention of lakes does not necessarily depend on the oxygen supply to their sediment surface. <u>Limnology and Oceanography</u>. Waco, TX, ETATS-UNIS, American Society of Limnology and Oceanography. **48:** 929-933.

Galvao, H. M., et al. (2008). "Cyanobacterial blooms in natural waters in southern Portugal: a water management perspective." <u>Aquatic Microbial Ecology</u> **53**(1): 29-140.

Gee, G. W., et al. (2005). "Chloride Mass Balance." <u>Vadose Zone J.</u> **4**(1): 72-78.

Gibson, J. J., et al. (1993). "Estimating Evaporation Using Stable Isotopes: Quantitative Results and Sensitivity Analysis forTwo Catchments in Northern Canada." <u>Nordic Hydrology</u> **24**: 79-94.

Hill, T. and C. Neal (1997). "Spatial and temporal variation in pH, alkalinity and conductivity in surface runoff and groundwater for the Upper River Severn catchment." <u>Hydrology and Earth System Sciences</u> **1**(3): 697-715.

Hölting, B. and W. G. Coldewey, Eds. (2013). <u>Hydrogeologie</u>. Berlin Heidelberg, Springer Verlag.

Holzer, S. (2012). <u>Desert or Paradise: Restoring Endangered Landscapes Using Water Management, including Lake and Pond Construction</u>. East Meon, England, Permanet Publications.

Jansson, M. (1988). Phosphate Uptake and Utilization by Bacteria and Algae. <u>Phosphorus in Freshwater Ecosystems</u>. G. Persson and M. Jansson, Springer Netherlands. **48:** 177-189.

Jochimsen, E. M., et al. (1998). "Liver Failure and Death after Exposure to Microcystins at a Hemodialysis Center in Brazil." <u>New England Journal of Medicine</u> **338**(13): 873-878.

Karlson, K., et al. (2002). <u>Temporal and spatial large-scale effects of eutrophication and oxygen deficiency on benthic fauna in Scandinavian and Baltic waters: A review</u>. Boca Raton, FL, ETATS-UNIS, CRC Press.

Keeney, D. R. (1973). "The Nitrogen Cycle in Sediment-Water Systems1." <u>J. Environ. Qual.</u> **2**(1): 15-29.

Knöller, K., et al. (2006). "Sulfur and Oxygen Isotope Fractionation during Benzene, Toluene, Ethyl Benzene, and Xylene Degradation by Sulfate-Reducing Bacteria." <u>Environmental Science & Technology</u> **40**(12): 3879-3885.

Krabbenhoft, D. P., et al. (1990). "Estimating groundwater exchange with lakes: 1. The stable isotope mass balance method." <u>Water Resources Research</u> **26**(10): 2445-2453.

Krom, M. D. (1980). "Spectrophotometric determination of ammonia: a study of a modified Berthelot reaction using salicylate and dichloroisocyanurate." <u>Analyst</u> **105**(1249): 305-316.

Liebe, J., et al. (2005). "Estimation of small reservoir storage capacities in a semi-arid environment: A case study in the Upper East Region of Ghana." Physics and Chemistry of the Earth, Parts A/B/C **30**(6–7): 448-454.

Lin, J., et al. (2001). "Study of corrosion material accumulated on the inner wall of steel water pipe." Corrosion Science **43**(11): 2065-2081.

Mez, K., et al. (1997). "Identification of a microcystin in benthic cyanobacteria linked to cattle deaths on alpine pastures in Switzerland." European Journal of Phycology **32**(2): 111-117.

Miao, Z., et al. (2012). "Sulfate reduction in groundwater: characterization and applications for remediation." Environmental Geochemistry and Health **34**(4): 539-550.

Morais, M. M., et al. (2007). Monitoring the water quality in Alqueva Reservoir, Guadiana River, southern Portugal. Berlin, Germany, Technische Uni Berlin.

Murphy, J. and J. P. Riley (1962). "A modified single solution method for the determination of phosphate in natural waters." Analytica Chimica Acta **27**(0): 31-36.

Neal, C. (1988). "Bicarbonate estimation from alkalinity determinations for neutral to acidic low alkalinity natural waters: theoretical considerations " Hydrological Sciences **33**(6): 619-624.

