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Abbreviations

ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
REE	Rare Earth Element
LTOW	Long term observation well
SD	Standard Deviation
MRI	Magnetic Resonance Imaging
MRA	Magnetic Resonance Angiography
LOQ	Limit of Quantification
WGWS	Western Groundwater Stream
EWGS	Eastern Groundwater Stream
EC	Electrical Conductivity
BFZ1	Bank Filtration Zone 1
BFZ2	Bank Filtration Zone 2
TZ	Transition Zone
Gd _{anth}	anthropogenic Gadolinium
Cl ⁻	Chloride
GIS	Geographic Information System
STP	Sewage treatment plant

1 Introduction

The sustainable production of drinking water is one of the major challenges for mankind in the coming decades. Demand is rising constantly and the supply needs to keep up (OECD 2012). Worldwide a third of the population is depending on groundwater for the supply of drinking water. Groundwater has a range of advantages over surface water. It is characterised to have a higher quality and better protection from pollution, contamination and evaporation (WHO 2006).

In Austria 100% of the drinking water is covered by groundwater (European Commission 2010). Around 50% originate from porous aquifers and 50% from karstic and crevice groundwater springs (Umweltbundesamt 2016).

Natural recharge of porous aquifers in alluvial settings is mainly caused by infiltration of waters from precipitation and infiltration of surface waters such as rivers and lakes (Hölting & Coldewey 2013). The water from the latter process is called bank filtrate. In extension, ground water management can utilise artificial recharge in order to guarantee the supply of drinking water in times of need (Fetter 2000).

The spatial distribution, quantification and residence time of river infiltration in the area of water works is important knowledge for drinking water suppliers. The knowledge of these parameters is important to outline water protection zones around production wells required by statutory rule like the ÖVGW-guideline in Austria and the DVGW-guideline in Germany (Zetinig 1997). An example is the 50-day border around a water catchment required in the DVGW for a protection zone class 2 (DVGW 1992) to avoid contamination with bacteria. In order to outline such zone information related to the spatial distribution, quantification and residence time of infiltrating water has to be known.

This information can be determined by using environmental, artificial tracers and pollution tracers. Environmental tracers are chemical or isotopic substances that can be of natural or anthropogenic origin that are present in the atmosphere and the soil (Plummer 2003).

Important environmental tracers used in Hydrology are stable isotopes like deuterium (^2H), oxygen-18 (^{18}O) or carbon-13 (^{13}C), radioactive isotopes like tritium (^3H), carbon-14 (^{14}C) and radon-222 (^{222}Rn), or geochemical compounds like chloride (Cl^-) and silicate (SiO_2) (Purtschert 2001; Leibundgut et al. 2009). They are implemented into aquifers by solution from minerals during infiltration processes or, in case of radon-222, by enrichment through geochemical decay mechanisms.

Artificial tracers are tracers that are actively introduced into the targeted aquifer. The most utilised artificial tracers are fluorescence tracers like uranine (disodium salt of fluo-

rescein) (IAEA 1990) followed by salt tracers like chloride (as NaCl or KCl) or bromide (as KBr or NaBr) (Leibundgut et al. 2009).

Pollution tracers can neither completely be classified as environmental tracers nor as artificial tracers. Pollution tracers are entering the water cycle by anthropogenic activity. They can either have a point source like leaking pollution deposits or the influx of treated or untreated wastewater, or they derive from the emission of pollution gases into the atmosphere. They are not of natural origin but share the same incorporation processes as environmental tracers. Important pollution tracers are nitrate and phosphate originating from fertiliser or radioactive compounds like cesium-134 (Leibundgut et al. 2009) that was set free after the Chernobyl accident.

Other pollution tracers of increasing importance are micropollutants (Hissler et al. 2014) originating from pharmaceuticals (WHO 2006), human drugs, veterinary drugs and food and feed additives. These substances are usually introduced into the wastewater systems or the soil through excretion. While human drugs and their products of decomposition enter the groundwater mainly via the pathway excretion → sewage system → sewage treatment plant → surface water, veterinary drugs and feed additives usually follow the path excretion → manure → top soil. Both have in common that they end up in drinking water (Leal et al. 2010; WHO 2011). The scope of substances originating from pharmaceuticals that can be found in drinking water is wide and increases from year to year due to increasing consumption of pharmaceuticals by a growing population (Deo & Halden 2013). Over 70,000 chemicals are discussed to have an endocrine disruptive potential (WHO 2006). Although the concentrations of pharmaceuticals in drinking water are more than 1000-fold below the minimum therapeutic dose (MTD) (WHO 2011) and effects on human health are unlikely, there is discussion if the extrapolation of short term high dosage studies to long term low dose exposure during drinking water consumption is sufficient (WHO 2006).

Among the pharmaceutical products that can be found in drinking water are antibiotics, beta-blocker, antihistamine, analgesics, lipid regulators and contrast media (WHO 2011). One of the compounds used as contrast media that can be found in drinking water is gadolinium. Gadolinium (Gd) is a heavy rare earth element (REE) with the atomic number 64. Among other, primarily military applications that reach from laser techniques and radar systems to nuclear marine propulsion (Grasso 2013; Clark & Reddy 1986; Bajor et al. 2011), gadolinium is used as a contrast agent in magnetic resonance imaging (MRI) and magnetic resonance angiography (MRA) as chelated compound. The patient gets injected with an intravenous agent prior to the examination (Bellin & Van Der Molen 2008). Later the gadolinium is removed from the body by urinary excretion usually a matter of a few hours after application and ends up in the waste water unaltered (Kümmerer & Helmers 2000). As gadolinium chelates are not degraded in sewage treatment plants they reach surface waters unhindered (Möller et al. 2000).

MRI is increasingly offered to out-patients in many areas. Anthropogenic gadolinium from MRI contrast agents can therefore be found even in headwater catchments without hospital facilities in the upstream region (Rabiet et al. 2009, Brünjes et al. 2016).

The investigated area has been subject to investigation before, evaluating various anthropogenic tracers such as artificial sweeteners and anthropogenic gadolinium (Bichler et al. 2015).

The goal of this work is to further investigate the spatial distribution, quantification and residence time of river infiltration. To get an integrated comprehension of the active dynamics and processes a multi tracer approach was conducted. Field samples were tested for anthropogenic gadolinium and chloride to map out the spatial distribution throughout the aquifer and to quantify mixing-ratios of bank filtrate and groundwater originating from natural recharge. Radon-222 was examined for estimating the residence time.

2 Site description

Due to a non-disclosure agreement the site description can in some areas only be schematic.

2.1 Description of the investigated area

The site investigated for this work lies within the Alpine Foreland within the catchment of a tributary of a major regional river. The area of interest covers approx. 3.45 km² and includes a river-valley with an adjacent tableland on one side of the valley. Within the catchment of the receiving water an annual mean air temperature of 7.7°C and an average annual precipitation of 1150 mm (Regional meteorological service). Other sources state an annual average precipitation between 1300 and 1500 mm with an evapotranspiration of over 600 mm and a groundwater recharge between 600 and 800 mm (Bichler et al. 2015).

The investigated area is divided in an agriculturally used tableland with pastures for livestock and a river valley that is mainly used as local recreation area and is covered by forest for the better part. On the tableland there are widespread homes and farms whereas the river-valley is not populated in the area of interest.

The river is lined with flood protection structures (impassable dykes) on both sides and is equipped with numerous groundsills. These structures were first erected between 1890 and 1910 and have since been object to maintenance and upgrading (Haselsteiner 2007). Along the upstream part of the river several small hydropower plants are in operation.

A few kilometres upstream the southern border of the investigation area a single municipal sewage treatment plant (STP) performs the sewage purification for the entire population of the head water. Due to a sewage ring system there is no overflow or discharge of untreated wastewater. The wastewater plant discharges the water into the river after treatment. The average discharge rate is almost constant at 0.11m³/s (Bichler et al. 2015).

The investigations took place along one river at its orographic right hand side river bank. Due to man-made reasons the riverbed in the area of interest lies considerably higher than the groundwater table. The river is therefore permanently infiltrating into the unconfined aquifer.

Hydraulic conductivities (K) are high and in a range of 1E-02 m/s - 5E-02 m/s. The mean value (MV) of the effective flow velocity is 85 m/d (11 hydraulic tests) (Bichler et al. 2015).

2.2 Geological frame

The investigated area is embedded in the Alpine Foreland and dominated by Quaternary and Holocene calcareous-dominated glacial and postglacial sandy gravel deposits covering sediments of the folded Paleogene and Neogene Molasse basin. These are mainly comprised by marls, calcareous sandstones, sandstones, conglomerates. Within the Paleogene layers chance coal can be embedded. The layers generally strike E-W and dip predominantly to the South, but due to the distinctive folding also northward dipping strata can be found.

The Pleistocene sheet gravels and moraine on top of the Molasse sediments are forming up the Quaternary plateaus. After the deposition, rivers and creeks subsequently incised into this tableland and formed valleys that were subdued to a cycle of fill-up due to sediments generated by the advancing Würm - glaciers and subsequent erosion. In the course of these cycles several terraces on descending levels were generated along the course of the river. The valley bottom is filled with alluvial sediments which constitute the porous medium for the groundwater. High flood loams are intercalated as laminar lenses and lenticular beds and may seal particular areas from interaction with surface water. The bedrock beneath the filling consists of Molasse sediments.

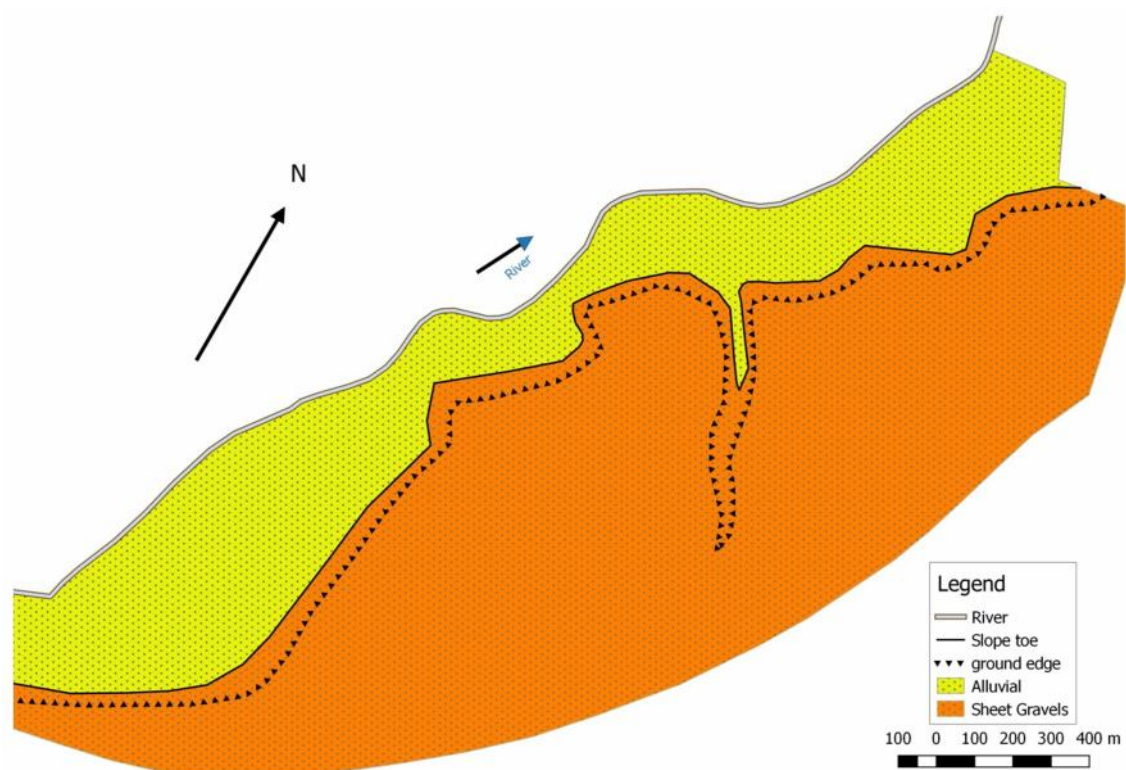


Figure 1: Simplified geological map of the investigated area. Sheet Gravels form up a tableland that lies approx. 50 m higher than the level of the river with its adjacent former floodplains which are here labelled as "Alluvial"

3 Methodology

3.1 Sampling

In general the sampling comprises two different sets of samples. In order to investigate temporal variations of the tracers anthropogenic gadolinium and chloride, continuous, weekly sampling of water from the river and a Long Term Observation Well (LTOW) was conducted for a time span of 1 year and 2 months. Those samples are important to determine mitigate variabilities and to acquire long term mean values of the anthropogenic gadolinium and chloride concentrations which serve as input parameter for mixing analysis.

The second set of samples originates from discrete sampling conducted between 4th and 8th of April 2016. Samples were taken from 23 different piezometers and wells (labelled 1 – 23 for this work) as well as daily samples from the river and the LTOW.

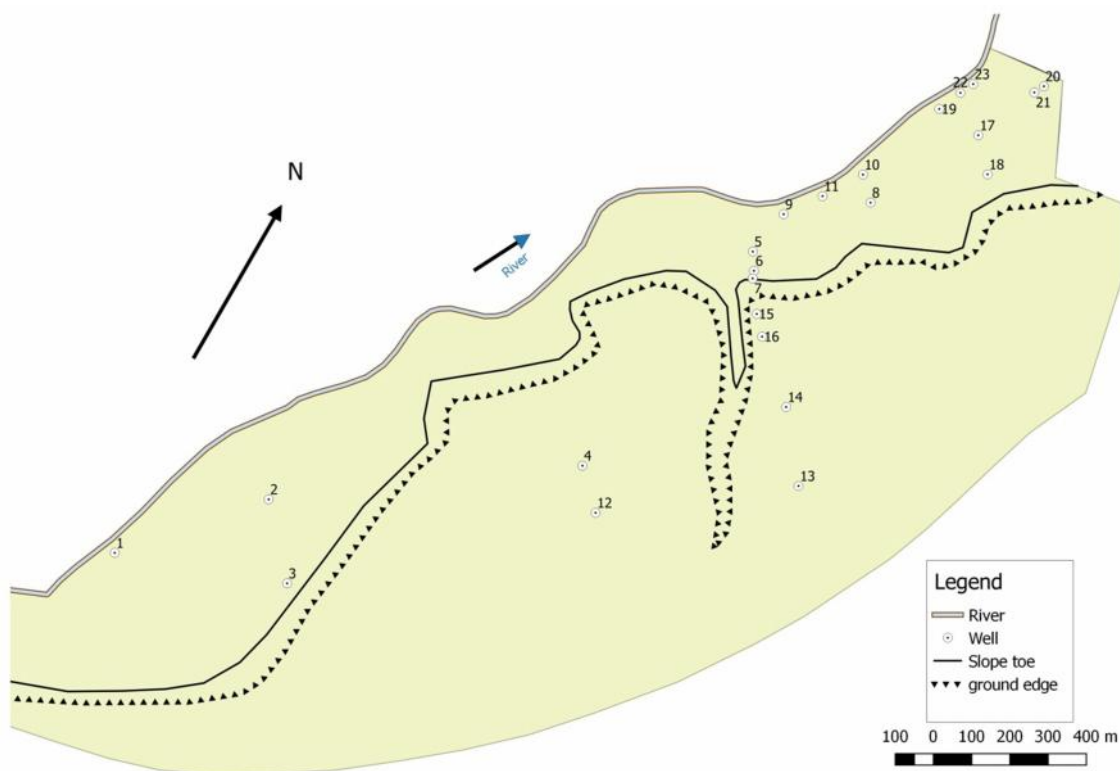


Figure 2: Schematic map of the investigated area with the sampled wells. All wells lie east of the river.

LTOW is further to the NE of the investigated area and is not displayed in the maps. It serves also as extraction well and therefore represents broader flow paths than the

sampling wells. All wells were pumped clear before sampling. The amount of water pumped out before sampling was at least three times the volume of the well.

3.1.1 Field parameters

In order to understand the spatial hydrochemical variability of the aquifer the distribution of the electrical conductivity (EC), pH and temperature were measured using a Hach multimeter (HQ40D).

3.1.2 Radon

Naturally occurring ^{222}Rn is isotope of radon with a half-life of 3.8 days a decay product in the U-238 decay chain. Radon has been used to estimate groundwater residence and infiltration times since in similar settings (Hoehn & Von Gunten 1989a) and in combination with chloride as natural tracers (Bertin & Bourg 1994). It has been described as a reliable method to describe the exchange processes between surface and ground waters (Atkinson et al. 2015; Dehnert et al. 1999).

Water samples for radon analysis can be collected by different means. Among other techniques bubblers, liquid scintillation and field screening methods can be used (Cecil & Gesell 1992).

For this work a field screening method was chosen. The portable radon detector RAD7 and the RAD H2O accessory by DurrIDGE were used to collect and analyse the samples. The water was sampled in absence of air in order to avoid degassing. This was accomplished by filling a large bucket with water at a low pumping rate to avoid the formation of blow holes with a hose that was kept at the bottom of the bin. The water overflowed the bucket when the vitreous 250 mL sample bottles were filled and flushed with freshly pumped water. The sample vials were then capped under water. All samples have been subsequently measured on site or latest a few hours later.



Figure 3: RAD7 field equipment with RAD7 H₂O accessory

The obtained data were then analysed using the RAD7 data acquisition and analysis software CAPTURE 5.5 by DurrIDGE.

3.1.3 Gadolinium, chloride

The sampling process comprised three steps. First a 250 mL sample of water freshly pumped out of the well was taken. The water was then filtered with nylon membrane filters with a pore size of 0.22 μm using a manually operated vacuum pump to remove any suspended particles (grain size of clay: 0.98–3.9 μm). The filtered water was then filled into acid-washed vials and subsequently stored for transport. In a later step the samples were prepared for the individual analysis in the laboratory.

3.2 Laboratory

The laboratory work was conducted between April and August 2016. With the exception of the radon samples which were tested in the field shortly after sampling all other samples were processed at the University of Vienna.

3.2.1 Chloride

Chloride (Cl^-) as well as other anions such as sulfate (SO_4^{2-}), nitrate (NO_3^-) were analysed by ion chromatography (IC 1000, Dionex) with a limit of quantification (LOQ) of 0.1 mg/L and a standard deviation (SD) of 0.05 mg/L. The major cations like sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}) or calcium (Ca^{2+}) were measured using an ICP-OES (Optima 5300DV, PerkinElmer) with a LOQ of 0.1 mg/L; the SD was 0.04 mg/L.

3.2.2 Anthropogenic gadolinium

The gadolinium content can be determined by performing a rare earth element analysis. The used instrument is an online pre-concentration system (SeaFAST 2, Elemental Scientific Inc.) together with an Triple Quad-ICP-MS (8800 ICP-QQQ, Agilent Technologies). LOQ of 0.1 ng/L with SD of 0.04 ng/L were reached.



Figure 4: The samples get loaded into a SC2 DX autosampler by Elemental Scientific

The amount of anthropogenic gadolinium cannot be analysed directly. As there is a background concentration of geogenic gadolinium, it has to be subtracted from the overall test result to determine the anthropogenic part. The geogenic gadolinium concentration was interpolated using europium (Eu) and neodymium (Nd) after the a modified method published by Kulaksiz and Bau (2013). The subscript UCC denotes normalisation to upper continental crust (Taylor et al. 1981) whereas the superscript * denotes the geogenic background.

Equation 1:

$$\log Gd_{UCC}^* = \frac{(4 \log Eu_{UCC} - \log Nd_{UCC})}{3}$$

The anthropogenic component was calculated using the formulas underneath:

Equation 2:

$$Gd^* = Gd_{UCC}^* \times [Gd_{UCC}]$$

Equation 3:

$$Gd_{anthropogenic} = Gd_{measured} - Gd^*$$

In one case the anthropogenic gadolinium was estimated after the method published by Bau and Dulski because of a Eu-anomaly in the respective sample. Other than the method by Kulaksiz and Bau presented above, the method by Bau and Dulski calculates the geogenic gadolinium using samarium (Sm) and terbium (Tb)(Bau & Dulski 1996).

