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# Title: Using $^{18}O/^{2}H$, $^{3}H/^{3}He$, $^{85}Kr$ and CFCs to determine mean residence times and water origin in the Grazer and Leibnitzer Feld groundwater bodies (Austria)

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A boron – nitrate differentiation plot shows more frequent boron-rich water in the more urbanized Grazer Feld and more frequent nitrate-rich water in the more agricultural used Leibnitzer Feld indicating that a some of the nitrate load in the Grazer Feld comes from urban sewer water. Several lumped parameter models based on tritium input data from Graz and monthly data from the river Mur (Spielfeld) since 1977 yield a Mean Residence Time (MRT) for the Mur-water itself between 3 and 4 years in this area. Data from $\delta^{18}O$, $^{3}H/^{3}He$

measurements at the Wagna lysimeter station supports the conclusion that 90% of the groundwaters in the Grazer Feld and 73% in the Leibnitzer Feld have MRTs of < 5 years. Only in a few groundwaters were MRTs of 6 - 10 or 11 – 25 years as a result of either a long-distance water inflow in the basins or due to longer flow path in somewhat deeper wells (> 20m) with relative thicker unsaturated zones. The young MRT of groundwater from two monitoring wells in the Leibnitzer Feld was confirmed by $^{85}Kr$-measurements. Most CFC-11 and CFC-12 concentrations in the groundwater exceed the equilibration concentrations of modern concentrations in water and are therefore unsuitable for dating purposes. An enrichment factor up to 100 compared to atmospheric equilibrium concentrations and the obvious correlation of CFC-12 with $SO_4$, Na, Cl and B in the ground waters of the Grazer Feld suggest that waste water in contact with CFC-containing material above and below ground is the source for the contamination. The dominance of very young groundwater (< 5 years) indicates a recent origin of the contamination by nitrate and many other components observed in parts of the groundwater bodies. Rapid measures to reduce those sources are needed to mitigate against further deterioration of these waters.

# Using $^{18}O/^{2}H$, $^{3}H/^{3}He$, $^{85}Kr$ and CFCs to determine mean residence times and water origin in the Grazer and Leibnitzer Feld groundwater bodies (Austria)

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**Abstract**

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A boron – nitrate differentiation plot shows more frequent boron-rich water in the more urbanized Grazer Feld and more frequent nitrate-rich water in the more agricultural used Leibnitzer Feld indicating that a some of the nitrate load in the Grazer Feld comes from urban sewer water. Several lumped parameter models based on tritium input data from Graz and monthly data from the river Mur (Spielfeld) since 1977 yield a Mean Residence Time (MRT) for the Mur-water itself between 3 and 4 years in this area. Data from $\delta^{18}O$, $^{3}H/^{3}He$ measurements at the Wagna lysimeter station supports the conclusion that 90% of the groundwaters in the Grazer Feld and 73% in the Leibnitzer Feld have MRTs of < 5 years. Only in a few groundwaters were MRTs of 6 - 10 or 11 – 25 years as a result of either a long-distance water inflow in the basins or due to longer flow path in somewhat deeper wells (> 20m) with relative thicker unsaturated zones. The young MRT of groundwater from two monitoring wells in the Leibnitzer Feld was confirmed by $^{85}Kr$-measurements. Most CFC-11 and CFC-12 concentrations in the groundwater exceed the equilibration concentrations of modern concentrations in water and are therefore unsuitable for dating purposes. An

enrichment factor up to 100 compared to atmospheric equilibrium concentrations and the obvious correlation of CFC-12 with $SO_4$, Na, Cl and B in the ground waters of the Grazer Feld suggest that waste water in contact with CFC-containing material above and below ground is the source for the contamination. The dominance of very young groundwater (< 5 years) indicates a recent origin of the contamination by nitrate and many other components observed in parts of the groundwater bodies. Rapid measures to reduce those sources are needed to mitigate against further deterioration of these waters.

## 1. Introduction

The Water Framework Directive (WFD) and the Austrian Water Act (WRG) require a ‘good status’ of groundwater by 2015. Therefore, remediation of groundwater bodies and the ability to estimate the timescales over which improvements in water quality are achieved is of utmost importance. The term groundwater body is used here as a hydrogeologically distinct volume of groundwater within an aquifer or aquifers (Directive 2000).

For drinking water supplies and other uses of groundwater where the recharge area is dominated by agricultural or urban land use, high nitrate and other pollutant concentrations are of major concern. Nitrate reaches groundwater by infiltration from soils under intensive agricultural use as well as from other sources.