Paralta, E., et al. (2007). Assessing agriculture pollution in the Beja aquifer using nitrogen isotopes, South Portugal. International Symposium on Advances in Isotope Hydrology and its Role in Sustainable Water Resources Management. Vienna, Austria, International Atomic Energy Agency.

Paralta, E. and M. Oliveira (2005). Assesing and modelling hard rock aquifer recharge based on complementary methodologies-a cas study in the "Gabbros of Beja" aquifer system (South Portugal). 2nd Workshop of the Iberian Regional Working Group on Hardrock Hydrogeology. Evora, Portugal.

Pereira, M. and D. Figueiredo (2009). "Effects of the Alqueva Dam Reservoir on the Distribution of Steppe Birds." Physical Geography **30**(1): 43-63.

Pereira, Z., et al. (2007). "Devonian and Carboniferous palynostratigraphy of the South Portuguese Zone, Portugal –An overview." Comunicações Geológicas **94**: 53-79.

Pinho, A. B., et al. (2007). The Baixo Alentejo (Portugal) flysch rocks. The Second Half Century of Rock Mechanics, Three Volume Set, Taylor & Francis.

Price, D. R. H. (1999). "Do reservoirs need ecological management?" Hydrobiologia **395-396**(0): 117-121.

Ramos, C. and E. Reis (2002). "Floods in southern Portugal: their physical and human causes, impacts and human response." Mitigation and Adaptation Strategies for Global Change **7**(3): 267-284.

Ribeiro, L. and L. V. daCunha (2010). Portuguese groundwater report. Groundwater in the Southern Member States of the European Union: an assessment of current knowledge and future prospects, European Academies Science Advisory Council.

Santos, M., et al. (2008). "Assessing dam implementation impact on threatened carnivores: the case of Alqueva in SE Portugal." Environmental Monitoring and Assessment **142**(1-3): 47-64.

Scanlon, B. R., et al. (2002). "Choosing appropriate techniques for quantifying groundwater recharge." Hydrogeology Journal **10**(1): 18-39.

Scanlon, B. R., et al. (2006). "Global Synthesis of Groundwater Recharge in Semiarid and Arid Regions." Hydrological Processes **20**: 3335-3370.

Sequeira, E. (2010). Desertification and salinisation in the Alentejo region, Portugal. Implementing the EU Water Framework Directive: A seminar series on water. Brussels, Belgium, WWF with the support of the European Commission and TAIEX.

Serafim, A., et al. (2006). "Spatial and temporal heterogeneity in the Alqueva reservoir, Guadiana river, Portugal." Limnetica **25**(3): 771-786.

Shade, A., et al. (2007). "Interannual dynamics and phenology of bacterial communities in a eutrophic lake." Limnology and Oceanography **52**(2): 487-494.

Simeonov, V., et al. (2003). "Assessment of the surface water quality in Northern Greece." Water Research **37**(17): 4119-4124.

Smith, S. V., et al. (2002). "Distribution and significance of small, artificial water bodies across the United States landscape." Science of The Total Environment **299**(1–3): 21-36.

Sonzogni, W. C., et al. (1982). "Bioavailability of Phosphorus Inputs to Lakes1." J. Environ. Qual. **11**(4): 555-563.

Stigter, T. Y., et al. (2006). "Impact of the shift from groundwater to surface water irrigation on aquifer dynamics and hydrochemistry in a semi-arid region in the south of Portugal." Agricultural Water Management **85**(1–2): 121-132.

Stookey, L. L. (1970). "Ferrozine---a new spectrophotometric reagent for iron." Analytical Chemistry **42**(7): 779-781.

UNESCO (2012). Managing Water under Uncertainty and Risk. The United Nations World Water Development Report 4. Paris, France, United Nations Educational, Scientific and Cultural Organization

Weather Station Beja, P. (2011). "Historical weather 2011." Retrieved 31.12.2013, 2013, from http://weatherspark.com/history/32364/2011/Beja-Portugal.

Weather Station Beja, P. (2012). "Historical weather 2012." Retrieved 31.12.2013 2013, from https://weatherspark.com/history/32364/2012/Beja-Portugal.

Weather Station Beja, P. (2013). "Historical weather 2013." Retrieved 31.12.2013, 2013, from https://weatherspark.com/history/32364/2013/Beja-Portugal.