3.2.3 Radon

Due to the decay of the radon the samples had to be analysed as soon as possible. Hence a RAD7 radon detector from DurrIDGE together with the RAD H2O accessory that enables the measurement of radon in water with high accuracy was used and the samples were analysed in the field.

As mentioned in 3.1.2 radon is a product of the uranium decay series. It emerges from mineral grains by alpha recoil or diffusion. The rate with which the radon is emitted depends on the microstructure of the grains, the grain size, the environmental conditions as well as the concentration of the parent isotope ²²⁶Radium, which in turn is a daughter of ²³⁸uranium(Hoehn & Von Gunten 1989b; Dehnert et al. 1999).

Only a fraction of the created radon is able to emanate from the mineral grains. It enters the pore volume which is either filled by gas or groundwater. It is then transported either by diffusion or in dissolved form in water or a carrier gas by advection over longer distances (Vaupoti et al. 2010). The problem of radon exhaust from the soil to the atmosphere in populated areas where radon can accumulate in basements and indoors has been covered on many accounts (Swedgemark & Mjönes 1984; Purtscheller et al. 1995). Even the radon emanation of building materials is recognised as a potential risk to health (Chen et al. 2010).

Radon in poriferous aquifers is usually of geogenic origin. In surface waters it is present as well and derives from sediment load or radon bearing groundwater that infiltrates into surface waters. As surface waters come in contact with the atmosphere radon discharges into the air, hence the concentration is lower than in groundwater. If surface water infiltrates into an aquifer the radon concentration will increase continuously until it reaches equilibrium between the rate of ²²²Rn loss due to radioactive decay and ²²²Rn resupply by the radioactive decay of ²²⁶Radium, the parent of ²²²Rn (Bertin & Bourg 1994). The concentration of radon in water is proportional to its measurable activity. This relationship can be exploited to analyse the age of bank filtrate(Hoehn et al. 1992; Hoehn & Von Gunten 1989a).

The increase of radioactivity from zero to the state of equilibrium is defined as

Equation 4:

$$A_t = A_e * (1 - e^{-\lambda t})$$

where

- A_t equals the activity at the time t
- A_e equals the activity in equilibrium
- λ equals the decay constant, $\lambda_{Rn} = 0.18 \text{ d}^{-1}$
- and t equals the time.

Rearranged, this equation can be used to calculate the residence time of the bank filtrate.

Equation 5:

$$t = \frac{1}{\lambda} * \ln\left(\frac{A_e}{A_e - A_t}\right)$$

As the radon activity of surface water is not negligible low the formula has to be supplemented with the activity of the initial infiltrating water (Dehnert et al. 1999).

Equation 6:

$$t_{res} = \frac{1}{\lambda} * \ln\left(\frac{A_e - A_0}{A_e - A_t}\right)$$

Where

- t_{res} is the residence time
- and A_0 is the radon activity at the time $t=0$.

Equation four, five and six were taken from Dehnert et al. (1999).

Several assumptions for the validity of the method should be taken into account:

- the average distribution of radon progenitors in the aquifer is homogeneous,
- the measured equilibrium concentration is representative for the flow path
- the losses of radon from the aquifer to the unsaturated zone and to the atmosphere is constant
- the distance of the flow path from the infiltration location to the sampling point does not change with varying water tables
- and the infiltrating water does not mix with older groundwater

The equilibrium activity A_e can be measured at a location that is far enough away from the surface water in order to make sure that it is not impacted by new infiltrating ^{222}Rn .

In general it has to be stated that due the radioactive half-life of ^{222}Rn the concentration reaches its asymptotic value within around 5 half-lives (Hoehn et al. 1992; Hoehn & Cirpka 2006).

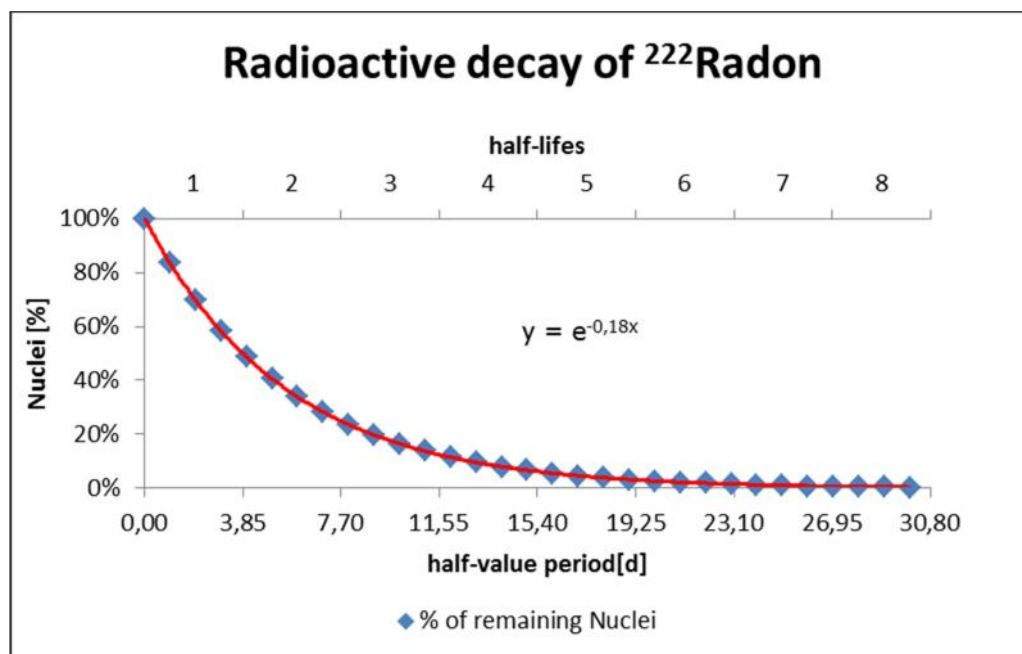


Figure 5: Radioactive decay of ^{222}Rn , half-life=3.85 days

Various sources (Hoehn & Von Gunten 1989b; Hoehn et al. 1992; Hoehn & Cirpka 2006; Dehnert et al. 1999) state that the method allows the dating of infiltrating surface water to groundwater up to a period of four half-lives which is about 15 days.

3.3 Mixing analysis

In order to access the spatial distribution of surface water infiltrate a two component mixing analysis was conducted using the concentrations of anthropogenic gadolinium and chloride in the analysed samples. Both species serve as conservative tracers (Davis et al. 1980; Möller et al. 2000) as they are not subjected to adsorbing effects within the porous aquifer.

One endmember of the mixing analysis for gadolinium is the river water as it is the medium that infiltrates. The MV of anthropogenic gadolinium concentration determined in the samples of the continuous sampling serves as the endmember. As the second endmember, pristine spring water was assumed as it is free of any anthropogenic gadolinium.

For the chloride mixing analysis the MV of the long term sample concentrations of chloride in the river water and the sample location "Well 7" with the highest Cl value was chosen.

The mixing ratios (MR) for bank filtrate to groundwater were determined with the modified equation (Małoszewski et al. 1990):

Equation 7:

$$MR = \frac{C_{GW} - C_S}{C_R - C_S}$$

Where

- MR is the mixing ratio, respectively the amount of surface water in the sample
- C_{GW} is the concentration in the water of the sampled well
- C_S is the concentration in river water and
- C_R is the concentration in river water.

A mixing ratio of 1 represents pure bank filtrate originating from the river whereas a mixing ratio of 0 represents pure ground water not influenced by any surface water.

The dynamic range (DR) is an important characteristic of a tracer. Usually it is defined by ratio of the maximum output signal to the minimum detection limit.

In this work the dynamic range (DR) of a tracer is the concentration range over which a tracer can be used. It is defined by the ratio of the two end member concentrations (here chloride: 1.49; 7.03–10.48 mg/L) or the ratio between the concentration in the river water and the limit of quantification (here gadolinium: 63.52; 0.1–6.35 ng/L), respectively. A small DR implies high uncertainties in the mixing ratio whereas a large DR reduces them (Bichler et al. 2015).

The accuracy of anthropogenic gadolinium as a tracer can be expected superior to chloride due to the larger dynamic range. The higher the DR, the larger the distance the tracer can be monitored from the initial entry point.

4 Results and Discussion

Mirroring the obtained results the project area can be divided into several zones. The first classification was made utilising the measured EC. In combination with the analysis of the concentration of anthropogenic gadolinium and chloride as tracers the aquifer in the investigated region can be subdivided into three main zones and one sub-zone.

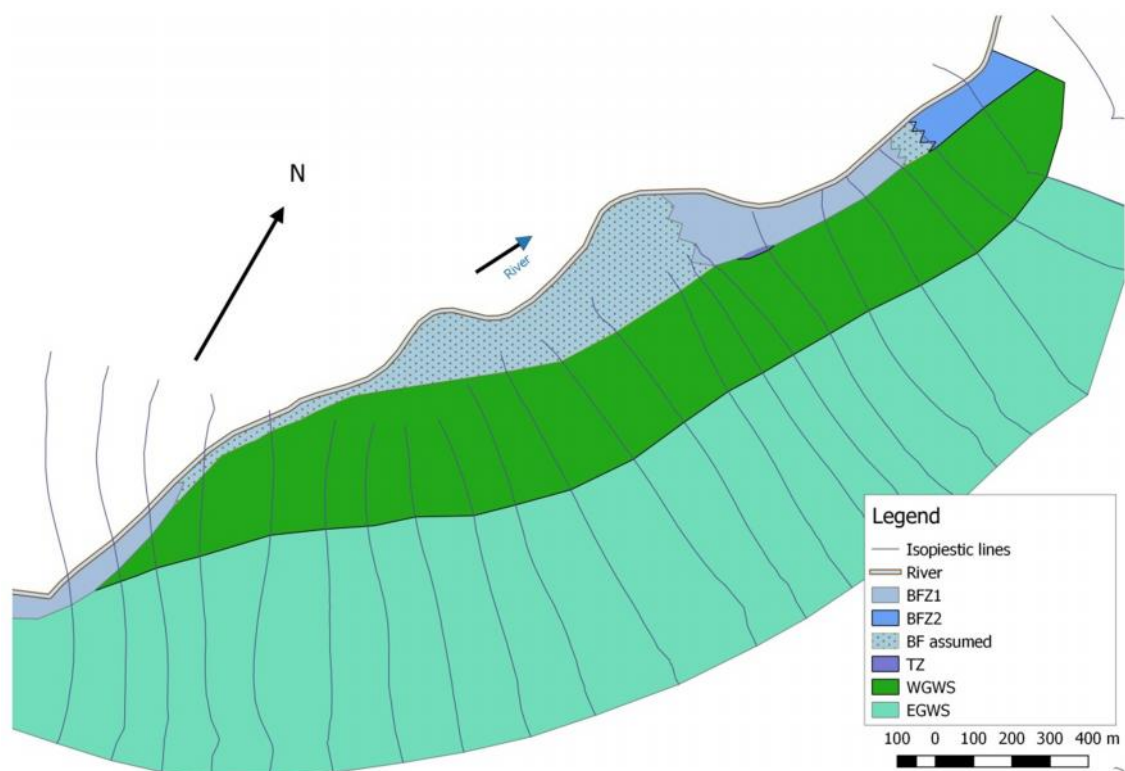


Figure 6: Spatial distribution of the investigated area in three main zones and one subzone; BFZ1 = Bank filtration zone 1; BFZ2 = Bank filtration zone 2; BF assumed= area of assumed bank filtration; TZ = Transition zone; WGWS = Western groundwater stream; EGWS = Eastern groundwater stream;

Along the right-hand shore of the river a strip can be identified where the river directly interacts with the aquifer and can be seen as a zone of direct river bank infiltration. It means that the infiltration of river water into the groundwater takes place inside the upstream and downstream border of the investigated area. The upstream area (well 1, 9, 10 and 11) hereafter Bank filtration zone 1 (BFZ1), and the downstream area (well 19, 22 and 23) hereafter Bank filtration zone 2 (BFZ2) have been identified based on hydrochemical parameters as well as on tracer data. This zone usually comprises the hyporheic zone in which river water penetrates into the alluvium and may mix with the groundwater that originates from hillslope (phreatic groundwater) or other groundwater

not directly recharged from the river (Stanford 2007). In the case at hand the hyporheic zone in the investigated area is formed only by infiltration of water beneath the river bed due to the artificially low groundwater table and the influent conditions. As we deal with an artificially embanked river there is no real parafluvial zone, hence no parafluvial flow.

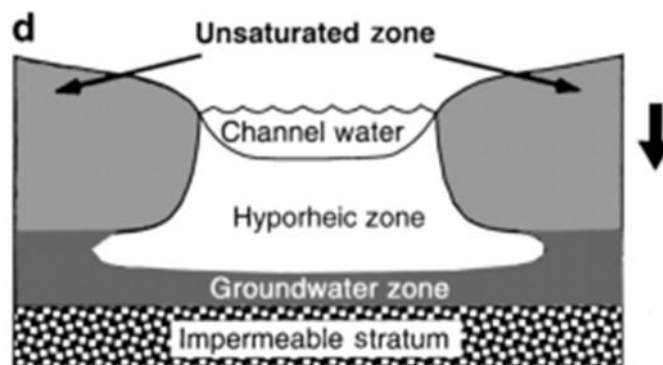


Figure 7: A hyporheic zone created only by infiltration of channel water beneath the stream bed (Culver & Pipan 2014) originally from (Malard et al. 2002)

Adjacent to the bank filtrate two different groundwater streams have been identified on the orographic east side of the river. The Western groundwater stream (WGWS) borders on the bank filtrate in the West and the Eastern groundwater stream (EGWS) in the East. A sub-zone between the bank filtrate and the WGWS was outlined for a well sample that showed high EC values found in the WGWS but did not show the corresponding tracer concentrations.

Alluvial aquifers usually have complex bed sediments with interstitial zones of preferential groundwater flow sometimes called paleo-channels. Therefore the model at hand is a simplification of the actual situation.

In absence of a groundwater flow model it is assumed, that the water moves more or less perpendicular to the isopiestic lines. The estimated lateral borders of the separate groundwater bodies follow that assumption. The longitudinal transitions of the different areas with direct river bank infiltration are displayed serrated (see Figure 6).

The process that resulted in the classification of the aquifer in the above mentioned zones is described below.

4.1 Field parameters

In general it can be stated that during the time of the sampling in April 2016 the river showed the highest pH (MV = 8.5 with SD 0.1) together with a relatively low values for the EC (MV = 377 $\mu\text{S}/\text{cm}$ with SD=2.6 $\mu\text{S}/\text{cm}$). The well samples showed lower pH (MV = 7.7 with SD 0.3) and higher (MV = 451 $\mu\text{S}/\text{cm}$ with SD=55.2 $\mu\text{S}/\text{cm}$) values for the

EC. A plot of the two parameters against each other revealed that a low pH-value correlates with a high EC. This suggests that the pH is influenced by the presence of carbonate present in the soil. The limestone in the alluvial gravels increases the buffering capacity of the groundwater and keeps the pH close to neutrality.

4.1.1 Electrical Conductivity

The EC of the well samples was used to preliminary classify the ground water using the Jenks natural breaks optimisation method implement in a GIS software used for visualisation of the data.

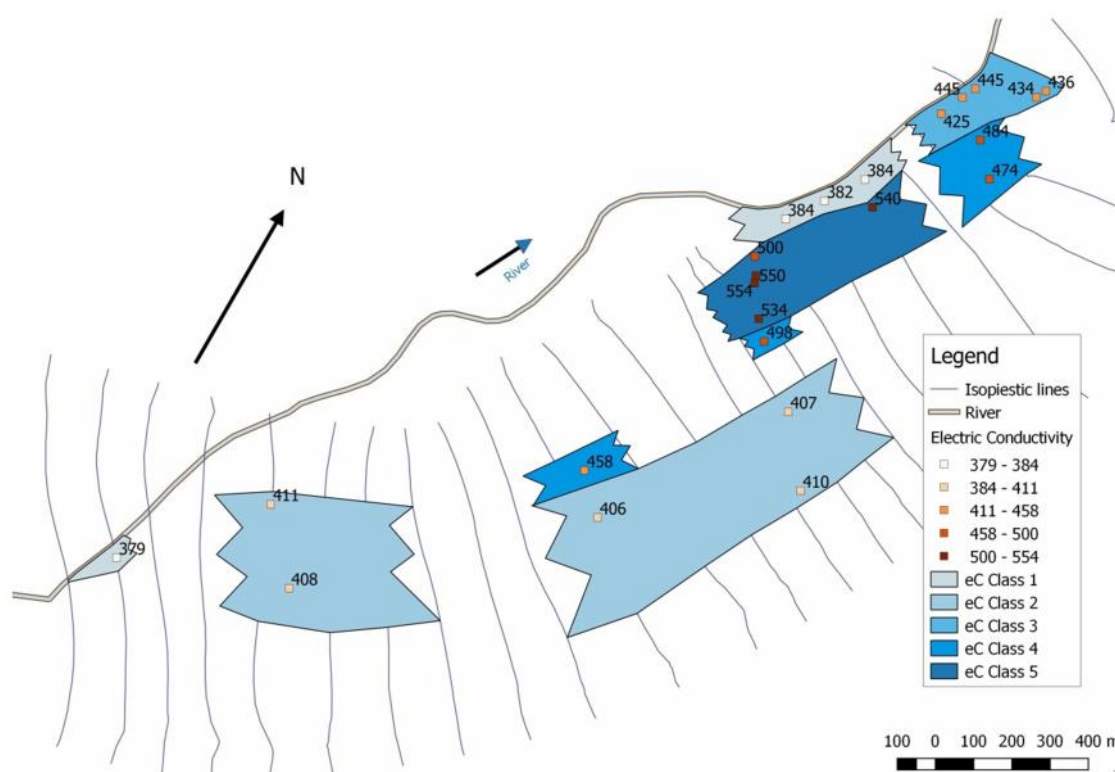


Figure 8: Classification of the measured EC using the Jenks natural breaks method; the respective classes were outlined to visualise areas with similar EC

The mean value of the measured EC of river water is 377 $\mu\text{S}/\text{cm}$. The well samples of eC Class 1 have very similar values. It can be assumed that they are directly influenced by recent river bank infiltrate. Higher values of EC can be caused by a longer residence time of the groundwater and is highly dependent on the sediment type present in the subsurface and the interaction with it.

4.1.2 Temperature and pH

Regarding the measured temperature in the field in line with the sampling, an increase in temperature by trend can be monitored with increasing lateral distance to the river.

The river water temperature is subdued to atmospheric changes and fluctuated during the five days of the investigation campaign in April 2016 between 6.7°C and 9.9°C. The SD amounts to 1.5 °C (n=4). The pH behaves opposite and shows a slight decline with increasing lateral distance to the river. The river water showed a mean pH of 8.5 with an SD of 0.1. In comparison the temperature the pH of the river is almost constant.

BFZ1 has a mean temperature of 6.3°C with a SD of 0.4°C and a mean pH of 8.2 with an SD of 0.2 (n=4). BFZ2 shows a mean temperature of 7.4°C with an SD of 0.4°C and a pH of 7.5 with an SD of 0.4 (n=3).

The WGWS (here together with the transition zone) shows an increase of the mean temperature to 10.2°C with an SD of 0.7°C which means that the temperature level is almost stable over the whole zone. The mean pH was determined with 7.5 with an SD of 0.15 (n=14).

The eastern part of the investigated area that was classified as EGWS shows also a mean temperature of 10.2°C but with a higher fluctuation and a SD of 2°C as one well (well 3 T= 7.3°C) showed a similar temperature as wells of the bank filtration zones. As the EGWS can be classified as distal bank filtration zone and well 3 is still the nearest one to the river this seems reasonable. The mean pH shows a slight decrease in comparison to the neighbouring WGWS to 7.8 with an SD of 0.1.