The Mean Residence Time (MRT) describes the transport time of a water between infiltration and the moment of sampling or natural discharge. Such a discharge area or point can be surface water, a spring, a monitoring well or an extraction borehole. The MRT of groundwater is an important parameter of the hydrological cycle and is related to the groundwater recharge rate, advective transport and the degree of water extraction. By understanding the MRT, measures to reduce the input of pollutants such as nutrients, pesticides and pharmaceuticals from agriculture and waste waters, can be put in context so that realistic timescales for improvement in water quality can be estimated.

The combination of different isotope measurements (oxygen-18, deuterium, tritium, tritium/helium-3, krypton-85 etc.), gas tracer measurements (CFCs, $SF_6$ etc.) allow for an assessment of the Mean Residence Time (MRT) of a groundwater. For relatively deep unsaturated zones the heavier gases krypton-85, CFC and $SF_6$ can be retarded as function of thickness and permeability of the unsaturated zone ( Cook and Solomon, 1995). Tritium/helium-3 records the time in the saturated zone only because of gas exchange between the unsaturated zone and the atmosphere (Solomon and Sudicky 1991). However, in some respects $^{85}Kr$ might be considered an ideal dating tracer, since as a noble gas no chemical reactions or adsorption processes can change its concentration in groundwater (Althaus et al. 2009). Since ratios of isotopes from the same element and with small relative mass difference are measured ($^{85}Kr/Kr_{tot}$), the method is insensitive to degassing during or before sampling or to variations in recharge temperature.

Few studies exist in young groundwater (< 10 yrs.) where whole groundwater bodies are covered with information about their MRT. Taylor et al. (1992), Ekwurzel et al. (1994), Michel (2004), Phillips and Castro (2005), Phillips and Castro (2005) used $^{18}O$ variation, $^{3}H$, $^{3}H/^{3}He$, $^{85}Kr$, CFC-11 and CFC-12 in different groundwater bodies of different geology and size. Visser et al. (2007) used $^{3}H/^{3}He$-data to demonstrate a trend reversal of agricultural pollutants based on the time of groundwater recharge.
The groundwater bodies in Grazer Feld and Leibnitzer Feld stretching along the river Mur in Austria (Fig. 1) were investigated. The sites are of particular interest because of evidence of urban impact from the city of Graz as well as agricultural impact from extensive farming of maize and oil seeds. Data from monitoring wells of the Austrian Quality Monitoring System (GZÜV, BGBL. II NR. 479/2006) show suspected agricultural pollution from high

concentrations of nitrate and historic residues of atrazine together with its degradation products, and urban contamination from chlorinated solvents such as trichloroethene and tetrachloroethene. In addition, fairly recent numerical groundwater models (Harum et al., 2011; Fank, 1999) offer the possibility to evaluate their results using isotope data and tracer gas results. Some background $^{18}O$-data were reported already by Harum et al. (2011) from the Grazer Feld and additional $^{18}O/^{2}H$, $^{3}H$-data from the Leibnitzer Feld have been previously collated (Papesch and Rank 1995).

The main purpose of this study was to obtain a statistical overview of the MRTs in the first few metres (0 – 10 m) of the saturated zone which is normally mixed by abstraction wells. This part of the aquifer is primarily monitored in the Quality Monitoring program (BGBL 2006) and is most sensitive to potential groundwater contamination.

To obtain further understanding of the processes along the vertical distribution in deeper parts of the saturated zone (>15 m) some deeper monitoring wells were sampled. In addition, a brief characterisation and a hydrogeological conceptual model of each investigated groundwater body has been compiled.

## 2. Methodologies

### *2.1Field Sampling*

Eighteen monitoring sites in the Grazer Feld and 13 at the Leibnitzer Feld of the Austrian Groundwater Quality Monitoring System (GZÜV, BGBL 2006) were sampled four times a year for $\delta\ ^{18}O$ and $^{2}H$ analyses mostly during 2009 (Tab. 1 - 5, Fig. 1 – 4). Nearly all the samples were taken with a submersible pump (Grundfos MP1). $^{3}H/^{3}He$ and CFCs were sampled once during summer 2009 from the same monitoring sites (Tab. 3 and 4). Samples for He isotope analysis were taken in clamped copper tube sample as described by Stute and

Schlosser (2000) and samples for CFC- analysis were filled under water in glass bottles (Oster, 1994). In addition, one deeper well was sampled simultaneously at depths of 13 m and 27 m with two pumps separated by inflatable packers in Gries (Graz), and the groundwater well ("Sonde II") close to the lysimeter station Wagna (Leibnitzer Feld) was also sampled in 2009 and 2011 (Tab. 1, Fig. 2 - 3).