Wisser, D., et al. (2010). "The significance of local water resources captured in small reservoirs for crop production – A global-scale analysis." Journal of Hydrology **384**(3–4): 264-275.

Wong, J. M. (1984). "Chlorination-filtration for iron and manganese removal." Journal of the American Water Works Association **76**(1): 76-79.

Wunderly, M. D., et al. (1996). "Sulfide mineral oxidation and subsequent reactive transport of oxidation products in mine tailings impoundments: A numerical model." Water Resources Research **32**(10): 3173-3187.

Appendix

Table 6 shows list of sampling data for temperature, conductivity, dissolved oxygen (DO) and pH of ground-and surface waters in November 2012:

Sample	Sampling date	Temp. [°C]	Conduct. [µS/ccm]	DO %	DO [mg/l]	pH
L1, 1m	11/11/2012	15.360	447	74.1	7.67	7.35
L1, 3m	11/11/2012	15.040	446	68.7	7.16	7.33
L1, 5m	11/11/2012	14.950	446	67.8	7.09	7.36
L1, 7m	11/11/2012	14.890	447	65.1	6.79	7.41
L2	11/11/2012	15.12	510	53.6	5.58	7.26
L4	11/11/2012	n.d.	n.d.	n.d.	n.d.	n.d.
DW1	06/11/2012	17.31	1096	11.80	1.18	6.82

Sample	Sampling date	Temp. [°C]	Conduct. [μS/ccm]	DO %	DO [mg/l]	pH
DW2	06/11/2012	17.66	832	4.00	0.39	6.37
DW3	07/11/2012	n.d.	n.d.	n.d.	n.d.	n.d.
DW4	08/11/2012	17.95	720	5.40	0.51	6.08
DW5	11/11/2012	19.11	1373	34.70	3.33	6.56
SW1	07/11/2012	16.94	375	5.10	0.51	6.70
SW2	08/11/2012	16.04	576	31.00	3.16	6.37
SW3	08/11/2012	n.d.	n.d.	n.d.	n.d.	n.d.
SW4	09/11/2012	16.21	505	33.30	3.37	6.84
SW5	09/11/2012	15.10	394	62.40	6.46	6.23
SW6	10/11/2012	16.53	429	43.70	4.41	6.30
SW7	11/11/2012	15.45	365	5,00	0.52	6.41

Sample	Sampling date	Temp. [°C]	Conduct. [µS/ccm]	DO %	DO [mg/l]	pH
SW8	11/11/2012	n.d.	n.d.	n.d.	n.d.	n.d.
SW9	11/11/2012	n.d.	n.d.	n.d.	n.d.	n.d.
S1	08/11/2012	16.68	595	63.30	6.34	6.54
S2	08/11/2012	16.21	626	46.90	4.74	6.55
S3	10/11/2012	n.d.	n.d.	n.d.	n.d.	n.d.
W1	07/11/2012	n.d.	n.d.	n.d.	n.d.	n.d.
W2	11/11/2012	n.d.	n.d.	n.d.	n.d.	n.d.
W3	09/11/2012	13.62	141	12.30	1.31	6.30

Table 6: List of sampling data for temperature, conductivity, dissolved oxygen (DO) and pH of ground-and surface waters in November 2012

Table 7 shows list of sampling data for ion concentrations of ground-and surface waters in November 2012

SRP=ortho phosphate; TP=total phosphate

Unit of ion concentrations is mg/l.