4.2 Hydrochemistry of major ions

The major anions and cations that were analysed are chloride, nitrate, sulfate (anions) and calcium, magnesium, sodium and potassium (cations).

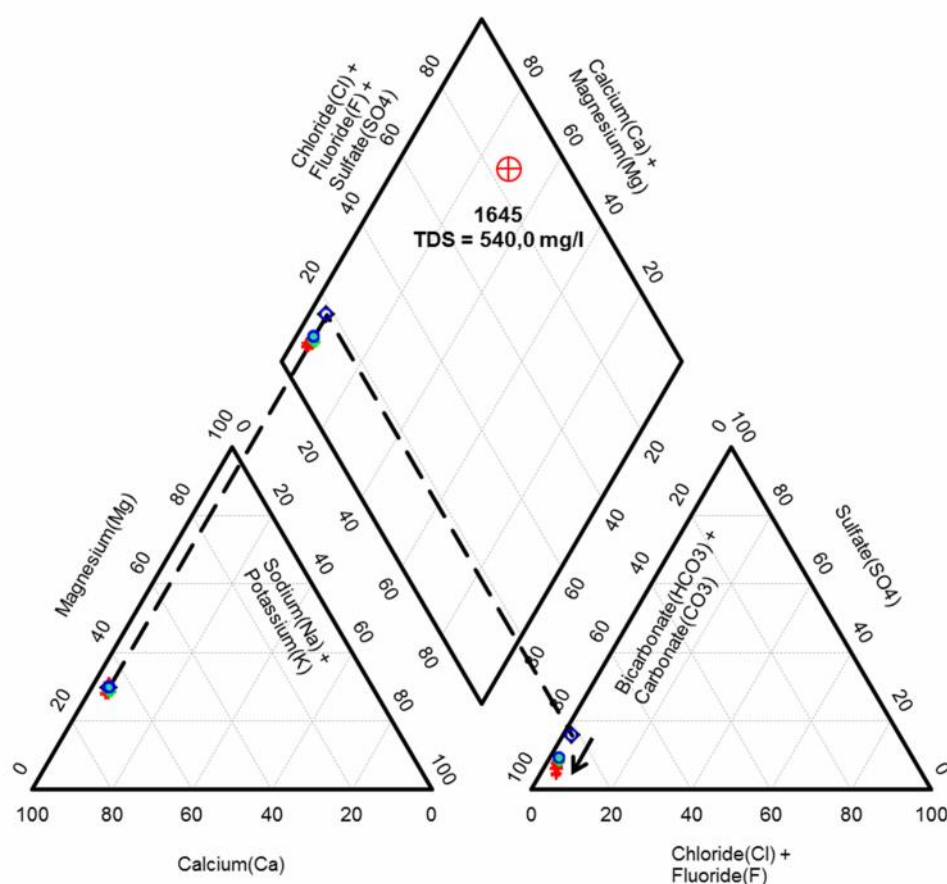


Figure 9: Piper diagram of the samples taken during the investigation campaign 2016; the arrow in the right triangle marks the trend from river water to groundwater

All samples in the piper diagram can be classified as calcium bicarbonate waters and are considered to be fresh shallow groundwater. All water samples in the diamond part lie on the same line. They can be traced back to river water as origin (blue marker). The HCO₃ values were calculated from the ion balance and provided by a third party. That means they are not determining for the groundwater classification but allow for a basic estimation of the evolution of the groundwater. The increase in bicarbonate however suggests calcium solution within the aquifer.

The total hardness (dH°) was calculated (Wikipedia 2016) with

Equation 8:

$$dH^{\circ} = (Ca * 1.4 + M_{\text{eq}} * 2.307) / 10$$

The equivalent mmol/L earth alkali content was calculated with:

Equation 9:

$$\text{mmol/L} = \frac{Ca}{40} + \frac{M_{\text{eq}}}{24.3}$$

Hydrochemically the aquifer can be divided in areas of moderate water hardness (2.21 – 2.5 mmol/L earth alkali respectively 12.41–14.0 dH°) and areas with hard water (>2.5 mmol/L earth alkali respectively >14 dH°). The highest chloride concentrations can be found in the areas with harder water whereas the highest gadolinium concentrations are bound to areas with moderate water hardness.

The hardest water was found within the samples of the WGWS (MV=2.93 mmol/L) and the transition zone (MV=2.96 mmol/L). The water with the lowest content of earth alkali (MV=2.23 mmol/L) was found in the “BFZ1” where direct bank infiltration occurs.

The values of the EGWS are slightly higher (MV=2.31 mmol/L) than in the bank filtration zones but considerably lower than in the adjacent WGWS. Due to the similarity it can be concluded that the EWGS is originating from river bank infiltration. The higher EC suggests an infiltration source further upstream of the investigated area.

The BFZ2 (MV=2.54 mmol/L for) shows a higher water hardness and EC. This is probably due to an influence of the bordering WGWS.

The ratio of chloride to the sum of all anions is well below 0.8 and therefore the source of chloride is likely rock-weathering in all well samples as well as in the river samples. The ratio between Na^+ , K^+ and Cl^- and Na^+ , K^+ , Cl^- and Ca_2^+ is below 0.2 which makes plagioclase weathering an unlikely source which is not unreasonable giving the limestone heavy characteristics of the alluvial gravels (regional environmental authority, 2016). The ratio of magnesium to the sum of calcium and magnesium, which is <0.5, hints for a limestone-dolomite weathering as source. This is supported by the ratio of calcium to calcium and sulfate that excludes gypsum as a source and also points to carbonate weathering. Dedolomitisation is also excluded as the ratio of calcium plus magnesium to sulfate (ranging 2.5 – 9.6) is well above the required range (>0.8, >1.2) (Hounslow 1996).

The MV of calcium in the river water was determined with 60.79 mg/L. All well samples showed a strong positive correlation of the calcium concentrations with the EC ($r=0.95$).

Sodium and potassium are released to the system during silicate weathering. As the catchment area is dominated by glacial and postglacial deposits on top of Molasse sediments these elements are most likely derived from weathering processes of the bedrock.

4.3 Chloride

The analysis of the major anions was conducted on two sets of samples. As mentioned in 3.1 one set comprises continuous samples of the river water (n=55) as well as continuous samples of the long term observation well LTOW (n=51). The second set is the batch of samples collected during the field campaign 2016.

4.3.1 Long-term samples

Over the course of the sampling period (Oct. 2014 – Dec. 2015) the chloride concentrations in the river water and the LTOW (representing a bulk aquifer in spatial elongation of the EGWS) show an overall increase. Divided in a hydrological winter (Nov. 2014 – Apr. 2015) and hydrological summer (May 2015 – Oct. 2015) there is a 20% increase of the chloride concentration in the summer.

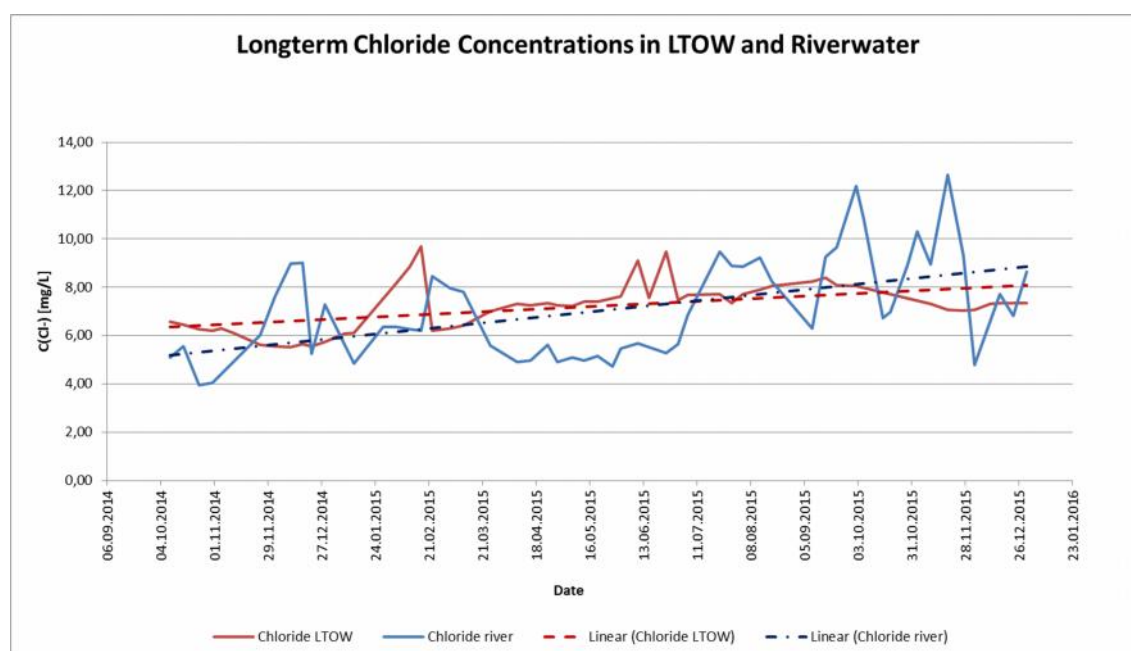


Figure 10: Concentration of chloride in long term samples of river water and the LTOW;

The MV of the chloride concentrations in the long term river samples is 7.03 mg/L with an SD of 2.1 mg/L (n=55). The MV of the chloride concentrations of the long term LTOW samples scores slightly higher and is calculated with 7.17 mg/L with an SD of 1.0 (n=51).

The chloride concentration in river water is connected to the discharge (see Figure 11) of the river. High concentrations in the river water coincide with low discharge values and vice versa. The Pearson correlation coefficient (Evans 1996) shows a strong negative correlation ($r=-0.7$). Nevertheless, the highest amounts of chloride are of course transported during periods of high discharge.

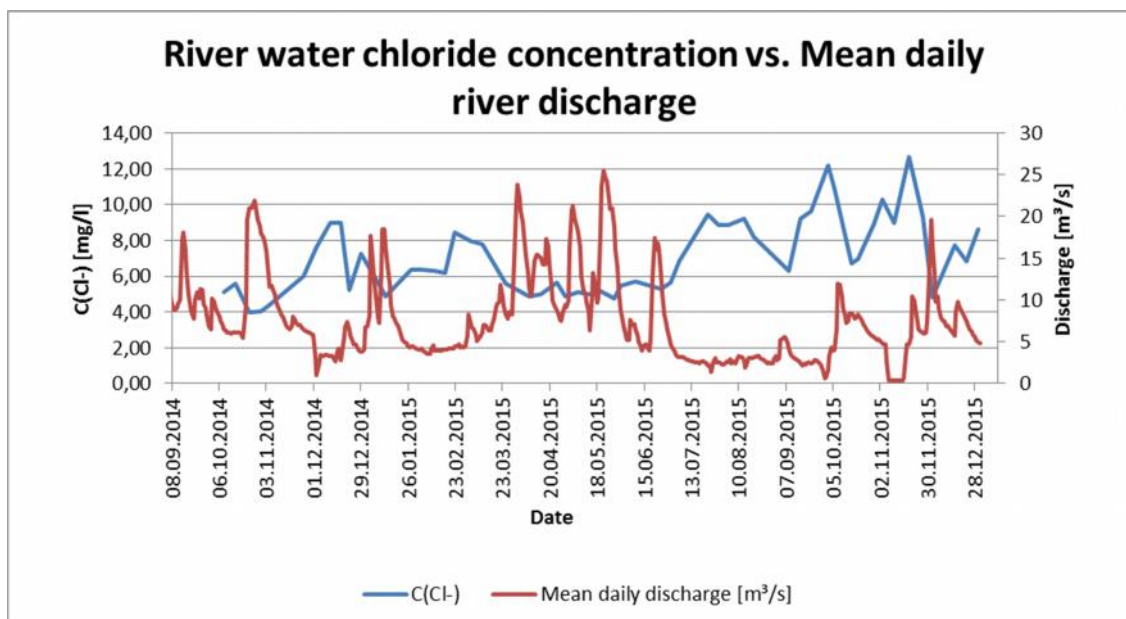


Figure 11: Concentration of Chloride in long term samples of river water against the Mean daily discharge of the river

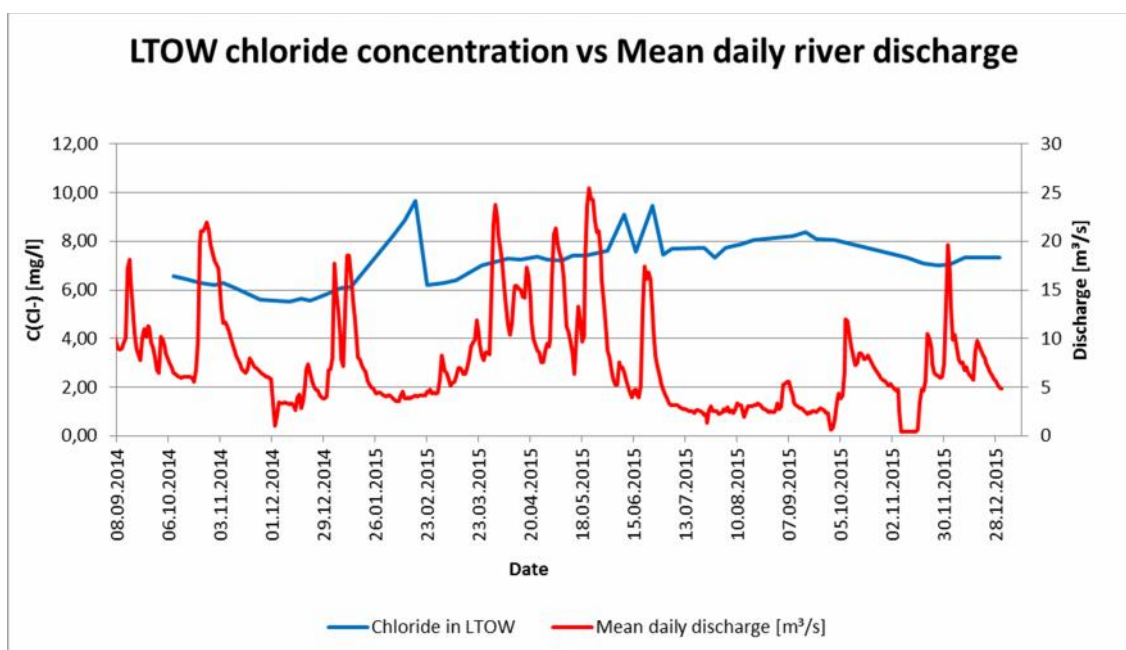


Figure 12: Concentration of chloride in long term samples of the LTOW against the mean daily discharge of the river

No such relation has been found for the water of the LTOW at first (see Figure 12). However, after calculating the dissolved chloride in river water related to the mean daily discharge of the river ($c(\text{Cl}^-)$ in mg/L times discharge in L/s) the three peaks in the LTOW chloride concentration can be correlated with three corresponding peaks in the in the river water. The time shift between the correlating peaks is between 34 and 36 days (see Figure 13).

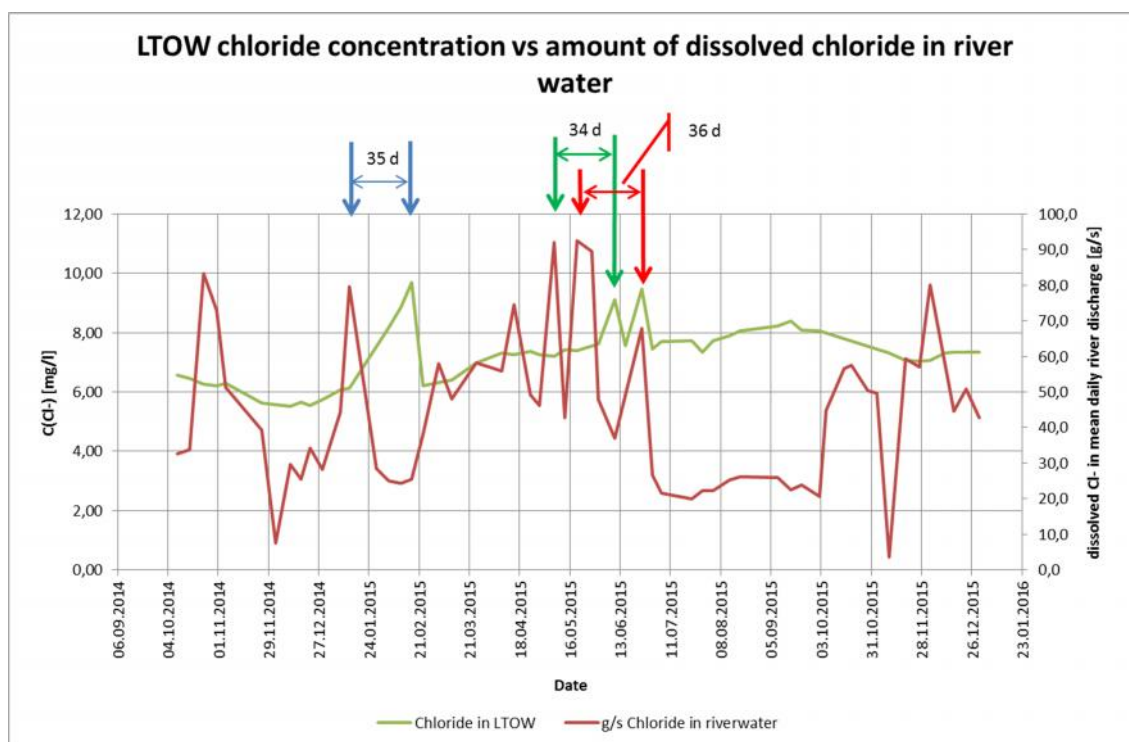


Figure 13: Long term chloride concentration in the LTOW in mg/L vs. the amount of dissolved chloride in the river discharge in g/s.

Although a theoretical travel time of infiltrating river water to the area of the LTOW can be stated (34 to 36 days) it is not exactly known where this water infiltrates. The distance perpendicular to the isopiestic lines (the assumed groundwater flow direction) between the the LTOW and the river is around 2750 m. The mean effective flow velocity for the aquifer was determined to be 85 m/d (see chapter 2.1). The calculated travel time for water along this path would be around 32 days. This matches the travel time depicted in Figure 13.

The fact that other peaks in the chloride curve of the river do not trigger a response in the chloride curve of the LTOW might has the reason that the continuous sampling of river water samples and samples of the LTOW was done in irregular intervals. Although taken in approx. intervals of one to one and a half weeks there are months with three samples and months with up to five samples. As the chloride concentration of the river water and the LTOW can vary from day to day it is possible that some peak concentrations were simply missed and not sampled.

4.3.2 Well samples of the field campaign 2016

The distribution of the chloride concentrations in the investigated area is not homogeneous. There is a tendency for higher chloride concentrations in parts of the aquifer that contains water infiltrated from further upstream. The EGWS and the WGWS both show similar MVs for the chloride concentration (MV EGWS = 8.40 mg/L with an SD =

1.64 mg/L; MV WGWS = 8.26 mg/L with SD = 0.9 mg/L) which are well above the chloride concentration of BFZ1 and BFZ2.

A Pearson correlation shows a strong positive correlation of the water hardness in mmol/l to the chloride concentration ($r=0.66$).

The concentrations measured within the BFZ1 and BFZ2 are even smaller than the mean concentration of the long term river samples which has been used as an input parameter for the mixing analysis.

The chloride concentrations found in the well samples (23 Wells) can be considered to be low. The MV of all samples is 7.19 mg/L with a standard deviation of 1.69 mg/L. According to the regional authorities the chloride concentrations in groundwater found in quaternary calcareous alluvial gravels ($n=723$) lies between 3.5 mg/L and 60 mg/L with a median of approx. 19 mg/L and a MV of approx. 27 mg/L.