For all the samples water temperature, conductivity, pH and dissolved oxygen content (WTW Multiline P4-meter) was measured after calibration in the field.

*2.2 Analysis of oxygen-18, hydrogen-2, tritium/helium-3, krypton-85, and CFC*

All stable isotope samples were analysed by laser-spectroscopy (CRDS – System, Types L1102-i Picarro) and tritium by liquid scintillation (LSC) by the Austrian Institute of Technology (AIT, Tulln). Noble gases $^{3}He$, $^{4}He$ and $^{20}Ne$ were measured at the Institute of Environmental Physics (IUP), University of Bremen, Germany. Water for CFC- analysis was analysed at the British Geological Survey (BGS). $^{85}Kr$ was collected by degassing of about 200L of water and measured by gas proportional counting at the University of Bern (Althaus et al., 2009; Purtschert et al. 2013). The long term standard deviation of ratios and concentrations of $\partial^{18}O$, $\partial^{2}H$, $^{3}H$, $^{3}He$, $^{4}He$, $^{20}Ne$ is better than 0.1‰, 1‰, 0.5 TU and 1% (noble gas isotopes). The precision of CFC and $^{85}Kr$ analyses is 4-5%. More analytical details are given by Kralik et al., 2011; Sültenfuß et al. 2009; Gooddy et al., 2006.

All tritium model ages were calculated by lumped parameter models (Maloszewski and Zuber 1996) using input data from the Graz precipitation station (ANIP 2012).

## 3. Hydrogeology and Climate of the Grazer and Leibnitzer Feld

### 3.1 Aquifer geometry, flow velocity and numeric models

The area of the groundwater body Grazer Feld encompasses 166 $km^2$ and stretches N – S from the city area of Graz to the mouth of the river Kainach along the river Mur (Fig. 1 and 2). The groundwater body Leibnitzer Feld continues from the mouth of the river Kainach south to the border of the Republic of Slovenia east of Strass (Fig. 1 and 3) and covers an area of roughly 100 $km^2$. In the South, the Leibnitzer Feld passes into the groundwater body "Unteres Murtal" (no clear hydrogeological border). Topography varies between 468 and 157 m above sea level.

The basin of Grazer Feld and the Leibnitzer Feld are both filled with fluvial Quaternary gravel and sand with relatively high permeability. Due to their relative thickness these sediments represent an important aquifer which is used for the drinking water supply for the city of Graz (270,000 inhabitants) and other smaller communities in both basins. The aquifer basically consists of Würm gravel terraces and Holocene floodplain areas along the rivers, but some terraces from higher Riss are preserved at the western border of the aquifer in the Grazer Feld and at the south-eastern border of the Leibnitzer Feld.

The underlying aquiclude is in both groundwater bodies generally formed by less permeable Tertiary sediments. The boundaries of the Graz basin, however, are formed in the Northern part by Palaeozoic limestone, dolomite and schist. Groundwater recharge is provided mainly by precipitation, as well as bank infiltration of the river Mur in the Northern part of both groundwater bodies and partly by infiltration from small tributary streams. Groundwater flow is generally directed from North to South (Fig. 2 and 3). Infiltrating water from the Western and Eastern boundaries is flowing towards the river Mur. In the Southern parts of the basins groundwater frequently discharges into the rivers.

In general, groundwater flow along the Mur river is also strongly influenced by several hydropower plants where infiltration and discharge processes are dominated by the level of impounded river water.

Land use is dominated by the urban city of Graz in the Northern part and by agriculture in the Southern part. The Schwarzl (Fig. 2) and Tillmitsch gravel pit lakes (Fig. 3) are filled with groundwater and do significantly reduce nitrate concentrations in the groundwater due to the high nitrogen consuming capacity of naturally occurring macrophytes.

The thickness of the aquifer in the Grazer Feld is in the range of 15 – 25 m in the North and at the main terraces 1 – 15 m. The thickest part is in the area of a deeper trough down to 32 m. To the South the thickness decreases to 16 – 18 m. The depth to groundwater varies between >15 m on the terraces down to 1 – 2 m in the Southern floodplain area.