Sample	Sampling date	Cl-	NO_2^-	NO_3^-	SRP	TP	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Fe^{2+}	HCO_3^-	Ion balance [%]
L1, 1m	11/11/2012	75.27	0	2.48	0.13	1.34	29.64	46.77	0.19	0	19.13	19.55	0	67.12	8.53
L1, 3m	11/11/2012	78.26	0	2.57	0.11	0.65	30.80	45.30	0.21	0	21.95	19.59	0.01	78.71	5.70
L1, 5m	11/11/2012	79.06	0	2.47	0.14	0.42	30.62	46.41	0.20	0	20.49	19.34	0	70.17	6.70
L1, 7m	11/11/2012	79.08	0	2.53	0.16	0.29	30.83	40.66	0.21	0	18.84	17.87	0.08	70.78	1.39
L4	11/11/2012	34.53	0	2.89	0.08	2.91	12.63	16.50	n.d.	1.62	6.31	8.52	n.d.	16.47	6.57
DW1	06/11/2012	208.65	0	0	0.03	0.48	28.87	96.51	0.11	0	59.04	45.88	0	273.05	-0.17
DW2	06/11/2012	193.79	0	1.61	0.03	0.09	33.56	90.18	0.10	0	35.42	48.51	1.71	160.17	5.02
DW3	07/11/2012	102.57	0	0	0.52	2.35	26.09	60.74	0.10	0	15.75	26.35	1.76	109.83	3.77
DW4	08/11/2012	154.44	0	0	0.73	2.07	40.85	69.38	0	0	16.53	27.28	3.25	77.98	-2.39
DW5	11/11/2012	301.98	0	0	0.33	0.91	41.08	145.55	0.11	0	33.86	61.08	0	176.95	3.04

Sample	Sampling date	Cl-	NO_2^-	NO_3^-	SRP	TP	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Fe^{2+}	HCO_3^-	Ion balance [%]
SW1	07/11/2012	68.42	0	0	0.50	4.55	27.23	43.90	0	2.81	16.34	16.59	1.29	131.49	-5.17
SW2	08/11/2012	113.95	0	0	0.48	0.49	36.32	66.70	0	0.00	18.36	24.77	0	73.83	5.97
SW3	08/11/2012	20.35	0	9.57	0.20	1.17	13.64	8.22	n.d.	0.31	7.50	4.81	n.d.	6.10	0.73
SW4	09/11/2012	93.13	0	3.60	0.08	0.11	20.89	60.74	n.d.	0.00	14.17	22.97	n.d.	87.86	6.90
SW5	09/11/2012	53.42	0	7.70	0.10	1.37	69.04	30.79	n.d.	0.00	15.82	19.54	n.d.	5.00	8.45
SW6	10/11/2012	81.07	0	5.56	0.13	0.17	44.05	39.00	n.d.	2.31	10.19	18.93	n.d.	38.14	-1.30
SW7	11/11/2012	82.26	0	4.64	0.09	0.21	18.49	42.31	n.d.	0	9.80	15.96	n.d.	26.85	6.11
SW8	11/11/2012	99.83	0	2.11	0.28	0.56	22.47	51.30	n.d.	0	18.45	21.78	n.d.	n.d.	n.d.
S1	08/11/2012	113.12	0	1.47	0.06	0.20	35.32	59.67	n.d.	0	22.30	27.98	n.d	88.47	5.34
S2	08/11/2012	124.51	0	0	0.18	0.25	36.35	67.05	n.d.	0	17.37	26.55	n.d	121.42	-2.42
S3	10/11/2012	98.54	0	0	0.08	0.27	33.59	54.85	n.d.	0	24.65	26.01	n.d	91.53	7.21
W1	07/11/2012	72.01	0	3.89	0.36	0.19	22.72	34.57	n.d	0.73	14.19	14.32	n.d	45.15	1.34
W2	11/11/2012	102.19	0	0	0.02	0.07	67.76	58.02	n.d	0	27.04	27.79	n.d	64.07	7.10

Sample	Sampling date	Cl^-	NO_2^-	NO_3^-	SRP	TP	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Fe^{2+}	HCO_3^-	Ion balance [%]
W3	09/11/2012	32.24	0	2.06	0.43	0.18	23.87	17.41	n.d.	0	6.32	5.83	n.d.	11.65	-2.88
I1	04/11/2012	61.74	0	0	0.39	0.60	20.02	34.67	n.d.	3.32	11.44	10.33	n.d.	n.d.	n.d.
I2	04/11/2012	59.82	0	2.09	0.35	0.16	35.55	32.45	n.d.	3.66	15.14	11.67	n.d.	32.64	3.42
I3	04/11/2012	109.16	0	1.80	0.05	0.15	29.35	54.69	n.d.	1.78	20.49	19.03	n.d.	38.56	7.05
I4	04/11/2012	54.92	0	2.65	0.21	0.26	19.07	35.68	n.d.	2.80	12.76	9.74	n.d.	24.53	12.17
R1	04/11/2012	21.74	0	1.69	0.72	n.d.	20.11	16.49	3.29	0	6.39	1.57	n.d.	n.d.	n.d.
R2	07/11/2012	12.41	0	0	0.44	n.d.	7.70	0	n.d.	0	0	0	n.d.	n.d.	n.d.
R3	07/11/2012	14.05	0	2.23	0.08	n.d.	7.87	0	n.d.	0	0	0	n.d.	n.d.	n.d.
R4	11/11/2012	15.91	0	0	0.10	n.d.	8.25	0	n.d.	0	0	0	n.d.	n.d.	n.d.
WW1	10/11/2012	136.11	0	22.80	22.67	53.63	18.97	95.85	13	45.75	72.88	25.25	n.d.	325.83	1.82
WW3	11/11/2012	2078.54	123.54	1265.60	170.45	267.48	332.41	1058.36	184.873	1210.78	101.28	7.00	n.d.	1443.36	n.d.