4.3.3 Chloride mixing analysis

The mixing analysis conducted with chloride yielded different MRs than the gadolinium mixing analysis. This was anticipated once the dynamic range, which is low for chloride but high for gadolinium was determined. The difference to the gadolinium MRs scored between minus 125% to plus 90% in certain samples. Only in wells where chloride concentrations were close to the upper endmember concentration (inside an 8% margin below the endmember concentration) the MRs yielded comparable results to the gadolinium MRs. In this manner only 4 wells yielded similar Cl^- MRs to the Gd_{anth} MRs (see Figure 15, red border).

Sample Location	n	%SWCl-	St.Dev.	Cl mg/L	St.Dev.
Bank Filtrate	7	139%	13%	5.69	0.41
Transition	1	93%	-	7.27	-
GW Stream West	11	65%	47%	8.24	1.62
GW Stream East	4	64%	26%	8.26	0.90

Table 1: Summary of the mixing analysis results for Cl^-

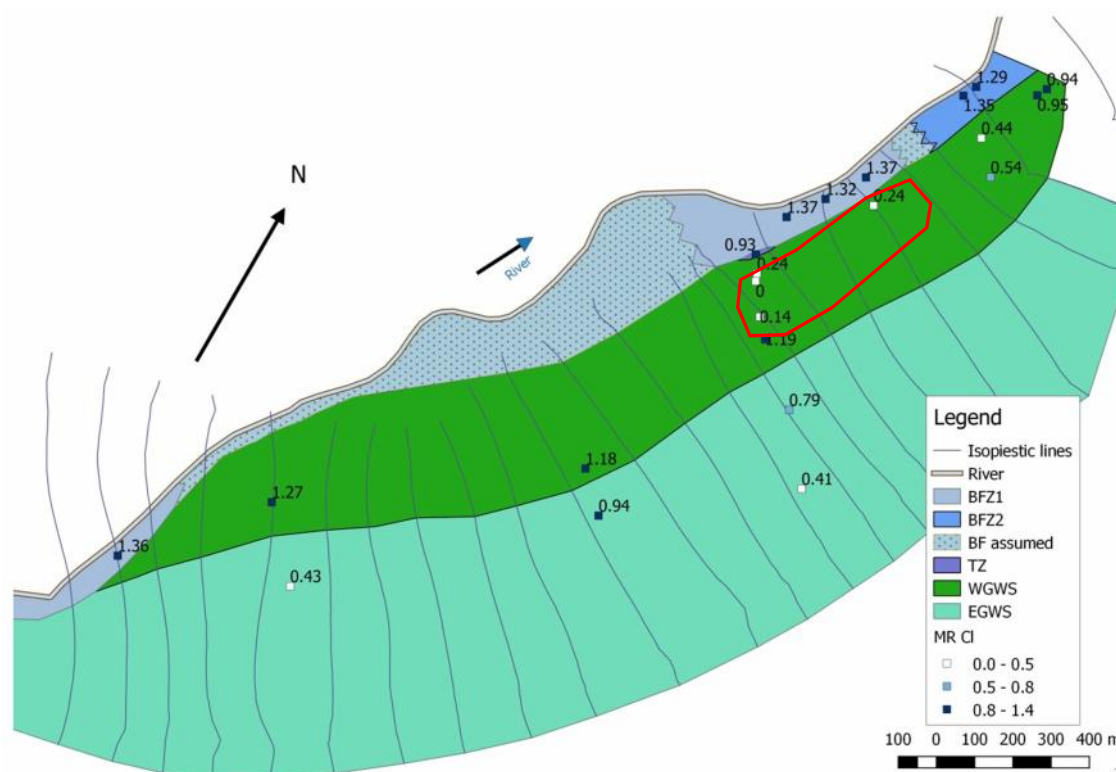


Figure 14: Mapping of the chloride concentration (Mixing ratio) within the investigated area; red border outlines wells with chloride MRs similar to Gd_{anth} MRs

The main problem is that the mean chloride concentration of the long term sample in the river water is higher than the chloride concentrations in several samples collected during the field investigation in April 2016. That makes a correct mixing analysis difficult as a mixing ratio yields values >1 in such cases. This concerns 10 wells, which means over 40% of all sample points. Another limiting factor is the absence of a real unaffected endmember (like pristine spring water) for the mixing analysis. Finally, as mentioned in chapter 3.3, the dynamic range of chloride as a tracer is small ($DR=1.5$). Therefore its applicability as natural tracer within the investigated area is very limited.

4.4 Anthropogenic gadolinium

The analysis of the REEs was conducted on two sets of samples. As mentioned in 3.1 one set comprises continuous samples of the river water ($n=59$) as well as continuous samples of the long term observation well LTOW ($n=50$). The second set is the batch of samples collected during the field campaign 2016.

Special focus was set on gadolinium as well as europium and neodymium, which were used to interpolate the value of geogenic gadolinium as it cannot be determined directly. The methodology is described in chapter 3.2.2.

4.4.1 Long-term samples

Over the course of the sampling period (Oct. 2014 – Dec. 2015) the concentrations of Gd_{anth} in the river water show an overall increase. The concentrations LTOW are stable for the most part and only show a very slight increase that is attributed to an isolated peak near the end of the timeline (see Figure 15). This isolated peak is no outlier though as elaborated in Figure 17. The increase in river water can be related to the constantly growing numbers of MRI examinations due to modern medical treatment guidelines MRI became a standard procedure for many illnesses (Vorbeck 2015).

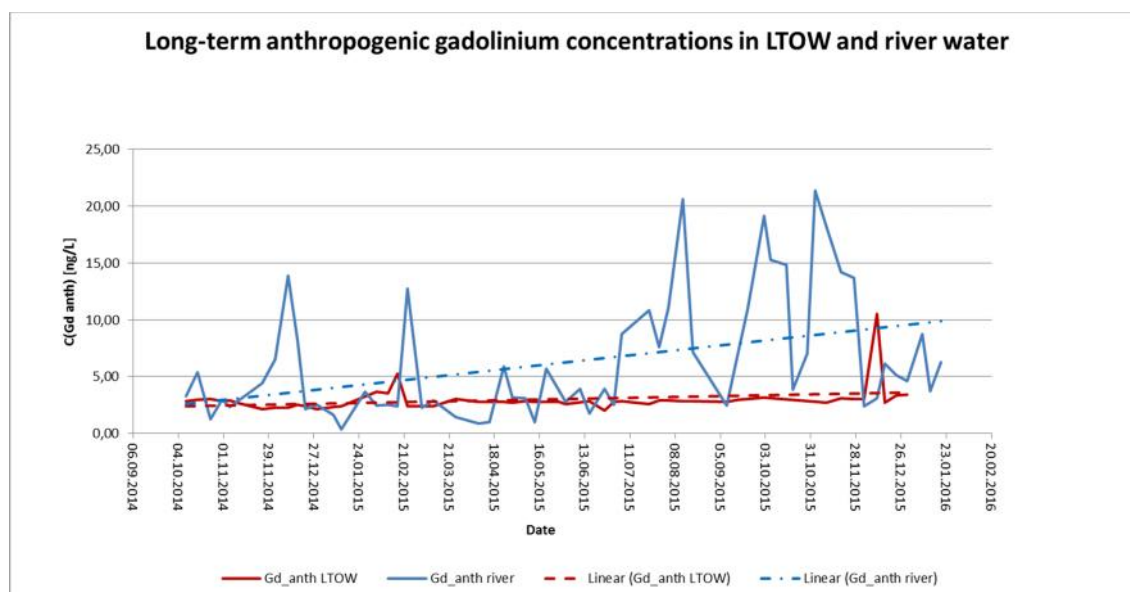


Figure 15: Concentration of Gd_{anth} in long term samples of river water and the LTOW;

The mean Gd_{anth} concentration in the long term river samples equals 6.35 ng/L with an SD of 5.37 ng/L ($n=59$). The mean value of the Gd_{anth} concentrations of the long term LTOW samples scores slightly higher and equals 2.97 mg/L with an SD of 1.2 mg/L ($n=50$).

The concentration of Gd_{anth} only shows a moderate negative correlation with the river discharge, which means that high concentrations likely occur when the discharge is low.

The Pearson correlation coefficient only equals -0.5. The controlling factor for the amount of Gdanth is the discharge of the STP upstream of the investigated area.

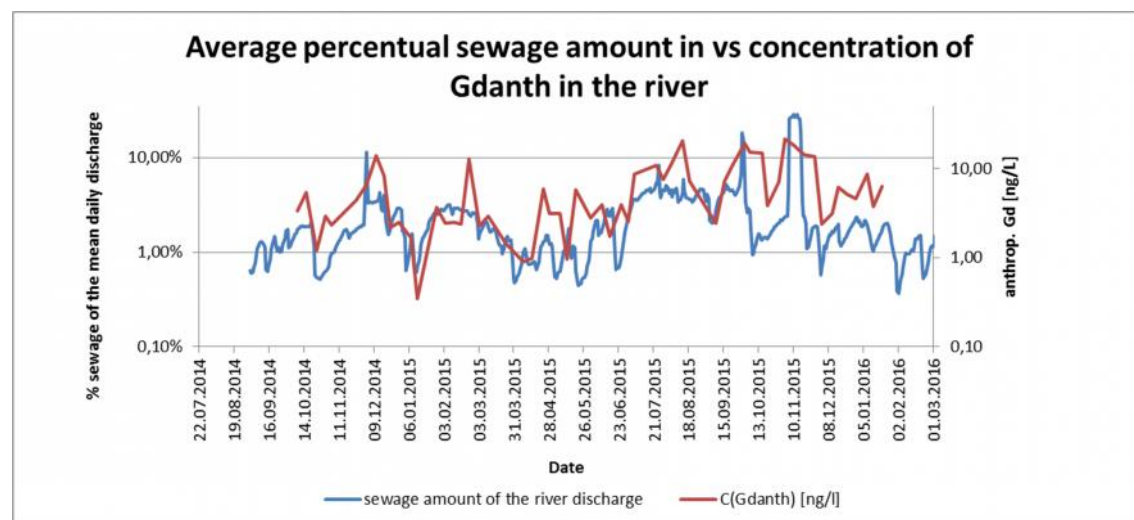


Figure 16: Average percentual amount of sewage in comparison to the concentration of anthropogenic gadolinium in the long term river samples

To estimate travel times between the river and the LTOW the percental amount of sewage in the mean daily river discharge was plotted against long term the Gd_{anth} concentration measurements from the LTOW.

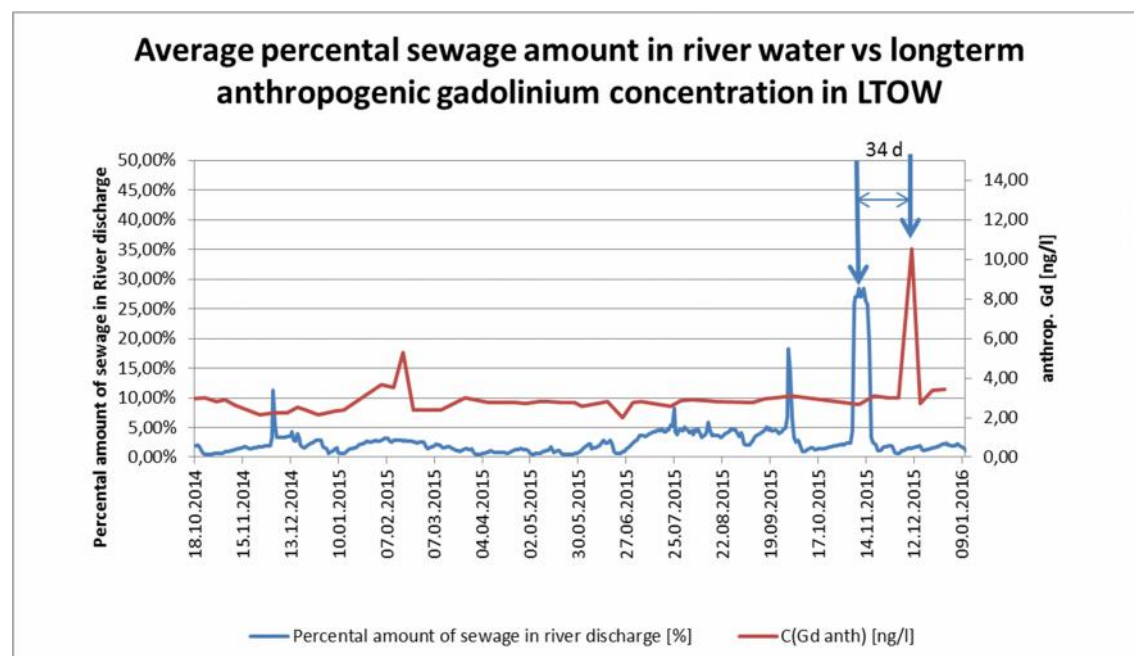


Figure 17: Average percental amount of sewage in the mean daily river discharge against the concentration of Gd_{anth} in LTOW

As seen in Figure 17 only one pair of distinctive peaks can be assumed to be related to each other. The temporal difference between the peaks is 34 days which would fit in the travel times mentioned in chapter 4.3.1. The peak in the LTOW ($c(\text{Gd}_{\text{anth}})=10.54 \text{ ng/L}$) was recorded at the 11th December 2015. The peak in the percental amount of sewage was recorded starting with the 7th November 2015. The temporal duration of the peak lasted for nine days until the 15th of November 2015. In the time around 34 days prior to the peak recorded for the LTOW, high concentrations of Gd_{anth} (mean=has been calculated using samples taken between the 3rd (21.4 ng/L) and 10th (18.16 ng/L) November 2015 (see A.2 Data Gadolinium, Table 6, Table 7, Table 8). If the peaks are corresponding, around 49% of the original Gd_{anth} river water concentration was recorded in the samples taken from the LTOW. Inserted into the mixture equation the MR equals 0.49 which accounts to an amount of river water of 49%. This is consistent with the mean value of the LTOW MRs ($n=50$) which is 0.47 (or 47% surface water) with an SD of 0.19.

4.4.2 Well samples of the field campaign 2016

In general it can be stated that high concentrations of anthropogenic gadolinium were associated with parts of the aquifer that showed a relatively low total hardness.

A Pearson correlation shows a high negative correlation coefficient (r) of the concentration of anthropogenic gadolinium to the water hardness ($r=-0.67$). That means that within the project area, lower values for Gd_{anth} are more likely to be found in hard water. The lowest concentrations of Gd_{anth} were measured within the WGWS where, with exception of the transition zone (only one well) the water hardness is the highest (see chapter 4.2).

The concentrations are high in the zones of direct bank infiltration (labelled BFZ1 and BFZ2) and in the EGWS (labelled Groundwater Stream East). One sample with an elevated level of Gd_{anth} was collected in well 5, which was classified as transition zone (Labelled "Transition zones") due to the fact that although it showed a high value for Gd_{anth} like the BFZ1 to the West, it had an EC and water hardness comparable to the WGWS to its East. In fact it has an intermediate position in all mentioned parameters. It can be assumed that well 5 lies within a zone where the hyporheic water of the BFZ1 is mixed with the groundwater from the WGWS. Although hints were only found in this particular well it can be assumed, that such transition zones are common along the whole border between areas of surface water infiltration and the groundwater.

4.4.3 Gadolinium mixing analysis

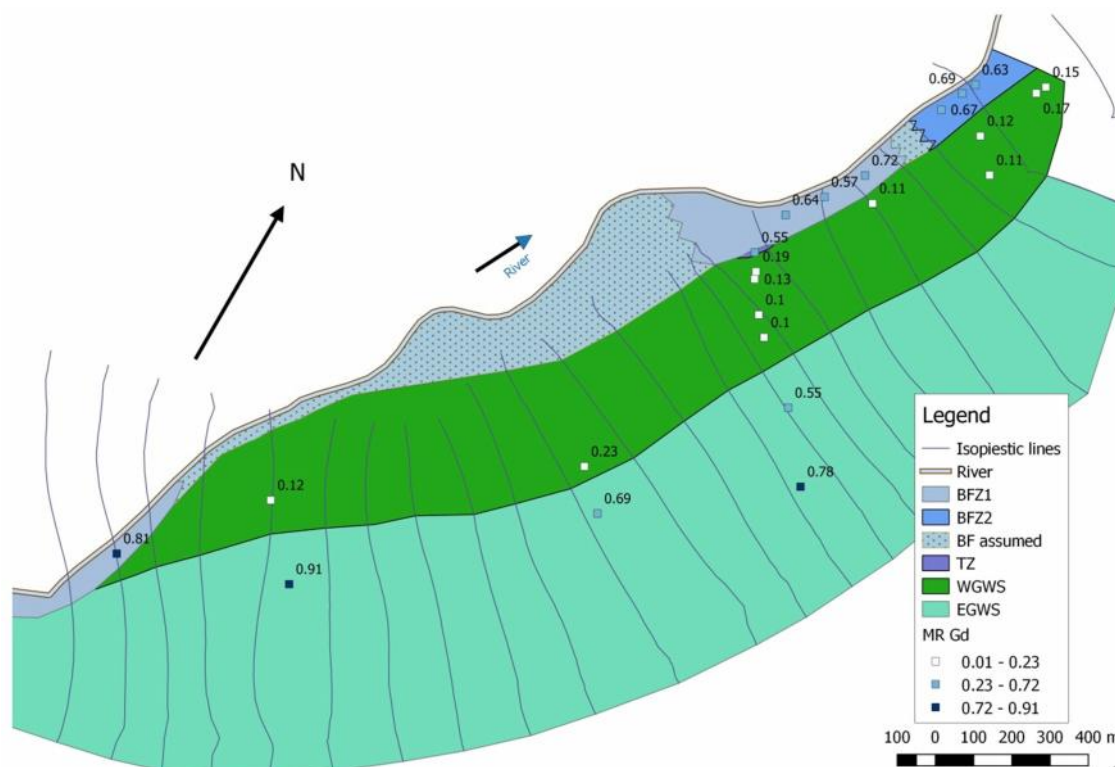


Figure 18: Mapping of the anthropogenic gadolinium MR within the investigated area;

BFZ1, BFZ2 and the EGWS show moderate to high Gd_{anth} MRs. That means that these areas are moderately to strongly impacted by bank infiltration processes as the amount of surface water in percent equals the MR times 100. The WGWS consistently shows very low MR for gadolinium. It can be assumed that the WGWS is only remotely influenced by bank infiltration processes.

Sample Location	n	% SWGd	St.Dev.	Gd ng/L	St.Dev.
Bank Filtrate	7	68%	8%	4.30	0.49
Transition	1	55%	-	3.49	-
GW Stream West	11	14%	4%	0.94	0.30
GW Stream East	4	73%	15%	4.66	0.96

Table 2: Summary of the mixing analysis results for Gd_{anth}

4.5 Radon

The calculation of the residence time and the related formulas are described in chapter 3.1.2.

A_0 is the MV of the ^{222}Rn activity measured in river water ($n=4$) equals 0.25 Bq/L. For A_t the activity of the sample was inserted.

The value for the equilibrium activity A_e was obtained utilising the results from the gadolinium mixture analysis. Well 15 (see Figure 2) which is located within the WGWS that shows consistently low MRs. Well 15 ($\text{MR}_{\text{Gd}} = 0.1$; 10% surface water) has the lowest concentration of Gd_{anth} of all field samples and therefore the lowest MR has also been calculated for this location. This means that at this location the smallest amount of surface water was determined throughout the investigated area. Results of the chloride mixing analysis ($\text{MR}_{\text{Cl}} = 0.13$; 13% surface water) supports the results Gd_{anth} mixing analysis at this location.

Other wells showed higher ^{222}Rn activities but they either showed high amount of surface water (high $c(\text{Gd}_{\text{anth}})$, high MR) or are too far away from the river to display reliable results.