The flow conditions within the aquifer are well known due to a well calibrated unsteady state model of groundwater flow (Harum et al., 2011). The modelled groundwater distance velocity ranges between 4 and 9 m/d for the most parts of the aquifer.

On the basis of the numerical model of groundwater flow (Feflow® software) the mean residence time in the saturated zone from the border of the groundwater body has been calculated for 4 sampling points in the range of 1.2 – 2.5 years. The thickness of the saturated aquifer in most parts of the Leibnitzer Feld varies between 1 and 10 m. The average groundwater thickness is approximately 3.5 m for the area of the lower Würm terrace (ranging between 3-8 m). Within the floodplain areas along Sulm River and the Southern part of the Mur river the groundwater depth decreases to below 2 m. Groundwater depths at the higher Riss terraces (N of well No. 20153) are between 7 and 9 m (Fank, 1999). The natural temporal fluctuation of the water table is 2.5 m, but no predominant inter-annual periods for groundwater recharge exist in the long term (evaluated at the Wagna lysimeter station, Fig. 3).

Infiltration- from and discharge to rivers affects the groundwater quantity and quality (e.g., dilution effects) significantly in several sub-regions of the Leibnitzer Feld. In the north eastern part, infiltrating water coming from the Tertiary hills also contributes to groundwater recharge. Soil particles are washed off and transferred into the aquifer and decrease hydraulic conductivity in this area (Fank, 1999).

In the region south of the Wagna Lysimeter station, the hydraulic gradients decrease and groundwater discharges into the Sulm or the Mur River. The area south-east of the Mur river (where Südbeton well is located; Fig.3) is affected by infiltrating water coming from the north-east. Fank (1999) describes a very homogeneous groundwater velocity (from 2.5 to 3 m/d) for the area of Würm terraces. Higher velocities up to 5 m/d occur along the outer border where the slope of the Tertiary basement is steeper. In the south-eastern part of the Leibnitzer Feld groundwater velocity may vary significantly between 1.3 and 8 m/d (Fank, 1999). According to a coupled unsaturated/saturated transient model simulation (Klammler et al., 2013) a maximum residence time in groundwater of approximately seven years was determined calculating over the distance from Lebring in the North to the confluence of the rivers Sulm and Mur South of the Wagna Lysimeter station.

Papesch and Rank (1995) analysed 1989-1990 $^{18}O/^{2}H$ and $^{3}H$ from roughly 50 domestic wells and surface waters. From the amplitude and phase shift of $^{18}O/^{2}H$-variations they concluded that the residence time of the groundwater is relatively short in the range of 4-5 years. Downstream of the gravel pit lakes an $^{18}O/^{2}H$-enrichment in the groundwater due to summer evaporation in the lakes has been observed. However, from the $^{3}H$-measurements some older groundwater up to 20 years and in one case in the NW even older than 40 years was found.

### *3.2 Long term climatic situation*

Both basins are situated in a moderate climate zone, marked by cold winters (lows of -10 °C) and hot summers (highs of 30 °C) with an average temperature of roughly 9° C. The annual precipitation ranges between 800 – 1000 mm/year. The monthly mean precipitation is low during winter month (22 to 42 mm/month) and are high during June to August (130 to 150 mm/month). Groundwater recharge is approximately 1/3 of the precipitation and generally higher during autumn (Harum et al. 2011; Fank 1999).

**4. Results**

The depth to the water table in the investigated monitoring sites varies between 1.3 – 15 m (mean 6 m) and 1.7 – 12.4 m (mean 5.4 m) below ground in the Grazer Feld and in the Leibnitzer Feld, respectively. In early 2009 the water table was generally 0.5 – 2 m higher compared to the long-time average due to 50% higher precipitation. The depth of the monitoring and production wells ranges between 6 – 43 m (mean 15 m) and 3.5 – 18 m (mean 8 m) in the two groundwater bodies reaching in most cases the Tertiary aquiclude. 7-9 of 19 monitoring wells and 10 of the sites are production wells for irrigation and industrial use in the Grazer and Leibnitzer Feld. Most of the wells have screens over the whole water column ranging between 1 – 22 m (mean 8.6 m) and 0.2 – 7.8 (mean 2.7 m) in the two groundwater bodies. This decrease in depth reflects the general trend of decreasing aquifer thickness from the Grazer groundwater body in the North to the Leibnitzer Feld in the South as well as a decrease in aquifer thickness from the river forests in the centre towards the lateral terraces of both fluvial aquifers.