Table 7: List of sampling data for ion concentrations of ground-and surface waters in November 2012

Table 8 shows list of sampling data for temperature, conductivity, dissolved oxygen (DO) and pH of ground-and surface waters in April 2013:

Sample	Sampling date	Temp. [°C]	Conduct. [μS/ccm]	DO %	DO [mg/l]	pH
L1, 0m	05/04/2013	16.76	251	89.00	8.89	7.12
L1, 1m	05/04/2013	16.15	250	85.40	8.65	7.25
L1, 3m	05/04/2013	15.68	255	77.20	7.89	7.19
L1, 5m	05/04/2013	14.81	250	64.50	6.70	7.15
L1, 7m	05/04/2013	12.78	325	17.20	1.88	6.97
L1, 9m	05/04/2013	11.75	404	1.50	0.16	6.91
L2	07/04/2013	14.26	275	4.40	4.73	6.62
L3	07/04/2013	16.82	283	93.30	9.41	6.60
L4, 0m	08/04/2013	19.25	238	104.00	10.09	7.01

Sample	Sampling date	Temp. [°C]	Conduct. [µS/ccm]	DO %	DO [mg/l]	pH
L4, 1m	08/04/2013	16.21	288	96.00	9.79	7.00
L4, 3m	08/04/2013	14.43	291	29.30	3.09	6.83
L4, 4m	08/04/2013	13.13	310	1.40	0.40	6.74
L4, 5m	08/04/2013	12.80	330	1.20	0.13	6.72
L5	06/04/2013	18.44	84	99.20	9.73	7.00
DW1	08/04/2013	17.43	568	20.50	2.02	6.63
DW2	08/04/2013	17.00	739	4.50	0.45	7.13
DW3	11/04/2013	18.17	687	37.40	3.50	6.53
DW4	-	n.d.	n.d.	n.d.	n.d.	n.d.
DW5	08/04/2013	18.88	1488	39.10	3.75	6.52
SW1	08/04/2012	17.16	404	1.10	0.11	6.53

Sample	Sampling date	Temp. [°C]	Conduct. [µS/ccm]	DO %	DO [mg/l]	pH
SW4	06/04/2012	16.56	611	6.50	0.65	6.39
SW5	06/04/2012	14.29	759	10.70	1.13	6.44
SW6	05/04/2012	14.73	476	17.50	1.82	6.27
SW7	06/04/2013	14.67	632	6.30	0.65	5.99
SW8	05/04/2012	14.52	848	14.20	1.46	6.28
SW10	06/04/2013	16.05	793	44.80	4.60	6.10
SW11	08/04/2013	14.87	1064	9.20	0.96	6.22
S3	05/04/2013	16.99	262	103.00	10.24	8.16
WW3	10/04/2013	16.87	7370	50.00	4.91	6.54
D1	10/04/2013	16.25	424	55.80	5.60	6.63
D2	08/04/2013	14.58	424	69.50	7.34	6.81

Sample	Sampling date	Temp. [°C]	Conduct. [μS/ccm]	DO %	DO [mg/l]	pH
D3	10/04/2013	16.86	413	61.30	5.79	6.53
D4	10/04/2013	16.68	417	105.30	10.65	6.99
D5	10/04/2013	28.26	434	83.20	6.72	6.77

Table 8: list of sampling data for temperature, conductivity, dissolved oxygen (DO) and pH of ground-and surface waters in April 2013

Table 9 shows list of sampling data for ion concentrations of ground-and surface waters in April 2013

SRP=ortho phosphate; TP=total phosphate

Unit of ion concentrations is mg/l.