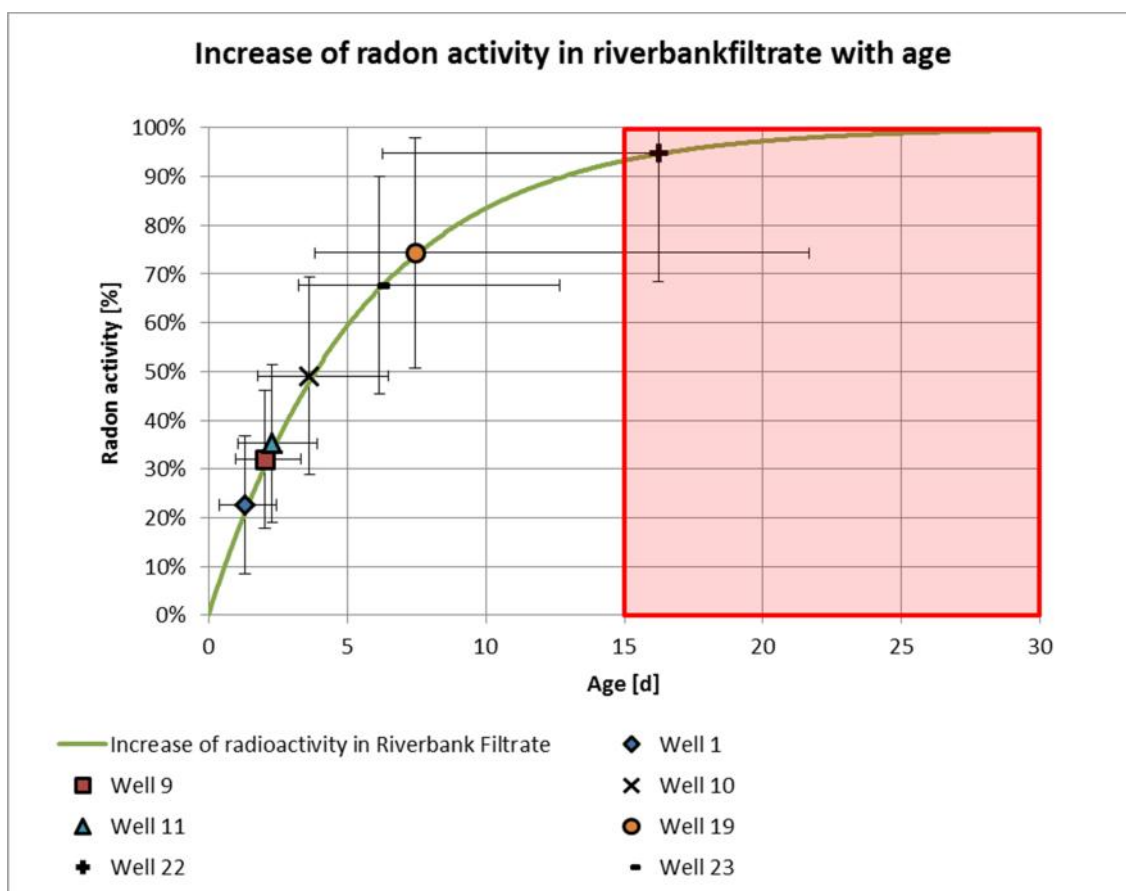


Figure 19: Wells in BFZ1 and 2 can be dated with ^{222}Rn ; error bar whiskers show the maximum uncertainty of measurement

The maximum uncertainty of measurements generally gets higher with increasing residence time. A Pearson correlation shows a very strong positive correlation ($r=0.98$) to the radon activity. The wells 1, 9, 10 and 11 are assigned to BFZ1. Wells 19, 22 and 23 are within BFZ2. The residence time recorded in BFZ1 is lower than in BFZ2. As seen in Figure 19 the residence time of well 22 is already marginal over the 15 day border. This shows the limitations of the ^{222}Rn method.

ID	% Activity of Ae	Residence time in days	% Surface Water (MR Gdanth)	Infiltration ratio [d^{-1}]
Well 1	23%	2.4	81%	0.33
Well 9	32%	2.0	64%	0.32
Well 11	35%	2.3	57%	0.25
Well 10	49%	3.6	71%	0.20
Well 19	74%	7.4	67%	0.09
Well 22	95%	16.2	69%	0.04
Well 23	68%	6.2	63%	0.10

Table 3: Data for Figure 19: Percent activity relative to the equilibrium value Ae ($A_e=12.02 \text{ Bq/L}$ =100%) and the calculated residence time in days; % SW derived from MR $G_{d_{anth}}$; Infiltration ratio = $\%SW/t_{res}$

Although all wells in the BFZ1 and 2 are more or less in the same distance (lateral distance 30-40 m) from the river the ages differ especially in respect of the drillings in the BFZ2. This can be caused by different geological conditions. No significant correlation between the amount of surface water and the calculated residence time was observed. Therefore the ratio of the percentage of surface water in the aquifer to the residence time was introduced and labelled as infiltration ratio (IR) [d^{-1}]. It decreases in downstream direction. This infiltration ratio has a very strong negative correlation ($r=-0.98$) with the %activity of Ae of the samples. That means that the more the radon activity of the sample converges to the equilibrium activity Ae, the lower the IR will be.

Wells 1, 9, 11 and 10 are located in BFZ1 and seem to be well connected to the hyporheic zone of the river and a high amount of infiltrated surface water can be measured after a short time (high infiltration ratio, $IR=0.33$ to 0.22). In contrast, the wells 19, 22 und 23 which are all in BFZ2 are not as well connected to the hyporheic zone of the river. Although the amount of surface water is similar to the wells in BFZ1 it either takes a longer time for the water to pass through the BFZ2 (lower hydraulic conductivity related to finer grained sediments) or the water has to pass a longer distance from the infiltration area to the sample wells. As the morphology of the well in BFZ1 and BFZ2 is

very similar the latter is excluded. It is therefore assumed that the BFZ1 is geologically dominated by rather course grained sediments with a high hydraulic conductivity and the BFZ2 comprises a higher amount of fine grained material which decreases the hydraulic conductivity.

4.6 Combined Map – Spatial distribution, quantification and residence time

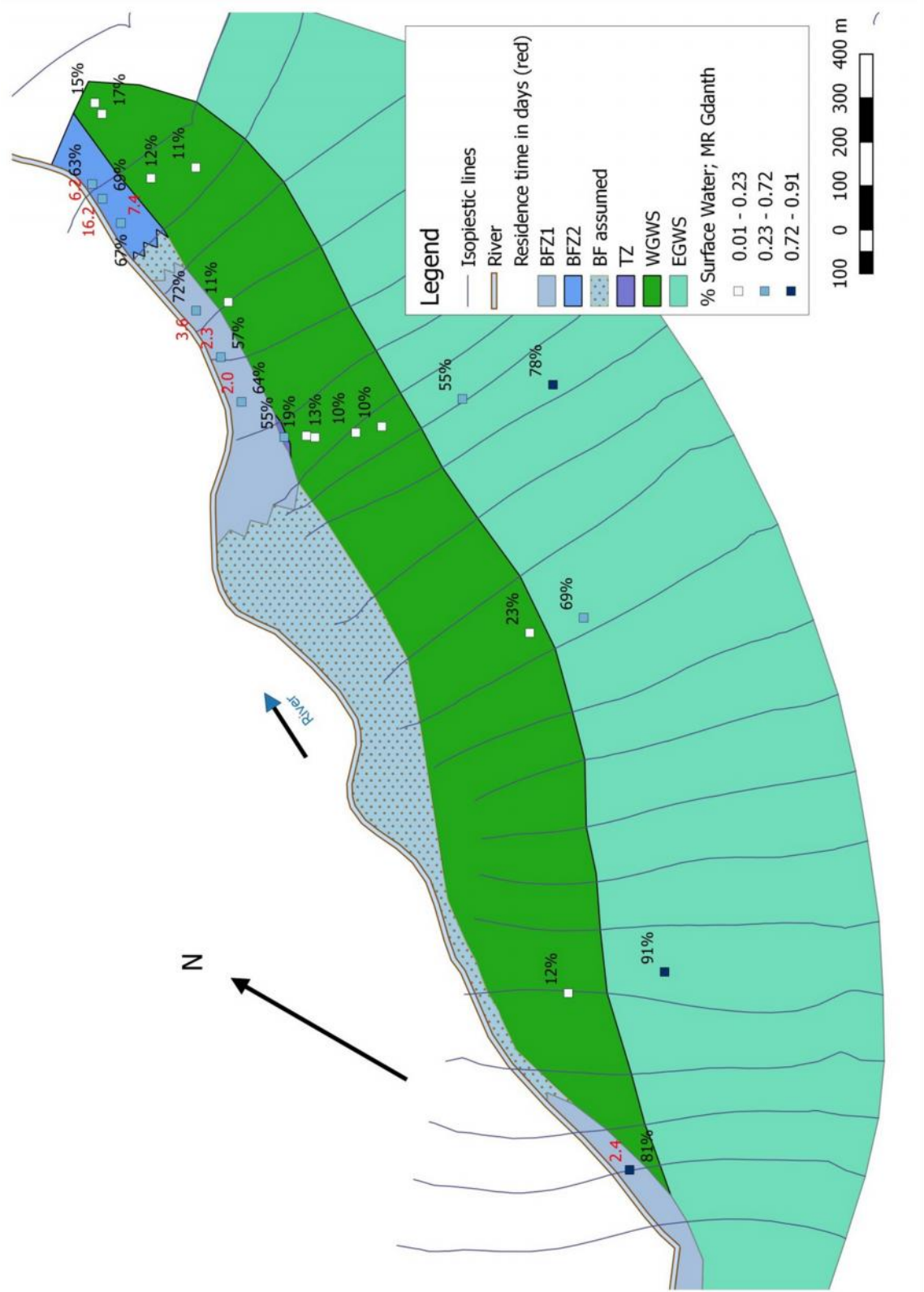


Figure 20: Combined map of spatial distribution, quantification of surface water and residence time within the investigated area; red figures represent the radon ages of the sampled wells

The combined map displays the spatial distribution of the different groundwater streams and the areas of direct bank infiltration. The distribution is based on the evaluation of the field parameters, the hydrochemistry of the major ions and the spatial distribution of the two utilised tracers chloride and anthropogenic gadolinium.

The quantification of surface water was achieved by using the mixing analysis of river water containing anthropogenic gadolinium as one end member and pristine spring water that does not contain any anthropogenic gadolinium as the other end member.

The residence time was determined by analysing the radioactive isotope ^{222}Rn . During evaluation of the data it was determined that radon dating is only applicable in areas of direct interaction with the surface water as only samples up to an age of 15 days can be dated sufficiently.

4.7 Sensitivity

The spatial distribution is based on the mixing ratios calculated with the concentrations of Gd_{anth} in the river water and unaffected spring water as endmembers. The variability of the spring water was assumed to be zero.

4.7.1 EGWS

The variability in the river water endmember for the Gd_{anth} mixing analysis is rather large as the long term Mv is 6.35 ng/L with an SD of 5.37 ng/L. It is therefore imperative to determine the sensitivity of the MR to a change in this particular parameter.

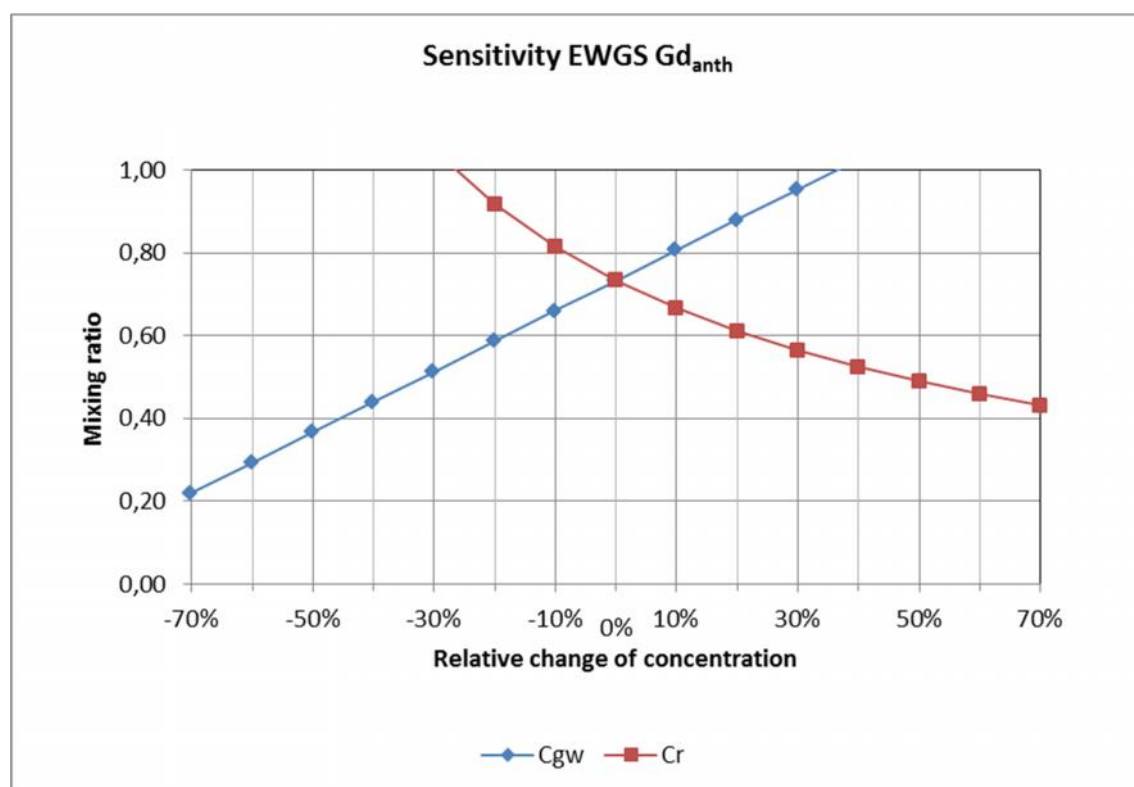


Figure 21: Sensitivity of the calculated mixing ratio to relative changes in the Gd_{anth} concentration in the endmembers river water (Cr) and ground water (Cgw) for the EWGS;

The sensitivity of the mixing ratio to a change in the river water concentration is larger if the concentration decreases. A decrease of 30% (to 4.45 ng/L) in the river water would already cause a 43% increase of the MR to a hydrologically impossible value >1 or over 100% surface water, because the mean concentration of the ground water in the EWGS lies above this value (4.66 ng/L). In the other direction even an increase of 70% would only cause the MR to drop by 41% from 0.73 to 0.43.

4.7.2 BFZ1 and BFZ2



Figure 22: Sensitivity of the calculated mixing ratio to relative changes in the Gd_{anth} concentration in the endmembers river water (Cr) and ground water (Cgw) for the BFZ1 and BFZ2;

A similar situation can be stated for BFZ1 and BFZ2. Since the mean ground water concentration of Gd_{anth} is slightly lower (4.3 ng/L) than within the EWGS mixing ratios >1 (approx. +44%) occur if the concentration in the river water drops by around 33%. At this point concentrations in the river water would be lower than the mean concentration in the ground water and the mixing analysis would not yield satisfying results. An increase of the river water concentration by 70% would yield a MR of 0.4 that accounts for a decrease of 41%.

The EGWS and the BFZ1 and BFZ2 are both affected by bank filtration and although spatially and temporally clearly divided still receptive to the same parameter change and subdued to the same sensitivity.

4.7.3 WGWS

The WGWS shows the lowest concentrations of Gd_{anth} and hence the lowest mean MR ($MR=0.15$) of all aquifer parts. Due to this it has the highest tolerance to change in concentrations.

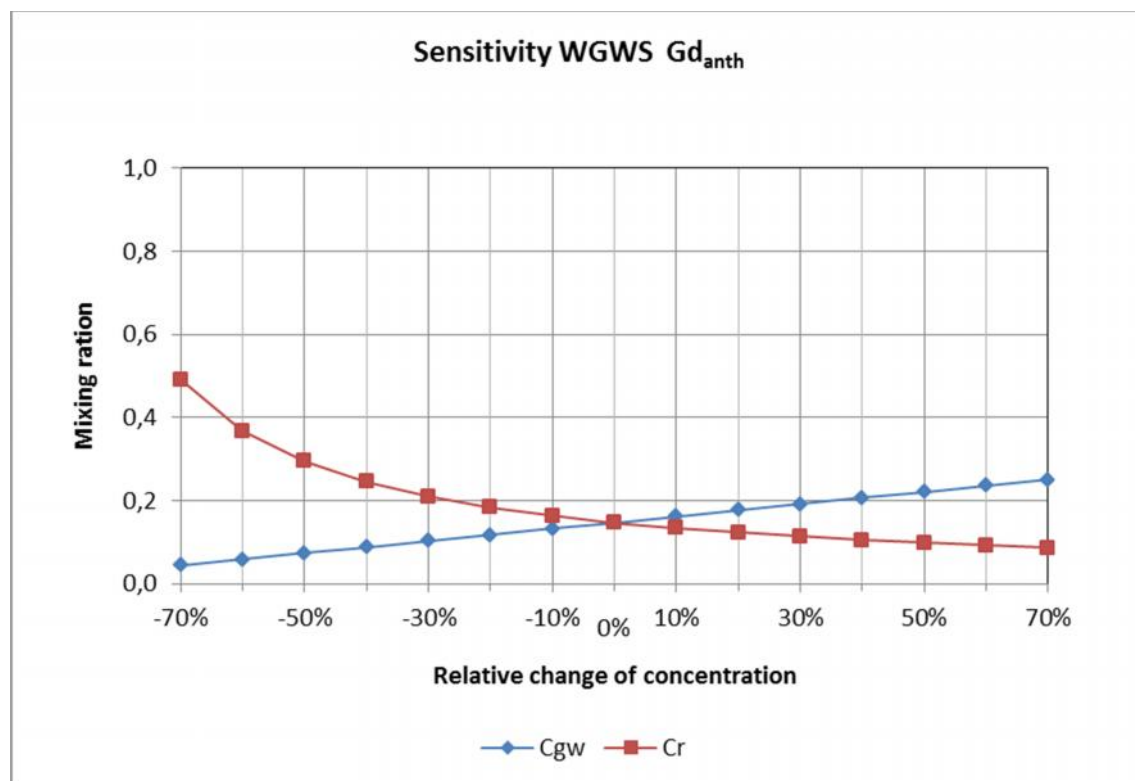


Figure 23: Sensitivity of the calculated mixing ratio to relative changes in the Gd_{anth} concentration in the endmembers river water (Cr) and ground water (Cgw) for the WGWS;

Due to the low concentration of Gd_{anth} in the ground water the concentration of the river water endmember can drop up to 86% until resulting MRs yield values >1 . At this point the concentration in the river water would drop below the mean Gd_{anth} concentration of the WGWS (0.94 ng/L). Nevertheless as there were a few examples of the long term river samples where values below 1 ng/L were observed, even such a scenario is in the realm of possibilities. An increase of river water concentration would not have big influence to the absolute value of the MR. Even a rise of river water concentration by 70% decreases the MR to 0.09 which accounts for a relative change of 41%.

5 Summary of the results - Conclusion

5.1 Spatial distribution and quantification

Due to the described limitations chloride proved not to be the appropriate tracer to determine the spatial distribution and quantification of infiltrated surface water for the hydrogeological setting at this specific site. The differences to the Gd_{anth} MRs scored between minus 125% to plus 90% for the individual samples. Nevertheless chloride was applicable as a tracer for the estimation of a residence time and groundwater distance velocity as elaborated below in chapter 5.2.

Anthropogenic gadolinium on the other hand is a reliable tracer for the hydrogeological setting at hand. The DR of Gd_{anth} in comparison to the DR of Cl^- within the investigated area is high (DR=63.5). That means that the range of concentration over which the tracer can be applied is larger and the uncertainties related to it are smaller than with chloride.

In general the whole investigated aquifer is influenced by the infiltration of river water to a variable degree.

BFZ1 and BFZ2 have their source within the investigated area and are directly infiltrated by river water. The water of the EGWS is also highly influenced by bank filtrate, but the infiltration takes place further upstream. The water of the WGWS is least affected but still influenced by the infiltration of surface water.