The $\delta^{18}O$ results range from -10.5 to -6.8 (mean -8.7) and from -9.5 to -5.2 (mean -8.8) (Tab. 3 -4, Fig. 2 – 4). The measured $\delta^{2}H$ values are well correlated to the $\delta^{18}O$-values forming a local precipitation line ($\delta\,^{2}H = 7.84x\delta^{18}O+7.19$) in agreement with the long-term precipitation station at the University of Graz (ANIP 2012). The monitoring wells downstream of the Schwarzl (Grazer Feld) and the Tillmitsch gravel pit lakes (Leibnitzer Feld) show isotope data evolving along an evaporation line ($\delta^{2}H = 4.38x\delta^{18}O-22.14$) (Fig. 4).

Based on the main hydrochemistry data of the Austrian Water Quality Monitoring System ($H_2O$ Fachdatenbank, 2009) and some additional chemical analyses (Tab.2) the majority of the groundwater is of alkaline earth-carbonate type (Piper, 1944; Furtak and Langguth, 1967;

Kralik et al., 2005). The groundwater of the Grazer Feld is dominated by the Ca-Mg-carbonate subtype whereas the groundwater of the Leibnitzer Feld is dominated by the Ca-carbonate subtype. Seven groundwater monitoring sites on the Westside of the Grazer Feld and on the Southeast side of the Leibnitzer Feld contain water of the alkaline earth-sulphate or alkaline earth-alkali-sulphate type (Fig. 5).

The electric conductivity ranges between 219 – 1150 µS/cm and 360 - 888 µS/cm (mean 723 and 621 µS/cm) in both groundwater bodies. Nitrate ranges between 6 – 113 mg/L and 12 – 91 mg/L (mean 39 and 52 mg/L) and boron between 6 – 235 µg/L as well as 6 – 82 µg/L (mean 63 and 28 µg/L) in the Grazer and in the Leibnitzer groundwater body, respectively. Boron rich groundwater is more frequent in the Grazer Feld and in contrast groundwater highly enriched in nitrate is more common in the Leibnitzer Feld (Fig. 6).

The tritium concentration (Tab. 3 and 4) varies from 6.0 to 10.1 tritium units [TU] (mean 8.0 TU) and 7.1 to 11.7 TU (mean 8.5 TU) in the Grazer Feld and Leibnitzer Feld, respectively. The mean tritium concentration in both groundwater bodies is somewhat lower than the weighted mean precipitation of 9.7 TU (Fig. 7).

The mean gas concentration of $^{3}He$, $^{4}He$ and $^{3}He$ from tritium decay $^{3}He_{trit}$ are 7.55 (7.71) $10^{-11}$, 5.39 (6.22) $10^{-5}$ cc STP/kg and 1.25 (0.4) TU in the two groundwater bodies, respectively. The gas samples have generally small amounts of excess air, as indicated by Delta-Neon (ΔNe) ranging from 1.7 – 30 % and 11-42% in both groundwater bodies. To calculate the excess of Ne from the solubility equilibrium concentration it was assumed that the recharge elevation and temperature is similar to the topographic elevation of the sampling sites (Grazer Feld 295 – 360 m; Leibnitzer Feld 295 – 360 m) and the recharge temperature corresponds to the mean air temperature over the last 10 years (10.6 °C).

The mean CFC-11 and CFC-12 concentrations vary from 0.9 to 132 (1.4 – 68), 1.3 to 214 (0.1 - 36) pmol/kg in the Grazer and Leibnitzer Feld, respectively (Tab. 3 and 4, Fig. 7). Nearly all CFC-data indicate considerable contamination compared to the atmospheric equilibrium concentrations which could not be assigned to excess atmospheric air. These data were not used for dating purposes.

As an additional age constraint, two monitoring wells were sampled for $^{85}$Kr (Tab. 5). The local modern atmospheric $^{85}$Kr level was determined by means of an atmospheric air sample and a sample from a gravel (fishing) pit lake. The latter represents a temporally averaged input value over timescales given by the gas exchange dynamics between the pond water and the atmosphere (days-weeks). The $^{85}$Kr activities in the groundwater samples ranged between 67.5-75.5 dpm/cc Kr and were very similar to the atmospheric input activity indicating short groundwater residence times (<3 years).