Sample	Sampling date	Cl^-	NO_2^-	NO_3^-	SRP	TP	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Fe^{2+}	HCO_3^-	Ion balance [%]
L1, 0m	05/04/2013	45.37	0	0.35	0	0.09	14.06	25.97	n.d.	1.81	8.50	8.95	n.d.	45.15	0.4
L1, 1m	05/04/2013	45.96	0	0.3	0	0.02	14.53	26.21	n.d.	1.79	9.01	9.33	n.d.	56.44	-2.57
L1, 3m	05/04/2013	46.00	0	0.34	0	0.05	15.74	26.07	n.d.	1.84	9.16	9.32	n.d.	45.76	0.50
L1, 5m	05/04/2013	46.49	0	0.33	0	0.12	14.32	26.33	0.18	1.77	9.29	9.47	0.15	45.76	1.64
L1, 7m	05/04/2013	46.16	0	0.41	0	0.06	14.20	26.37	0.16	1.78	9.27	9.50	0.16	45.76	1.87
L1, 9m	05/04/2013	60.15	0	0.71	0	0.07	18.05	31.46	0.15	2.1	10.88	11.42	0.13	68.64	-4.83
L4, 0m	08/04/2013	56.92	0	1.15	0	0.06	12.45	30.63	n.d.	1.74	7.12	10.03	n.d.	42.59	-0.47
L5	06/04/2013	13.54	0	0.49	0.02	0.06	6.43	11.04	n.d.	0	2.61	2.12	n.d.	16.78	-0,91
SW1	08/04/2012	75.13	0	0	n.d.	0.06	20.02	41.05	0.36	0.82	13.44	14.25	2.00	79.32	-2.29
SW4	06/04/2012	140.03	0	0	0	0.03	19.60	67.66	0.33	0	12.73	25.16	0.28	112.88	-4.55

Sample	Sampling date	Cl^-	NO_2^-	NO_3^-	SRP	TP	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Fe^{2+}	HCO_3^-	Ion balance [%]
SW5	06/04/2012	219.57	0	0.16	0	0.05	30.66	75.23	0.39	0	15.70	31.76	2.36	64.07	-8.19
SW7	06/04/2013	185.83	0	0.48	n.d.	0	19.22	65.20	0.35	0	12.27	25.10	2.29	48.81	-7.65
SW10	06/04/2013	261.42	0	1.21	0	0.01	22.14	81.69	0.29	0	8.98	36.78	0	38.14	-9.24
S3	05/04/2013	45.34	0	0.39	0.01	0.04	18.44	25.68	0.33	1.73	9.19	9.62	0.13	46.68	-0.09
WW1	10/04/2013	111.95	0	5.42	23.46	36.10	85.84	82.69	8.89	27.12	93.10	31.39	0.26	n.d.	n.d.
WW2	10/04/2013	145.19	0	3.56	36.85	19.28	68.57	118.01	16.36	52.06	59.43	40.25	0.49	n.d.	n.d.
WW3	10/04/2013	1025.69	13.35	1316.20	945.79	950.93	251.69	637.73	114.85	778.94	133.48	150.88	0.43	n.d.	n.d.
D1	10/04/2013	84.05	0	0	0	0.09	20.50	43.94	0	0	11.91	15.91	0.52	74.75	-2.66
D2	08/04/2013	84.38	0	0	0.01	0.11	21.12	44.02	0.08	0	12.27	15.83	0.95	82.37	-4.20
D3	10/04/2013	83.71	0	0	0.02	0.03	19.76	43.95	0.13	0	11.88	15.93	0	76.88	-2.68
D4	10/04/2013	82.16	0	0	0.01	0.02	19.41	43.93	0.09	0	12.06	15.73	0	76.27	-2.05
D5	10/04/2013	84.77	0	0	0	0.03	19.92	44.31	0.05	0	12.25	15.99	0	77.19	-2.69

Table 9: list of sampling data for ion concentrations of ground-and surface waters in April 2013