Sample Location	n	% SW Gd_{anth}	St.Dev.	Gd_{anth} ng/l	St.Dev.	% SW Cl^-	St.Dev.	Cl^- mg/l	St.Dev.
BFZ 1&2	7	68%	8%	4.30	0.49	139%	13%	5.69	0.41
TZ	1	55%	-	3.49	-	93%	-	7.27	-
WGWS	11	14%	4%	0.94	0.30	65%	47%	8.24	1.62
EGWS	4	73%	15%	4.66	0.96	64%	26%	8.26	0.90

Table 4: Summary of the mixing analysis results; Comparison of Gd_{anth} to Cl^-

Gd_{anth} as tracer yields homogeneous and reasonable results for all aquifer subdivisions of the investigated area with SDs not exceeding 15%. The result of the mixing analysis conducted with Gd_{anth} is seen as representative for the aquifer.

Bichler (2015) identified an area of bank filtration referred as BF 1 that overlaps with the BFZ2 outlined in this work.

The results of this work extend the known area of bank infiltration along the river by approx. 700 m in upstream direction. This additional area was labelled BFZ1 (see map in Figure 20).

5.2 Estimation of residence time, groundwater distance velocity

Radon can be used to date river bank filtrate in the hydrogeological setting presented, if applied to areas of direct infiltration close to the river where the water has not travelled further than approx. 200 m in groundwater flow direction. The same observation was also made by Dehnert et al (1999).

The ages acquired in BFZ1 are ranging from 2 to 3.6 days. The maximum uncertainty of measurements of the radon activity in relation to the chosen equilibrium activity is in a range of 14% to 20% which accounts for systematic and random errors with a confidence level of 95.4%.

The ages calculated for BFZ2 are ranging from 6.2 to 16.2 days. The maximum uncertainty of measurements of the radon activity in relation to the chosen equilibrium activity is in a range of 14% to 26% which accounts for systematic and random errors with a confidence level of 95.4%.

The results are seen as acceptable for the aquifer and the circumstances. Comparable studies found SD percentages of the radon activity ranging from 5 – 20 % (Bertin & Bourg 1994) and from 5 – 27% (Dehnert et al. 1999).

Based on the evaluation of long term river data and well data a residence time respectively a travel time for water reaching the extraction well was estimated to be between 34 and 36 days for a distance of 2800 m. This accounts for a groundwater distance velocity of 81 m/d (MV, n=4). This is supported flow velocities determined in prior works in the area (Bichler et al. 2015) that were slightly higher (85 m/d). The results are afflicted with some uncertainties. The intervals between the collection of the individual long term samples are irregular and too long, as the concentration of chloride or Gd_{anth} in the river water and the LTOW can vary from day to day. Therefore it is possible that some peak concentrations were simply missed and not sampled.

The consequence is that due to the high temporal variability of both, chloride (SD=30%) and anthropogenic gadolinium (SD=85%) and the strong fluctuation in the mean daily river discharge (SD=60%) a correlation of concentration peaks in long term river and well data can only be applicable with good conscience if the measurement intervals is similar and high.

Nevertheless, due to the arguments discussed in chapter 4.4.1 in relation to Figure 17 the estimated groundwater distance velocity is reasonable and seen as representative.

6 Acknowledgements

Firstly I want to express my gratitude to my supervisor Prof. Thilo Hofmann for continuous support of this master thesis.

This work would not have been possible without the constant guidance and tutelage of Robert Brünjes, MSc and the support of Philipp Höhn, MSc. Their great knowledge in this matter helped me to understand and finish this work.

I also want to thank my loved ones who supported me throughout the whole time. I thank my wife for her pragmatism and firm motivation. I want to thank my parents and my parents in law who spend many hours watching our children.

I thank my two children for reminding me of the really important things, like making dinner and changing diapers.

Appendix A: Laboratory Data

A.1 Data Chlorid

Location	Date	Sample ID	C(Cl ⁻)[mg/l]	Location	Date	Sample ID	C(Cl ⁻)[mg/l]	Location	Date	Sample ID	C(Cl ⁻)[mg/l]
River	09.10.2014	1537	5.08	LTOW	09.10.2014	1571	6.56	River	04.04.2016	1610	6.39
River	16.10.2014	1538	5.56	LTOW	16.10.2014	1572	6.46	1	04.04.2016	1611	5.79
River	24.10.2014	1539	3.96	LTOW	24.10.2014	1573	6.27	2	04.04.2016	1612	6.10
River	31.10.2014	1540	4.05	LTOW	31.10.2014	1574	6.20	3	04.04.2016	1613	8.99
River	05.11.2014	1541	4.41	LTOW	05.11.2014	1575	6.28	LTOW	04.04.2016	1614	7.44
River	25.11.2014	1651	6.00	LTOW	11.11.2014	1576	6.10	4	05.04.2016	1616	6.41
River	03.12.2014	1653	7.61	LTOW	25.11.2014	1650	5.61	5	05.04.2016	1617	7.27
River	11.12.2014	1655	8.99	LTOW	03.12.2014	1652	5.56	6	05.04.2016	1618	9.65
River	17.12.2014	1657	9.00	LTOW	11.12.2014	1654	5.53	7	05.04.2016	1619	10.48
River	22.12.2014	1659	5.26	LTOW	17.12.2014	1656	5.65	8	05.04.2016	1620	9.66
River	29.12.2014	1661	7.28	LTOW	22.12.2014	1658	5.54	River	05.04.2016	1622a	5.88
River	08.01.2015	1663	5.63	LTOW	29.12.2014	1660	5.75	River	06.04.2016	1622b	6.10
River	13.01.2015	1665	4.85	LTOW	08.01.2015	1662	6.07	9	06.04.2016	1623	5.75
River	28.01.2015	1667	6.35	LTOW	13.01.2015	1664	6.12	10	06.04.2016	1624	5.75
River	04.02.2015	1669	6.35	LTOW	04.02.2015	1668	8.17	11	06.04.2016	1625	5.92
River	11.02.2015	1671	6.27	LTOW	11.02.2015	1670	8.86	LTOW	06.04.2016	1627	7.60
River	17.02.2015	1673	6.19	LTOW	17.02.2015	1672	9.67	12	06.04.2016	1628	7.23
River	23.02.2015	1675	8.44	LTOW	23.02.2015	1674	6.20	13	06.04.2016	1629	9.05
River	04.03.2015	1677	7.96	LTOW	04.03.2015	1676	6.30	14	06.04.2016	1630	7.76
River	11.03.2015	1679	7.80	LTOW	11.03.2015	1678	6.41	15	07.04.2016	1631	10.01
River	25.03.2015	1542	5.60	LTOW	25.03.2015	1577	6.99	16	07.04.2016	1632	6.36
River	08.04.2015	1543	4.89	LTOW	08.04.2015	1578	7.30	5	07.04.2016	1633	7.53
River	15.04.2015	1544	4.97	LTOW	15.04.2015	1579	7.24	7	07.04.2016	1634	10.16
River	24.04.2015	1545	5.63	LTOW	24.04.2015	1580	7.35	17	07.04.2016	1635	8.98
River	29.04.2015	1546	4.89	LTOW	29.04.2015	1581	7.24	18	07.04.2016	1636	8.61
River	07.05.2015	1547	5.08	LTOW	07.05.2015	1582	7.21	LTOW	07.04.2016	1637	7.58
River	13.05.2015	1548	4.97	LTOW	13.05.2015	1583	7.42	19	08.04.2016	1640	4.79
River	20.05.2015	1549	5.16	LTOW	20.05.2015	1584	7.39	20	08.04.2016	1641	7.23
River	28.05.2015	1550	4.73	LTOW	01.06.2015	1586	7.62	21	08.04.2016	1642	7.20
River	01.06.2015	1551	5.46	LTOW	10.06.2015	1587	9.10	22	08.04.2016	1643	5.82
River	10.06.2015	1552	5.68	LTOW	16.06.2015	1588	7.55	23	08.04.2016	1644	6.01
River	25.06.2015	1554	5.26	LTOW	25.06.2015	1589	9.46	River	08.04.2016	1645	5.97
River	01.07.2015	1555	5.64	LTOW	01.07.2015	1590	7.46			Mean	7.36
River	06.07.2015	1556	6.85	LTOW	06.07.2015	1591	7.69			SD	1.6
River	23.07.2015	1557	9.46	LTOW	23.07.2015	1592	7.73			Median	7.23
River	29.07.2015	1558	8.88	LTOW	29.07.2015	1593	7.34				
River	04.08.2015	1559	8.85	LTOW	04.08.2015	1594	7.72				
River	13.08.2015	1560	9.21	LTOW	13.08.2015	1595	7.89				
River	19.08.2015	1561	8.23	LTOW	19.08.2015	1596	8.05				
River	09.09.2015	1562	6.28	LTOW	09.09.2015	1597	8.23				
River	16.09.2015	1563	9.24	LTOW	16.09.2015	1598	8.37				
River	22.09.2015	1564	9.66	LTOW	22.09.2015	1599	8.09				
River	02.10.2015	1565	12.19	LTOW	02.10.2015	1600	8.05				
River	06.10.2015	1566	10.86	LTOW	10.11.2015	1680	7.31				
River	16.10.2015	1567	6.73	LTOW	19.11.2015	1682	7.07				
River	20.10.2015	1568	6.96	LTOW	27.11.2015	1684	7.03				
River	29.10.2015	1569	8.93	LTOW	03.12.2015	1686	7.06				
River	03.11.2015	1570	10.31	LTOW	11.12.2015	1688	7.31				
River	10.11.2015	1681	8.95	LTOW	16.12.2015	1690	7.34				
River	19.11.2015	1683	12.65	LTOW	23.12.2015	1692	7.34				
River	27.11.2015	1685	9.31	LTOW	30.12.2015	1694	7.34				
River	03.12.2015	1687	4.79			Mean	7.17				
River	16.12.2015	1691	7.71			SD	1.0				
River	23.12.2015	1693	6.82			Median	7.31				
River	30.12.2015	1695	8.64								
		Mean	7.03								
		SD	2.1								
		Median	6.35								

Table 5: Long-term river; LTOW chloride data; Field investigation campaign 2016 data; Results of the IC analysis

A.2 Data Gadolinium

	UCC:		0.88	26	3.8								Gd _{anthr}	Gd _{anthr}
Location	Sample ID	Datum	Eu	Nd	Gd	Eu UCC	Nd _{ucc}	Gd _{UCC}	log Gd _{*ucc}	Gd _{*ucc}	Gd*	Gducc/ Gd*ucc	[ng/L]	[%]
River	1537	09.10.14	0.04	0.13	3.68	0.05	0.01	0.97	-1.01	0.10	0.37	9.82	3.31	89.8%
River	1538	16.10.14	0.02	0.11	5.51	0.02	0.00	1.45	-1.48	0.03	0.13	43.59	5.39	97.7%
River	1539	24.10.14	0.01	0.13	1.31	0.02	0.00	0.34	-1.59	0.03	0.10	13.52	1.21	92.6%
River	1540	31.10.14	0.01	0.13	3.02	0.01	0.01	0.79	-1.73	0.02	0.07	43.01	2.95	97.7%
River	1541	05.11.14	0.01	0.12	2.37	0.01	0.00	0.62	-1.72	0.02	0.07	32.76	2.30	96.9%
River	1651	25.11.14	0.01	0.17	4.47	0.01	0.01	1.18	-1.79	0.02	0.06	72.12	4.40	98.6%
River	1653	03.12.14	0.03	0.12	6.77	0.03	0.00	1.78	-1.19	0.06	0.24	27.77	6.53	96.4%
River	1655	11.12.14	0.02	0.12	14.03	0.02	0.00	3.69	-1.38	0.04	0.16	88.32	13.87	98.9%
River	1657	17.12.14	0.06	0.45	8.59	0.07	0.02	2.26	-0.98	0.10	0.40	21.70	8.20	95.4%
River	1659	22.12.14	0.01	0.22	2.21	0.01	0.01	0.58	-1.88	0.01	0.05	44.44	2.16	97.7%
River	1661	29.12.14	0.01	0.11	2.59	0.02	0.00	0.68	-1.62	0.02	0.09	28.53	2.50	96.5%
River	1663	08.01.15	0.00	0.06	1.65	0.00	0.00	0.43	-2.62	0.00	0.01	179.54	1.64	99.4%
River	1665	13.01.15	0.01	0.20	0.40	0.01	0.01	0.11	-1.85	0.01	0.05	7.43	0.35	86.5%
River	1667	28.01.15	0.01	0.08	3.69	0.01	0.00	0.97	-1.98	0.01	0.04	93.41	3.65	98.9%
River	1669	04.02.15	0.00	0.04	2.46	0.00	0.00	0.65	-2.56	0.00	0.01	233.68	2.45	99.6%
River	1671	11.02.15	0.01	0.15	2.55	0.01	0.01	0.67	-1.83	0.01	0.06	45.26	2.49	97.8%
River	1673	17.02.15	0.01	0.08	2.42	0.01	0.00	0.64	-2.04	0.01	0.03	69.07	2.38	98.6%
River	1675	23.02.15	0.01	0.13	12.79	0.01	0.01	3.37	-1.85	0.01	0.05	238.67	12.74	99.6%
River	1677	04.03.15	0.01	0.10	2.30	0.01	0.00	0.60	-2.15	0.01	0.03	84.91	2.27	98.8%
River	1679	11.03.15	0.03	0.30	3.07	0.03	0.01	0.81	-1.37	0.04	0.16	18.86	2.91	94.7%
River	1542	25.03.15	0.01	0.09	1.49	0.01	0.00	0.39	-1.98	0.01	0.04	37.87	1.45	97.4%
River	1543	08.04.15	0.01	0.14	0.95	0.01	0.01	0.25	-1.76	0.02	0.07	14.46	0.89	93.1%
River	1544	15.04.15	0.01	0.15	1.04	0.01	0.01	0.27	-1.78	0.02	0.06	16.49	0.98	93.9%
River	1545	24.04.15	0.01	0.16	5.93	0.01	0.01	1.56	-2.01	0.01	0.04	158.26	5.90	99.4%
River	1546	29.04.15	0.01	0.14	3.20	0.01	0.01	0.84	-1.76	0.02	0.07	48.20	3.13	97.9%
River	1547	07.05.15	0.01	0.15	3.20	0.02	0.01	0.84	-1.62	0.02	0.09	35.10	3.11	97.2%
River	1548	13.05.15	0.01	0.15	1.00	0.01	0.01	0.26	-2.11	0.01	0.03	33.64	0.97	97.0%
River	1549	20.05.15	0.22	2.55	7.01	0.25	0.10	1.84	-0.46	0.34	1.31	5.35	5.70	81.3%
River	1551	01.06.15	0.02	0.27	2.90	0.02	0.01	0.76	-1.57	0.03	0.10	28.48	2.79	96.5%
River	1552	10.06.15	0.02	0.24	4.03	0.02	0.01	1.06	-1.47	0.03	0.13	31.53	3.91	96.8%
River	1553	16.06.15	0.02	0.37	1.88	0.03	0.01	0.49	-1.46	0.03	0.13	14.19	1.74	93.0%
River	1554	25.06.15	0.03	0.31	4.08	0.03	0.01	1.07	-1.41	0.04	0.15	27.38	3.93	96.3%
River	1555	01.07.15	0.01	0.18	2.56	0.01	0.01	0.67	-1.90	0.01	0.05	54.16	2.52	98.2%
River	1556	06.07.15	0.02	0.22	8.83	0.02	0.01	2.32	-1.60	0.03	0.10	92.68	8.73	98.9%
River	1557	23.07.15	0.02	0.14	10.94	0.02	0.01	2.88	-1.47	0.03	0.13	84.56	10.81	98.8%
River	1558	29.07.15	0.01	0.13	7.64	0.01	0.01	2.01	-1.98	0.01	0.04	193.19	7.60	99.5%
River	1559	04.08.15	0.03	0.13	11.33	0.03	0.00	2.98	-1.23	0.06	0.22	50.45	11.10	98.0%
River	1560	13.08.15	0.04	0.15	21.03	0.05	0.01	5.53	-0.98	0.10	0.40	52.76	20.63	98.1%
River	1561	19.08.15	0.02	0.10	7.35	0.02	0.00	1.93	-1.34	0.05	0.17	42.76	7.17	97.7%
River	1562	09.09.15	0.01	0.14	2.49	0.01	0.01	0.66	-1.77	0.02	0.06	38.91	2.43	97.4%
River	1563	16.09.15	0.03	0.23	7.30	0.03	0.01	1.92	-1.35	0.05	0.17	42.55	7.13	97.7%
River	1564	22.09.15	0.03	0.16	11.18	0.04	0.01	2.94	-1.16	0.07	0.26	42.82	10.92	97.7%
River	1565	02.10.15	0.04	0.12	19.50	0.04	0.00	5.13	-1.04	0.09	0.34	56.54	19.15	98.2%
River	1566	06.10.15	0.06	0.14	15.86	0.07	0.01	4.17	-0.80	0.16	0.60	26.36	15.26	96.2%
River	1567	16.10.15	0.03	0.24	15.01	0.03	0.01	3.95	-1.32	0.05	0.18	82.06	14.83	98.8%
River	1568	20.10.15	0.01	0.13	3.92	0.02	0.01	1.03	-1.62	0.02	0.09	43.38	3.83	97.7%
River	1569	29.10.15	0.02	0.11	7.19	0.02	0.00	1.89	-1.40	0.04	0.15	48.05	7.04	97.9%
River	1570	03.11.15	0.02	0.25	21.51	0.02	0.01	5.66	-1.52	0.03	0.12	186.66	21.40	99.5%
River	1681	10.11.15	0.02	0.13	18.31	0.02	0.00	4.82	-1.42	0.04	0.14	126.31	18.16	99.2%
River	1683	19.11.15	0.05	0.22	14.57	0.05	0.01	3.84	-1.02	0.10	0.36	40.00	14.21	97.5%
River	1685	27.11.15	0.02	0.22	13.84	0.03	0.01	3.64	-1.42	0.04	0.14	95.92	13.70	99.0%
River	1687	03.12.15	0.04	0.48	2.58	0.04	0.02	0.68	-1.25	0.06	0.21	12.17	2.37	91.8%
River	1689	11.12.15	0.01	0.05	3.20	0.01	0.00	0.84	-1.61	0.02	0.09	34.09	3.11	97.1%
River	1691	16.12.15	0.02	0.20	6.24	0.02	0.01	1.64	-1.46	0.03	0.13	46.96	6.11	97.9%
River	1693	23.12.15	0.02	0.22	5.24	0.02	0.01	1.38	-1.52	0.03	0.11	46.08	5.13	97.8%
River	1695	30.12.15	0.02	0.16	4.76	0.02	0.01	1.25	-1.41	0.04	0.15	32.32	4.61	96.9%
River	1697	08.01.16	0.03	0.18	8.95	0.04	0.01	2.36	-1.19	0.06	0.24	36.72	8.71	97.3%
River	1699	13.01.16	0.04	0.29	4.01	0.05	0.01	1.06	-1.12	0.08	0.29	14.06	3.73	92.9%
River	1701	20.01.16	0.02	0.17	6.38	0.02	0.01	1.68	-1.42	0.04	0.15	43.95	6.23	97.7%

Mean Value	6.35	ng/l
Standard Deviation	5.37	ng/l
Median	3.93	ng/l

Table 6: Long term river Gadolinium data; Results of the ICP analysis for REE with focus on Eu, Nd and Gd; the anthropogenic Gadolinium is calculated as described in chapter 3.2.2