Based on the variation in $\delta^{18}$O and apparent $^{3}$H/$^{3}$He ages in 19 of the 21 investigated monitoring sites (90%) in the Grazer Feld, MRT's of less than 5 years were determined. One sample from a site close to Wundschuh (No. 656342) was11 – 25 years old. The deeper part (13 – 27 m) of the drill-hole KB01/09 (Gries /Graz) yields groundwater with a MRT in the range of 6 – 10 years. In the Leibnitzer Feld 11 of the 15 investigated monitoring sites (73%) are younger than 5 years. Only the monitoring sites in area of St. Georgen an der Stiefing (No. 331082) and Wildon (No. 40102) in the North and St. Veit am Vogau in the South (No. 36322; 36032) are somewhat older in the range of 6 – 10 years.

## 5. Discussion

### *5.1. Origin of waters*

Monthly precipitation samples for stable isotopes have been determined from the meteorological station at the University in the centre of Graz ($\delta^2H = 7.84*\delta^{18}O + 7.19$, ANIP 2012) (Fig. 4) and provide the rainfall signature for the Grazer and Leibnitzer Feld. The weighted mean (2000 – 2011) winter precipitation ($\delta^{18}O/\delta^2H$ = - 12.0 $\pm$ 1.7 / - 85.8 $\pm$ 15.2 ‰) is isotopically lighter than the summer ($\delta^{18}O/\ \delta^2H$ = - 6.8 $\pm$ 0.7 / - 47.1 $\pm$ 5.3 ‰). The majority of stable isotope $\delta^{18}O$ data in both groundwater bodies range between -9 and -8 ‰. Assuming the weighted yearly mean of the meteorological station Graz ($\delta\ ^{18}O$ = - 8.0 ‰) is representative of local precipitation to the two groundwater bodies, the contribution of Mur-water to the groundwater in the Grazer Feld and Leibnitzer Feld would be between 0 – 30 % based on a mean $\delta\ ^{18}O$-value of - 11.2 ‰ for this section of river (Tab. 3, Fig. 4; Papesch and Rank, 1995; Harum et al. 2011). A small contribution of preferential winter precipitation in some years cannot be excluded, but a larger portion of winter precipitation would be detected from lower tritium values in the range of 6-7 TU (see Fig. 7 and section 5.2).

Four monitoring sites in the Grazer Feld and two monitoring sites in the Leibnitzer Feld show a dominant Mur-water contribution. The wells in Lend (No. 104472), Gries (No. KB09/01, 105462,) and in particular in Andritz (No. 613162) indicate a Mur water contribution in the range of 55 – 70% flowing through gravel conduits beneath the city of Graz. In the Leibnitzer Feld just the wells in Obergralla (No. 12292) and in Unter Hasendorf (No. 45212), not far from the river Mur, seem to have an elevated river water portion (36 – 43%) in the groundwater (Fig.2).

In areas where infiltration from precipitation dominates the summer half-year contributed 65 – 75 % in 2009. The estimated proportion of recharge from the summer half-year could be even higher if depleted river water ($\delta\ ^{18}O$ = -11.2 ‰) or water originating from slightly higher altitude outside of the basins is present. Such lower $^{18}O$-values are indicated from springs north of Graz, (Hammerbach, Ursprung, $\delta^{18}O$ = - 9.32 and- 9.11 ‰, Kralik and Schartner,

2010) or (KK61033012, $\delta\ ^{18}O$ = - 9.34, West of the Leibnitzer Feld (Fig. 2 - 3) as well as from small rivers e.g. Kainach, Laßnitz or Sulm ($\delta^{18}O$ = - 9.32 ‰; Tab. 4; Papesch and Rank, 1995, Kralik et al., 2011, Fig. 4).

In contrast to the unusual high recharge in the summer half-year 2009 with 50% higher precipitation rates (2009: 1204 mm/a) than the long term mean in the year 1990 the amount of precipitation was 12% lower than usual (1990: 840 mm/a). The mean summer half-year recharge, calculated from the groundwater data (1990) of Papesch and Rank (1995) and from the precipitation station at Graz (1987-90), are in the range of 45-50 %. In these humid unconfined aquifers precipitation during summer half-years have at least the same importance as winter precipitation and snow-melt recharge. Obviously, during summer half year water of heavy precipitation events is only partly lost by evapotranspiration and contributes to groundwater recharge.

The well documented evaporation effect of the gravel pit lakes “Schwarzl” (Grazer Feld, Yehdegho and Probst, 2000) and “Tillmitsch” (Leibnitzer Feld, Papesch and Rank, 1995; Müllegger et al., 2011) is evident in several monitoring wells with an obvious evaporation trend ($\delta^2H = 4.38x\delta^{18}O - 22.14$). Clear indication of evaporitic $\delta^{18}O$ enrichment can be seen 4 - 5 km downstream of the Schwarzl Lakes in the monitoring site close to Kalsdorf (No. 624372, Fig. 2 and 4). An even greater enrichment is observed 2 – 3 km downstream of the Tillmitsch gravel pit lakes in the monitoring well Tillmitsch (No. 12022, Fig. 3 and Fig. 4).

Most groundwater samples in the Grazer Feld are significantly more enriched in magnesium, sulphate and chlorine compared to the groundwater samples in the Leibnitzer Feld (Fig. 5). The higher magnesium content may be derived from the Palaeozoic (Devonian) dolomites, which surround the Northern parts of the Grazer Feld. The sulphate and chlorine may be the influence of urban sewer water from the densely populated city of Graz (270,000 inhabitants). Groundwater in heavily urbanised areas is not only impacted by leakage of sewer water, but also by leaching construction material above and below ground, which is also documented by a general higher conductivity of 723±28 µS/cm compared to 621±90 µS/cm in the Leibnitzer Feld.

Four groundwater samples at the South-Western border of the Grazer Feld Hautzendorf (No. 652092), Unterpremstätten (No. 652532), Wundschuh (No. 656342) and partly Werndorf (No. 655192) have a different major ion composition with a depletion in bicarbonate and a relative enrichment in sulphate, chlorine, sodium and potassium (Fig. 5).

The site close to Lang (No. 20152) in the North-West and three close to St. Veit (No. 36322, 25262 + 36032) in the South-East of the Leibnitzer Feld are of similar composition. For all these sites contact with a carbonate poor host rock as in the Upper Terraces (pre-Würm) (pers. communication P. Rauch) as well as variable degrees of agricultural inputs may have largely influenced the hydrochemistry of these sites. The indication of a different chemistry in the NW in the area of an older Riss terrace and in the SE was reported by Zötl (1968) showing lower pH (6.0-6.6) and lower water hardness (dH=<6.9°, approx.<100 mg/L $HCO_3$) in these areas. A pure contamination effect is very unlikely, because in most cases of contamination the general mineralisation is elevated and not lowered in these groundwaters as indicated by an EC range of 220-400 µS/cm.

The diagram of nitrate *vs.* boron (Fig. 6) shows the impact of sewage and agriculture in the two groundwater bodies. This differentiation is based on the assumption that boron is predominantly derived from detergents in sewer waters and nitrate from both agricultural fertilizers and sewer waters. The frequent monitoring sites with high boron and elevated nitrate concentrations in the north of the Grazer Feld indicate a dominant sewer water impact. The more frequent medium to high nitrate and low boron concentration in the Leibnitzer Feld seem to delineate the dominant agricultural fertilizer input. The only site with high boron content (Obergralla, No. 12292) lies in a fairly urbanized area of the Leibnitzer Feld. Samples with high boron and nitrate content could be a mixture of both sources (Fig. 6). The monitoring sites with low nitrate and boron composition are either diluted by a high proportion of the river Mur-water or are the two sites with low oxygen content in the groundwater where nitrate concentrations are lower due to denitrification e.g. Andritz, No. 613162; Wagna, No. 45242).

The previously mentioned CFC-11 and CFC-12 contamination is generally higher in the groundwater of the Grazer Feld compared to measurements in the Leibnitzer Feld (Fig. 7). The enrichment is particular high in CFC-12 (up to 214 pmol/kg). The highest concentrations are found in the monitoring wells in Graz itself (Gries, No. 105462; Liebenau, No. 107402 and Neuseiersberg, No. 116142). An obvious correlation of CFC-12 with the concentrations in sulphate, sodium, chlorine and boron (regression analysis; $r^2 = 0.4 - 0.6$) indicate a similar source as the sewer water of this area. As shown in Fig. 7 such excess values are found in Austria in several basins with a high population rate underlain by groundwater bodies. The source of CFC-12 and probably of CFC-11 is leaching from CFC-containing material above and below ground as well is mixing with waste water. Just two monitoring sites with nearly no dissolved oxygen (Andritz, No. 613162; Wagna, No. 45242) show concentrations much lower than equilibration values (Fig. 7), but these cannot be used for dating purposes as CFCs are known to degrade biologically under reducing conditions (Horneman et al. 2008). Most wells in the Leibnitzer Feld show CFC-11 values lower than expected for recent groundwaters. Variable reducing and oxidizing condition in parts of the Leibnitzer Feld could be the reason for the low CFC-11 values (Darling et al., 2012).