	UCC:		0.88	26	3.8									
Location	Sample ID	Datum	Eu	Nd	Gd	Eu UCC	Nd ucc	Gd UCC	log Gd*ucc	Gd*ucc	Gd*	Gducc/Gd*ucc	Gdanthr [ng/L]	Gdanthr [%]
LTOW	1571	09.10.14	0.01	0.13	2.89	0.01	0.00	0.76	-1.85	0.01	0.05	53.66	2.84	98.1%
LTOW	1572	16.10.14	0.01	0.10	3.01	0.01	0.00	0.79	-1.89	0.01	0.05	62.11	2.96	98.4%
LTOW	1573	24.10.14	0.01	0.14	3.06	0.01	0.01	0.80	-1.88	0.01	0.05	61.63	3.01	98.4%
LTOW	1574	31.10.14	0.01	0.17	2.90	0.01	0.01	0.76	-1.75	0.02	0.07	42.66	2.83	97.7%
LTOW	1575	05.11.14	0.01	0.11	2.93	0.01	0.00	0.77	-1.94	0.01	0.04	67.97	2.89	98.5%
LTOW	1576	11.11.14	0.01	0.11	2.65	0.01	0.00	0.70	-2.03	0.01	0.04	75.10	2.62	98.7%
LTOW	1650	25.11.14	0.03	0.12	2.43	0.04	0.00	0.64	-1.15	0.07	0.27	8.97	2.16	88.8%
LTOW	1652	03.12.14	0.01	0.12	2.29	0.01	0.00	0.60	-2.03	0.01	0.04	63.80	2.25	98.4%
LTOW	1654	11.12.14	0.00	0.05	2.28	0.01	0.00	0.60	-2.10	0.01	0.03	74.99	2.25	98.7%
LTOW	1656	17.12.14	0.00	0.06	2.52	0.00	0.00	0.66	-2.50	0.00	0.01	209.23	2.51	99.5%
LTOW	1660	29.12.14	0.02	0.04	2.37	0.03	0.00	0.62	-1.21	0.06	0.24	10.05	2.13	90.1%
LTOW	1662	08.01.15	0.00	0.04	2.34	0.01	0.00	0.62	-2.08	0.01	0.03	74.82	2.31	98.7%
LTOW	1664	13.01.15	0.00	0.03	2.42	0.01	0.00	0.64	-2.04	0.01	0.03	70.10	2.38	98.6%
LTOW	1668	04.02.15	0.01	0.08	3.69	0.01	0.00	0.97	-1.98	0.01	0.04	93.41	3.65	98.9%
LTOW	1670	11.02.15	0.04	0.13	3.94	0.05	0.01	1.04	-0.99	0.10	0.39	10.04	3.55	90.0%
LTOW	1672	17.02.15	0.02	0.13	5.41	0.02	0.01	1.42	-1.44	0.04	0.14	39.11	5.27	97.4%
LTOW	1674	23.02.15	0.00	0.07	2.41	0.01	0.00	0.63	-2.16	0.01	0.03	91.21	2.38	98.9%
LTOW	1676	04.03.15	0.01	0.06	2.44	0.01	0.00	0.64	-1.98	0.01	0.04	61.80	2.40	98.4%
LTOW	1678	11.03.15	0.01	0.11	2.44	0.01	0.00	0.64	-1.84	0.01	0.05	44.38	2.38	97.7%
LTOW	1577	25.03.15	0.00	0.07	3.02	0.00	0.00	0.80	-3.45	0.00	0.00	2245.60	3.02	100.0%
LTOW	1578	08.04.15	0.05	0.59	3.07	0.06	0.02	0.81	-1.08	0.08	0.31	9.77	2.75	89.8%
LTOW	1579	15.04.15	0.01	0.12	2.82	0.01	0.00	0.74	-1.79	0.02	0.06	46.18	2.76	97.8%
LTOW	1580	24.04.15	0.01	0.16	2.85	0.01	0.01	0.75	-1.72	0.02	0.07	39.13	2.77	97.4%
LTOW	1581	29.04.15	0.01	0.12	2.75	0.01	0.00	0.72	-2.08	0.01	0.03	86.69	2.72	98.8%
LTOW	1582	07.05.15	0.01	0.09	2.89	0.01	0.00	0.76	-1.66	0.02	0.08	34.42	2.80	97.1%
LTOW	1583	13.05.15	0.01	0.15	2.85	0.01	0.01	0.75	-1.84	0.01	0.06	51.76	2.80	98.1%
LTOW	1584	20.05.15	0.02	0.25	2.89	0.02	0.01	0.76	-1.59	0.03	0.10	29.28	2.79	96.6%
LTOW	1585	28.05.15	0.00	0.06	2.77	0.00	0.00	0.73	-2.81	0.00	0.01	468.52	2.77	99.8%
LTOW	1586	01.06.15	0.01	0.06	2.63	0.01	0.00	0.69	-2.06	0.01	0.03	78.51	2.59	98.7%
LTOW	1587	10.06.15	0.00	0.10	2.14	0.00	0.00	0.56	no input values					0.0%
LTOW	1588	16.06.15	0.01	0.09	2.86	0.01	0.00	0.75	-1.96	0.01	0.04	68.04	2.82	98.5%
LTOW	1589	25.06.15	0.00	0.06	2.03	0.01	0.00	0.54	-2.13	0.01	0.03	72.24	2.01	98.6%
LTOW	1590	01.07.15	0.01	0.09	2.82	0.01	0.00	0.74	-2.05	0.01	0.03	83.90	2.78	98.8%
LTOW	1591	06.07.15	0.01	0.06	2.94	0.02	0.00	0.77	-1.49	0.03	0.12	23.88	2.81	95.8%
LTOW	1592	23.07.15	0.01	0.07	2.65	0.01	0.00	0.70	-1.63	0.02	0.09	30.07	2.56	96.7%
LTOW	1593	29.07.15	0.00	0.06	2.90	0.00	0.00	0.76	-2.24	0.01	0.02	133.53	2.88	99.3%
LTOW	1594	04.08.15	0.00	0.09	2.90	0.00	0.00	0.76	-2.85	0.00	0.01	540.90	2.90	99.8%
LTOW	1595	13.08.15	0.00	0.08	2.86	0.01	0.00	0.75	-2.20	0.01	0.02	118.69	2.84	99.2%
LTOW	1596	19.08.15	0.00	0.07	2.80	0.00	0.00	0.74	-2.89	0.00	0.00	569.36	2.80	99.8%
LTOW	1597	09.09.15	0.01	0.05	2.87	0.01	0.00	0.75	-1.67	0.02	0.08	35.70	2.79	97.2%
LTOW	1598	16.09.15	0.01	0.10	3.01	0.01	0.00	0.79	-1.85	0.01	0.05	55.92	2.96	98.2%
LTOW	1599	22.09.15	0.01	0.11	3.07	0.01	0.00	0.81	-1.92	0.01	0.05	67.61	3.03	98.5%
LTOW	1600	02.10.15	0.01	0.08	3.17	0.01	0.00	0.83	-1.85	0.01	0.05	58.46	3.12	98.3%
LTOW	1680	10.11.15	0.03	0.10	2.96	0.04	0.00	0.78	-1.14	0.07	0.28	10.68	2.69	90.6%
LTOW	1682	19.11.15	0.02	0.28	3.22	0.03	0.01	0.85	-1.41	0.04	0.15	22.00	3.08	95.5%
LTOW	1684	27.11.15	0.01	0.06	3.10	0.01	0.00	0.82	-1.71	0.02	0.07	41.96	3.03	97.6%
LTOW	1686	03.12.15	0.01	0.07	3.07	0.01	0.00	0.81	-1.68	0.02	0.08	38.47	2.99	97.4%
LTOW	1688	11.12.15	0.02	0.17	10.66	0.02	0.01	2.80	-1.52	0.03	0.11	93.70	10.54	98.9%
LTOW	1690	16.12.15	0.03	0.07	3.07	0.04	0.00	0.81	-1.03	0.09	0.36	8.61	2.71	88.4%
LTOW	1692	23.12.15	0.01	0.06	3.43	0.01	0.00	0.90	-1.79	0.02	0.06	55.77	3.37	98.2%
LTOW	1694	30.12.15	0.01	0.06	3.47	0.01	0.00	0.91	-1.87	0.01	0.05	68.09	3.42	98.5%
	UCC		4.50	0.64	3.80									
Location	Sample ID	Datum	Sm	Tb	Gd tot	Gd*	Gdanthr [ng/L]	Gdanthr [%]						
LTOW	1658	22.12.14	0.01	0.00	2.39	0.02	2.36	99.1%						
													Mean	2.96
													SD	1.19
													Median	2.80

Table 7: Long term LTOW Gadolinium data; Results of the ICP analysis for REE with focus on Eu, Nd and Gd; the anthropogenic Gadolinium is calculated as described in chapter 3.2.2

	UCC	0.88	26	3.8									
Location	Sample ID	Eu	Nd	Gd	Eu UCC	Nd ucc	Gd UCC	log Gd*UCC	Gd*UCC	Gd*	Gducc/Gd*UCC	Gdanthr [ng/L]	Gdanthr [%]
River	1610	0.13	1.19	2.93	0.14	0.05	0.77	-0.67	0.21	0.81	3.63	2.12	72.5%
1	1611	0.05	0.53	5.45	0.05	0.02	1.43	-1.12	0.08	0.29	19.09	5.17	94.8%
2	1612	0.03	0.28	0.94	0.03	0.01	0.25	-1.37	0.04	0.16	5.83	0.78	82.9%
3	1613	0.04	0.42	6.07	0.05	0.02	1.60	-1.14	0.07	0.28	21.91	5.80	95.4%
4	1614	0.02	0.26	3.78	0.03	0.01	0.99	-1.45	0.04	0.13	28.06	3.64	96.4%
5	1615	0.03	0.27	3.89	0.03	0.01	1.02	-1.33	0.05	0.18	22.15	3.72	95.5%
6	1616	0.04	0.67	1.65	0.05	0.03	0.43	-1.23	0.06	0.22	7.46	1.43	86.6%
7	1617	0.03	0.43	3.69	0.04	0.02	0.97	-1.28	0.05	0.20	18.66	3.49	94.6%
8	1618	0.11	0.32	1.27	0.13	0.01	0.33	-0.56	0.28	1.05	1.21	0.22	17.5%
9	1619	0.02	0.32	0.89	0.02	0.01	0.23	-1.64	0.02	0.09	10.10	0.80	90.1%
10	1620	0.04	0.48	0.94	0.05	0.02	0.25	-1.20	0.06	0.24	3.90	0.70	74.4%
River	1622a	0.08	1.03	1.65	0.09	0.04	0.43	-0.91	0.12	0.47	3.51	1.18	71.5%
River	1622b	0.08	0.90	1.48	0.09	0.03	0.39	-0.93	0.12	0.44	3.35	1.04	70.1%
11	1623	0.06	0.84	4.40	0.07	0.03	1.16	-1.06	0.09	0.33	13.21	4.06	92.4%
12	1624	0.05	0.83	4.84	0.06	0.03	1.27	-1.13	0.07	0.28	17.23	4.56	94.2%
13	1625	0.05	0.69	3.89	0.06	0.03	1.02	-1.15	0.07	0.27	14.36	3.62	93.0%
LTOW	1627	0.03	0.29	3.75	0.04	0.01	0.99	-1.23	0.06	0.22	16.82	3.53	94.1%
14	1628	0.03	0.33	4.52	0.03	0.01	1.19	-1.41	0.04	0.15	30.49	4.38	96.7%
15	1629	0.03	0.41	5.15	0.04	0.02	1.36	-1.28	0.05	0.20	25.78	4.95	96.1%
16	1630	0.02	0.27	3.64	0.03	0.01	0.96	-1.44	0.04	0.14	26.41	3.51	96.2%
17	1631	0.03	0.27	0.83	0.04	0.01	0.22	-1.26	0.06	0.21	3.92	0.62	74.5%
18	1632	0.02	0.24	0.75	0.02	0.01	0.20	-1.54	0.03	0.11	6.85	0.64	85.4%
7	1633	0.03	0.35	3.93	0.03	0.01	1.04	-1.34	0.05	0.17	22.72	3.76	95.6%
9	1634	0.02	0.34	0.95	0.02	0.01	0.25	-1.55	0.03	0.11	8.86	0.84	88.7%
19	1635	0.02	0.28	0.86	0.02	0.01	0.23	-1.67	0.02	0.08	10.63	0.78	90.6%
20	1636	0.02	0.29	0.85	0.03	0.01	0.22	-1.44	0.04	0.14	6.15	0.71	83.7%
LTOW	1637	0.03	0.33	3.70	0.04	0.01	0.97	-1.30	0.05	0.19	19.32	3.50	94.8%
21	1638	0.03	0.35	4.09	0.04	0.01	1.08	-1.30	0.05	0.19	21.39	3.90	95.3%
22	1639	0.07	0.44	4.65	0.08	0.02	1.22	-0.90	0.12	0.47	9.82	4.18	89.8%
23	1640	0.05	0.76	4.55	0.06	0.03	1.20	-1.12	0.08	0.29	15.69	4.26	93.6%
24	1641	0.04	0.34	1.20	0.05	0.01	0.32	-1.13	0.07	0.28	4.29	0.92	76.7%
25	1642	0.03	0.29	1.28	0.03	0.01	0.34	-1.29	0.05	0.19	6.61	1.08	84.9%
26	1643	0.05	0.66	4.66	0.05	0.03	1.23	-1.16	0.07	0.26	17.70	4.39	94.4%
27	1644	0.04	0.51	4.25	0.04	0.02	1.12	-1.24	0.06	0.22	19.53	4.03	94.9%
River	1645	0.09	1.08	5.81	0.10	0.04	1.53	-0.88	0.13	0.50	11.66	5.31	91.4%

Mean	2.79
SD	1.74
Median	3.51

Table 8: Field investigation campaign April 2016 Gadolinium Data; Results of the ICP analysis for REE with focus on Eu, Nd and Gd; the anthropogenic Gadolinium is calculated as described in chapter 3.2.2

A.3 Radon data

222RADON Sampling April 2016										Corrected for Humidity					Corrected for humidity and decay			
ID	Location	Sampling [S]	Analyse [A]	Bq/m³ (not corr.)				Hours between S and A	Decay correction factor	Avg. Radon		S.D.	Av. RH	Av C/A count	Avg. Air Temp	Avg. Radon		Δx max. uncert. o. measurement (systematic + random error)
				Mean:	S.D.	High	Low			corr [Bq/m³]	Bq/m³					pCi/L	±	
1610	River	04.04.2016 16:13	04.04.2016 18:40	304	278	608	0	02:27:00	1.019	333	240	13.5%	0.125	25.2	339	0.34	9	0.59
1611	1	04.04.2016 17:40	04.04.2016 22:05	2438	549	2900	1820	04:25:00	1.034	2630	700	14.3%	0.0782	20.9	2719	2.72	73	1.71
1612	2	04.04.2016 18:35	05.04.2016 00:23	11800	525	12300	11100	05:48:00	1.045	12800	1500	13.3%	0.0121	20.9	13373	13.37	361	3.66
1623	9	06.04.2016 10:05	06.04.2016 18:57	3550	710	4280	2600	08:52:00	1.070	3600	700	11.5%	0.1181	13.3	3849	3.85	104	1.71
1624	10	06.04.2016 11:23	06.04.2016 23:57	5533	772	6110	4410	12:34:00	1.100	5370	1000	11.8%	0.0761	17.5	5905	5.90	160	2.44
1625	11	06.04.2016 12:45	07.04.2016 00:39	3743	491	4300	3190	11:54:00	1.095	3870	800	10.3%	0.0653	19.6	4234	4.23	114	1.95
1626	8	06.04.2016 12:32	07.04.2016 02:07	8315	926	9520	7370	13:35:00	1.109	8480	1200	10.0%	0.2621	19.7	9396	9.40	254	2.93
1628-1	12_1	06.04.2016 17:22	07.04.2016 05:26	9040	1184	10700	7990	12:04:00	1.096	9380	1200	10.8%	0.1321	19.7	10275	10.28	278	2.93
1628-2	12_2	06.04.2016 17:22	07.04.2016 06:40	9343	1243	11000	7990	13:18:00	1.106	9560	1200	9.0%	0.3841	19.6	10570	10.57	286	2.93
1628-3	12_3	06.04.2016 17:22	07.04.2016 07:10	8318	1609	10600	6910	13:48:00	1.110	8450	1200	8.0%	0.7721	19.8	9378	9.38	253	2.93
1629-1	13_1	06.04.2016 19:30	07.04.2016 09:54	7785	1000	9060	6910	14:24:00	1.116	7860	1100	10.3%	0.2071	13.3	8763	8.76	237	2.68
1629-2	13_2	06.04.2016 19:30	07.04.2016 10:46	7925	1219	9580	6760	15:16:00	1.123	7930	1100	7.5%	0.4701	12.4	8899	8.90	241	2.68
1629-3	13_3	06.04.2016 19:30	07.04.2016 11:33	8620	1397	10000	7070	16:03:00	1.130	8630	1200	7.0%	0.5671	12.1	9742	9.74	263	2.93
1630	14	06.04.2016 22:03	07.04.2016 12:12	8718	747	9420	7880	14:09:00	1.113	8720	1200	6.5%	0.7611	12.1	9704	9.70	262	2.93
1631	15	07.04.2016 10:20	07.04.2016 13:57	11690	1948	13400	9060	03:37:00	1.028	11700	1300	8.0%	0.3251	12.7	12024	12.02	325	3.17
1632	16	07.04.2016 12:10	07.04.2016 15:12	11033	1042	12000	9830	03:02:00	1.023	11000	1300	8.0%	0.4881	12.9	11255	11.25	304	3.17
1633-1	5_1	07.04.2016 13:45	07.04.2016 15:48	12075	793	12900	11000	02:03:00	1.016	12100	1400	7.0%	0.551	13.3	12289	12.29	332	3.41
1633-2	5_2	07.04.2016 13:45	07.04.2016 16:26	11385	1676	13700	9940	02:41:00	1.021	11400	1300	6.5%	0.8661	13.2	11633	11.63	314	3.17
1633-3	5_3	07.04.2016 13:45	07.04.2016 17:07	11825	737	12700	10900	03:22:00	1.026	11800	1400	6.5%	0.7331	13	12104	12.10	327	3.41
1634	7	07.04.2016 14:00	07.04.2016 18:09	11178	1441	12300	9110	04:09:00	1.032	11200	1300	7.0%	0.7261	11.8	11557	11.56	312	3.17
1635	17	07.04.2016 15:33	07.04.2016 19:00	13275	2304	15900	10300	03:27:00	1.026	13300	1400	6.8%	0.521	11.3	13651	13.65	369	3.41
1636	18	07.04.2016 16:25	07.04.2016 19:47	9335	966	10700	8340	03:22:00	1.026	9540	1200	5.5%	0.8911	10.8	9786	9.79	264	2.93
1640-1	19_1	08.04.2016 09:10	08.04.2016 10:09	7405	1060	8600	6420	00:59:00	1.007	7400	1100	9.0%	0.2231	10	7455	7.46	201	2.68
1640-2	19_2	08.04.2016 09:10	08.04.2016 10:44	8230	845	8910	7070	01:34:00	1.012	8230	1100	7.0%	0.4491	9.25	8328	8.33	225	2.68
1640-3	19_3	08.04.2016 09:10	08.04.2016 12:09	10848	2028	13100	8190	02:59:00	1.023	10800	1300	7.5%	0.3671	8.05	11046	11.05	299	3.17
1641	20	08.01.2016 09:40	08.04.2016 13:21	11850	1066	12700	10400	03:41:00	1.028	11800	1400	6.0%	0.7691	8.8	12133	12.13	328	3.41
1642	21	08.04.2016 10:40	08.04.2016 13:59	11225	802	12400	10600	03:19:00	1.025	11200	1300	5.5%	0.9071	9.7	11484	11.48	310	3.17
1643	22	08.04.2016 11:40	08.04.2016 12:43	9990	1006	12100	9990	01:03:00	1.008	11300	1300	6.5%	0.541	8.5	11390	11.39	308	3.17
1644	23	08.04.2016 14:00	08.04.2016 14:38	8095	2082	9780	5100	00:38:00	1.005	8100	1100	5.0%	1.161	9.4	8138.8	8.14	220	2.68
1645	River	08.04.2016 11:45	09.04.2016 13:26	163	188	326	0	01:41:00	1.013	164	160	11.5%	1.25	24.5	166	0.17	4	0.39
1647-1	3_1	08.04.2016 14:37	08.04.2016 21:35	11355	1278	12400	9820	06:58:00	1.054	12000	1400	11.0%	0.0263	20.1	12648	12.65	342	3.41
1647-2	3_2	08.04.2016 14:37	09.04.2016 14:03	9730	968	9980	7950	23:26:00	1.195	9850	1300	10.5%	0.0171	24.6	11757	11.76	318	3.17
1647-3	3_3	08.04.2016 14:37	09.04.2016 14:53	9215	416	9830	8910	24:16:00	1.202	9760	1300	9.8%	0.4381	24.6	11723	11.72	317	3.17

Table 9: Radon sampling campaign April 2016

A.4 Major Ions and field parameters

ID	Location	Temp °C	pH	LF [μS/cm]	HCO (from balance) [mg/l]	Oxygen [mg/l]	Oxygen [%]	Cl ⁻	NO3 ⁻	SO ₄ ²⁻	Ca ²⁺ [mg/l]	Mg ²⁺	Na ⁺	K ⁺	total hardness [°dH]	earth alkali [mmol/l]
1610	River	9.9	8.5	373	401.63	-	100%	6.39	2.56	32.64	59.90	16.47	4.27	0.84	12.18	2.18
1645	River	6.7	8.7	377	387.48	12.00	100%	5.97	2.56	31.20	61.61	16.83	4.27	0.83	12.51	2.23
1622a	River	9.8	8.5	378	381.08	10.36	100%	5.88	2.45	31.16	60.88	16.50	4.18	0.76	12.33	2.20
1611	1	5.8	8.2	379	382.18	8.82	78%	5.79	3.07	30.80	61.21	16.64	4.26	1.03	12.41	2.21
1622b	River	8.1	8.4	379	385.96	10.90	100%	6.10	2.51	31.27	60.77	16.84	4.26	0.85	12.39	2.21
1625	11	6.6	8.3	382	391.31	8.37	73%	5.92	2.92	31.42	61.34	16.90	4.22	1.01	12.49	2.23
1623	9	6.5	8.5	384	381.56	9.10	80%	5.75	3.14	30.50	61.67	17.07	4.08	1.00	12.57	2.24
1624	10	6.1	8.1	384	385.87	9.15	79%	5.75	3.33	30.71	61.74	17.07	4.10	1.03	12.58	2.25
1628	12	10.3	7.7	406	405.28	8.40	81%	7.23	3.81	29.47	64.58	16.91	5.13	1.03	12.94	2.31
1630	14	11.5	7.7	407	415.63	7.67	76%	7.76	3.48	30.26	63.84	16.68	5.41	1.06	12.79	2.28
1613	3	7.3	7.8	408	427.30	8.21	75%	8.99	4.01	28.57	66.34	17.27	5.89	0.94	13.27	2.37
1629	13	11.6	7.7	410	429.79	8.43	85%	9.05	3.76	29.96	63.60	16.81	5.77	1.08	12.78	2.28
1637	LTOW	11.2	7.9	410	410.54	-	-	7.58	3.48	29.67	64.75	16.87	5.47	1.12	12.96	2.31
1612	2	10.7	7.7	411	371.42	6.38	64%	6.10	3.06	27.36	67.63	16.64	4.82	1.12	13.31	2.38
1627	LTOW	11.2	7.6	420	416.73	7.80	78%	7.60	3.57	30.08	64.82	16.79	5.31	1.10	12.95	2.31
1640	19	7.0	7.8	425	308.12	8.53	76%	4.79	3.55	22.55	68.49	19.01	4.26	1.08	13.97	2.49
1642	21	11.3	7.7	434	395.57	6.46	64%	7.20	3.35	26.30	71.76	18.30	5.44	1.26	14.27	2.55
1641	20	11.2	7.7	436	389.53	6.22	60%	7.23	3.44	25.83	70.81	19.60	4.27	1.08	14.44	2.58
1614	LTOW	10.6	7.6	438	395.09	7.91	76%	7.44	3.36	28.52	65.08	16.81	5.38	1.11	12.99	2.32
1643	22	7.8	7.7	445	378.19	9.60	88%	5.82	5.22	25.87	70.11	17.78	5.31	1.24	13.92	2.48
1644	23	7.5	7.0	445	388.94	9.80	90%	6.01	5.01	25.53	72.46	20.10	4.42	1.09	14.78	2.64
1616	4	10.2	-	458	339.21	-	-	6.41	4.92	18.65	81.36	20.57	5.25	1.47	16.14	2.88
1636	18	10.6	7.6	474	389.97	7.84	76%	8.61	4.35	21.63	77.60	19.80	5.94	1.39	15.43	2.75
1635	17	10.4	7.6	484	389.08	7.66	74%	8.98	4.46	21.09	77.44	20.02	6.10	1.39	15.46	2.76
1634	7	9.7	7.2	495	369.54	-	-	10.16	6.68	12.49	90.76	25.61	6.13	1.40	18.61	3.32
1632	16	10.4	7.6	498	276.12	8.33	81%	6.36	3.27	14.45	82.56	21.22	6.40	1.47	16.45	2.94
1617	5	9.1	7.3	433	378.31	7.95	80%	7.27	6.73	19.88	78.91	22.83	4.68	1.11	16.31	2.91
1633	5	9.3	7.5	500	399.48	8.93	84%	7.53	6.48	20.43	81.81	23.59	4.67	1.12	16.90	3.02
1631	15	10.6	7.4	534	389.06	9.10	88%	10.01	6.32	15.36	87.61	23.65	6.23	1.49	17.72	3.16
1620	8	10.1	7.4	540	380.53	7.90	77%	9.66	6.28	15.06	87.67	24.31	6.03	1.37	17.88	3.19
1618	6	9.6	7.3	550	370.73	8.03	81%	9.65	6.36	13.71	89.36	25.75	5.66	1.29	18.45	3.29
1619	7	9.5	7.5	554	385.39	-	-	10.48	6.74	13.42	90.13	25.42	6.09	1.38	18.48	3.30

Table 10: Listing of the major ions and the field parameters

A.5 Endmember Mixing Analysis

Location	Sample ID	Date	Gadolinium [ng/l]				Cl [mg/l]			
			Cgw	Cs	Cr	MR	Cgw	Cs	Cr	MR
1	1611	04.04.2016	5.17	0.00	6.35	0.81	5.79	10.48	7.03	1.36
2	1612	04.04.2016	0.78	0.00	6.35	0.12	6.10	10.48	7.03	1.27
3	1613	04.04.2016	5.80	0.00	6.35	0.91	8.99	10.48	7.03	0.43
4	1616	05.04.2016	1.43	0.00	6.35	0.23	6.41	10.48	7.03	1.18
5	1617	05.04.2016	3.49	0.00	6.35	0.55	7.27	10.48	7.03	0.93
6	1618	05.04.2016	1.18	0.00	6.35	0.19	9.65	10.48	7.03	0.24
7	1619	05.04.2016	0.80	0.00	6.35	0.13	10.48	10.48	7.03	0.00
8	1620	05.04.2016	0.70	0.00	6.35	0.11	9.66	10.48	7.03	0.24
9	1623	06.04.2016	4.06	0.00	6.35	0.64	5.75	10.48	7.03	1.37
10	1624	06.04.2016	4.56	0.00	6.35	0.72	5.75	10.48	7.03	1.37
11	1625	06.04.2016	3.62	0.00	6.35	0.57	5.92	10.48	7.03	1.32
12	1628	06.04.2016	4.38	0.00	6.35	0.69	7.23	10.48	7.03	0.94
13	1629	06.04.2016	4.95	0.00	6.35	0.78	9.05	10.48	7.03	0.41
14	1630	06.04.2016	3.51	0.00	6.35	0.55	7.76	10.48	7.03	0.79
15	1631	07.04.2016	0.62	0.00	6.35	0.10	10.01	10.48	7.03	0.14
16	1632	07.04.2016	0.64	0.00	6.35	0.10	6.36	10.48	7.03	1.19
5	1633	07.04.2016	3.76	0.00	6.35	0.59	7.53	10.48	7.03	0.85
7	1634	07.04.2016	0.84	0.00	6.35	0.13	10.16	10.48	7.03	0.09
17	1635	07.04.2016	0.78	0.00	6.35	0.12	8.98	10.48	7.03	0.44
18	1636	07.04.2016	0.71	0.00	6.35	0.11	8.61	10.48	7.03	0.54
19	1640	08.04.2016	4.26	0.00	6.35	0.67	4.79	10.48	7.03	1.65
20	1641	08.04.2016	0.92	0.00	6.35	0.15	7.23	10.48	7.03	0.94
21	1642	08.04.2016	1.08	0.00	6.35	0.17	7.20	10.48	7.03	0.95
22	1643	08.04.2016	4.39	0.00	6.35	0.69	5.82	10.48	7.03	1.35
23	1644	08.04.2016	4.03	0.00	6.35	0.63	6.01	10.48	7.03	1.29
		Mean	2.66	0.00	6.35	0.42	7.54	10.48	7.03	0.85
		SD	1.82	0.00	0.00	0.29	1.69	0.00	0.00	0.49

Table 11: Results of the endmember mixing analysis for the field campaign 2016

Sample ID	Location	Date	Gadolinium [ng/l]				Date	Cl [mg/l]			
			Cgw	Cs	Cr	MR		Cgw	Cs	Cr	MR
LTOW	1571	09.10.14	2.84	0.00	6.35	0.45	09.10.2014	6.56	10.48	7.03	1.14
LTOW	1572	16.10.14	2.96	0.00	6.35	0.47	16.10.2014	6.46	10.48	7.03	1.16
LTOW	1573	24.10.14	3.01	0.00	6.35	0.47	24.10.2014	6.27	10.48	7.03	1.22
LTOW	1574	31.10.14	2.83	0.00	6.35	0.45	31.10.2014	6.20	10.48	7.03	1.24
LTOW	1575	05.11.14	2.89	0.00	6.35	0.46	05.11.2014	6.28	10.48	7.03	1.22
LTOW	1576	11.11.14	2.62	0.00	6.35	0.41	11.11.2014	6.10	10.48	7.03	1.27
LTOW	1650	25.11.14	2.16	0.00	6.35	0.34	25.11.2014	5.61	10.48	7.03	1.41
LTOW	1652	03.12.14	2.25	0.00	6.35	0.35	03.12.2014	5.56	10.48	7.03	1.42
LTOW	1654	11.12.14	2.25	0.00	6.35	0.35	11.12.2014	5.53	10.48	7.03	1.43
LTOW	1656	17.12.14	2.51	0.00	6.35	0.39	17.12.2014	5.65	10.48	7.03	1.40
LTOW	1660	29.12.14	2.13	0.00	6.35	0.34	22.12.2014	5.54	10.48	7.03	0.79
LTOW	1662	08.01.15	2.31	0.00	6.35	0.36	29.12.2014	5.75	10.48	7.03	0.82
LTOW	1664	13.01.15	2.38	0.00	6.35	0.38	08.01.2015	6.07	10.48	7.03	0.86
LTOW	1668	04.02.15	3.65	0.00	6.35	0.58	13.01.2015	6.12	10.48	7.03	0.87
LTOW	1670	11.02.15	3.55	0.00	6.35	0.56	04.02.2015	8.17	10.48	7.03	1.16
LTOW	1672	17.02.15	5.27	0.00	6.35	0.83	11.02.2015	8.86	10.48	7.03	1.26
LTOW	1674	23.02.15	2.38	0.00	6.35	0.37	17.02.2015	9.67	10.48	7.03	1.38
LTOW	1676	04.03.15	2.40	0.00	6.35	0.38	23.02.2015	6.20	10.48	7.03	0.88
LTOW	1678	11.03.15	2.38	0.00	6.35	0.37	04.03.2015	6.30	10.48	7.03	0.90
LTOW	1577	25.03.15	3.02	0.00	6.35	0.48	11.03.2015	6.41	10.48	7.03	0.91
LTOW	1578	08.04.15	2.75	0.00	6.35	0.43	25.03.2015	6.99	10.48	7.03	0.99
LTOW	1579	15.04.15	2.76	0.00	6.35	0.43	08.04.2015	7.30	10.48	7.03	1.04
LTOW	1580	24.04.15	2.77	0.00	6.35	0.44	15.04.2015	7.24	10.48	7.03	1.03
LTOW	1581	29.04.15	2.72	0.00	6.35	0.43	24.04.2015	7.35	10.48	7.03	1.05
LTOW	1582	07.05.15	2.80	0.00	6.35	0.44	29.04.2015	7.24	10.48	7.03	1.03
LTOW	1583	13.05.15	2.80	0.00	6.35	0.44	07.05.2015	7.21	10.48	7.03	1.03
LTOW	1584	20.05.15	2.79	0.00	6.35	0.44	13.05.2015	7.42	10.48	7.03	1.06
LTOW	1585	28.05.15	2.77	0.00	6.35	0.44	20.05.2015	7.39	10.48	7.03	1.05
LTOW	1586	01.06.15	2.59	0.00	6.35	0.41	01.06.2015	7.62	10.48	7.03	1.08
LTOW	1587	10.06.15	no value				10.06.2015	9.10	10.48	7.03	1.29
LTOW	1588	16.06.15	2.82	0.00	6.35	0.44	16.06.2015	7.55	10.48	7.03	1.07
LTOW	1589	25.06.15	2.01	0.00	6.35	0.32	25.06.2015	9.46	10.48	7.03	1.35
LTOW	1590	01.07.15	2.78	0.00	6.35	0.44	01.07.2015	7.46	10.48	7.03	1.06
LTOW	1591	06.07.15	2.81	0.00	6.35	0.44	06.07.2015	7.69	10.48	7.03	1.09
LTOW	1592	23.07.15	2.56	0.00	6.35	0.40	23.07.2015	7.73	10.48	7.03	1.10
LTOW	1593	29.07.15	2.88	0.00	6.35	0.45	29.07.2015	7.34	10.48	7.03	1.04
LTOW	1594	04.08.15	2.90	0.00	6.35	0.46	04.08.2015	7.72	10.48	7.03	1.10
LTOW	1595	13.08.15	2.84	0.00	6.35	0.45	13.08.2015	7.89	10.48	7.03	1.12
LTOW	1596	19.08.15	2.80	0.00	6.35	0.44	19.08.2015	8.05	10.48	7.03	1.14
LTOW	1597	09.09.15	2.79	0.00	6.35	0.44	09.09.2015	8.23	10.48	7.03	1.17
LTOW	1598	16.09.15	2.96	0.00	6.35	0.47	16.09.2015	8.37	10.48	7.03	1.19
LTOW	1599	22.09.15	3.03	0.00	6.35	0.48	22.09.2015	8.09	10.48	7.03	1.15
LTOW	1600	02.10.15	3.12	0.00	6.35	0.49	02.10.2015	8.05	10.48	7.03	1.15
LTOW	1680	10.11.15	2.69	0.00	6.35	0.42	10.11.2015	7.31	10.48	7.03	1.04
LTOW	1682	19.11.15	3.08	0.00	6.35	0.48	19.11.2015	7.07	10.48	7.03	1.01
LTOW	1684	27.11.15	3.03	0.00	6.35	0.48	27.11.2015	7.03	10.48	7.03	1.00
LTOW	1686	03.12.15	2.99	0.00	6.35	0.47	03.12.2015	7.06	10.48	7.03	1.00
LTOW	1688	11.12.15	10.54	0.00	6.35	1.66	11.12.2015	7.31	10.48	7.03	1.04
LTOW	1690	16.12.15	2.71	0.00	6.35	0.43	16.12.2015	7.34	10.48	7.03	1.04
LTOW	1692	23.12.15	3.37	0.00	6.35	0.53	23.12.2015	7.34	10.48	7.03	1.04
LTOW	1694	30.12.15	3.42	0.00	6.35	0.54	30.12.2015	7.34	10.48	7.03	1.04
		Mean	2.97	0.00	6.35	0.47	Mean	7.17	10.48	7.03	1.11
		SD	1.20	0	0	0.19	SD	1.00	0.00	0.00	0.16

Table 12: Results of the endmember mixing analysis for the long term samples of the LTOW

Appendix B: Abstract / Kurzfassung

B.1 Abstract

This master thesis addresses the investigation of an alluvial aquifer in a subalpine headwater catchment by utilising environmental and pollution tracers to determine the spatial distribution and portion of infiltrated surface water as well as its residence time. The tracers that have been used comprise chloride as an environmental geochemical compound tracer, radon-222 as an environmental radioactive isotope tracer and anthropogenic gadolinium as a pollution tracer. The spatial distribution and quantification of infiltrated river water to the groundwater (bank filtrate) was determined by calculating mixing ratios from the concentration of anthropogenic Gadolinium in the groundwater and mapping them with GIS software. In combination with the hydrochemical analysis the results lead to the spatial classification of the aquifer in 3 zones that show different characteristics. Chloride proved to be not of the anticipated use as the dynamic range turned out to be too small. The resulting mixing ratios differ from the related results of gadolinium by minus 125% to plus 90%. The residence time of the bank filtrate was determined by the analysis of radon-222, a radioactive isotope that is part of the U-238 decay chain. In particular bank filtration zones directly adjacent to the river proved to be dateable and showed ages between around 2 and 16 days. By analysing and comparing long term timelines of chloride and gadolinium concentrations in river water and a long term observation well which lies downstream to the investigated area, a groundwater distance velocity of approx. 81 m/d has been determined.

Keywords: Tracer, Gadolinium, Chloride, 222-Rn

B.2 Kurzfassung

Diese Masterarbeit befaßt sich mit der Untersuchung eines alluvialen Grundwasserleiters im Oberlauf eines subalpinen Quellgebietes unter Einsatz von umweltbedingten und verschmutzungsbedingten Spurenstoffen um die räumliche Verteilung und den Anteil des infiltrierenden Oberflächenwassers am Grundwasser, sowie dessen Verweilzeit zu bestimmen. Die verwendeten Spurenstoffe sind Chlorid als natürlicher geochemischer Spurenstoff, radon-222 als radioaktives Isotop sowie anthropogenes Gadolinium als anthropogener Spurenstoff. Die räumliche Verteilung und Quantifizierung von infiltriertem Flußwasser (Uferfiltrat) in das Grundwasser wurde durch die Berechnung der Mischungsverhältnisse mit Hilfe des anthropogenen Gadoliniums im Grundwasser bestimmt und

durch den Einsatz einer GIS Software visualisiert. In Kombination mit der hydrochemischen Analyse führten die Ergebnisse zur räumlichen Aufteilung des Grundwasserleiters in drei Zonen, die unterschiedliche Eigenschaften aufweisen. Es stellte sich heraus, dass Chlorid nicht wie erhofft eingesetzt werden konnte, da sich dessen dynamische Reichweite als zu klein erwies. Die resultierenden Mischungsverhältnisse unterscheiden sich von den entsprechenden Ergebnissen mit Gadolinium in einem Bereich von minus 125% bis plus 90%. Die Verweilzeit des Uferfiltrats wurde durch die Analyse von radon-222, einem radioaktiven Isotop das Teil der U-238 Zerfallskette ist, bestimmt. Insbesondere direkt an den Fluß grenzende Zonen mit Uferfiltrat konnten datiert werden und zeigten Wasser Verweilzeiten zwischen etwa 2 und 16 Tagen. Durch die Analyse von Langzeitprobenreihen eines Flusses und eines abstromig vom Untersuchungsgebiet liegenden Beobachtungsbrunnens, konnte mittels Chlorid und Gadolinium-Konzentrationen eine Grundwasserabstandsgeschwindigkeit von ca. 81 m/d ermittelt werden.

Schlagwörter: Tracer, Gadolinium, Chlorid, 222-Rn

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