Höhener et al. (2002) reported that in 12 of 16 aquifers groundwater was locally contaminated with CFCs in concentrations exceeding equilibrium with respect to modern air. Pathways of CFC input to groundwater such as local atmospheric pollution (Darling and Gooddy, 2007), landfills (Darling et al. 2010), and industrial solvent spills (Morris et al., 2006) are widely reported throughout the literature.

*5.2 Estimation of mean residence time*

The majority of the groundwater samples in the Grazer and Leibnitzer Feld have slightly lower tritium concentrations than the weighted mean precipitation value in Graz (Fig. 8). This is in agreement with the $\delta^{18}O$ evidence that the groundwater contains variable amounts of Mur-river water and/or of other small rivers which originate from outside of the groundwater basins. From 2006 on due to the input of older bomb-tritium from groundwater, the nearly complete disappearance of the bomb tritium and the decay of "natural tritium" produced by cosmic rays, the tritium concentrations in the river Mur are now lower than the weighted mean precipitation values of Graz (Fig. 8).

The tritium content of the river Mur has been measured on a monthly basis 5 km downstream of the investigation area at the Austrian – Slovenian border (Spielfeld) (ANIP 2012) since 1977 (Fig. 3 and 8). Based on the input data from the University of Graz the several lumped parameter models (Maloszewski and Zuber, 1996) yielded MRTs of the Mur-water between 3 and 4 years.

However, tritium in the monitoring site close to Wundschuh (10.1 TU; No. 656342) exceeds the weighted mean precipitation (9.7 TU; wt. mean 1997-2011) whereas the monitoring wells Wildon, St. Georgen a. Stiefing, St. Veit (No. 40102, 31082, 36322, KK61036032) show lower tritium concentrations (7.1 -7.8 TU). The higher tritium value at the Wundschuh site indicates the influence of the bomb peak resulting in a dispersion model age older than 11 years (Fig. 9). The derived $^{3}H/^{3}He$ age is 20.5 yrs. (see below and Tab. 3) and in agreement with lumped parameter ages calculated in the range of 19 – 23 years. The CFC-11 value of 1.5

pmol/kg of the Wundschuh well is the only site with oxygen content above 1.5 mg/L in the Grazer Feld, which do not exceed equilibration values of the present global atmospheric concentration (Fig. 7) and therefore may provide a valid age. This value support the older MRT, but the calculated age indicate an even older residence time (38 years) which might suggest at least partial degradation of the CFC-11.

The highest measured tritium concentration of 11.7 TU at the St. Veit site (No. 25262) is not consistent with a tritiogenic $^{3}$He concentration of 0 TU. Potentially this water has been re-equilibrated with atmospheric air and thereby lost its $^{3}$He excess. However, this theory, is not supported by the Ne data as this shows an excess of 7%. Alternatively the high tritium concentration is a result of pure summer recharge water entering the aquifer, but again this is not supported by high summer- $\delta^{18}$O values. Another possibility could be a local $^{3}$H high caused by contamination due to an unmarked landfill site as these are known to be sources of tritium (Robinson and Gronow 1996).

The monitoring wells sampled by Papesch and Rank (1995) in the years 1989-1990 in the Leibnitzer Feld are all from different domestic wells than the ones sampled in this study, but still indicate that, with the exception of two sites, they are all just above or close to the precipitation curve shown in red in Fig. 8, suggesting low MRT’s of less than 5 years.

The $^{3}$He, $^{4}$He and Ne measurements are combined to derive $^{3}$He from tritium decay, so called tritiogenic $^{3}$He ($^{3}$He$_{trit}$). Most groundwater samples have $^{3}$He$_{trit}$ below 0.25 TU indicating that the time elapsed since the separation of atmospheric exchange in the unsaturated zone or in the river water is less than several months. A mean unsaturated zone thickness of 5 – 6 m and a mean vertical infiltration rate of 2.2 – 2.8 m/y, measured at the lysimeter station Wagna (Stumpp et al., 2009), lead to a transfer time from the surface to the water table of 2-3 years. The high precipitation rate in 2009 (1204 mm/a) may have shortened the MRTs to a small extent. This may be indicated in the lysimeter station as the measurement in 2009 showed no

$^{3}He_{trit.}$ (depth to the groundwater 2.95 m) whereas the repetition in the dry year 2011 (depth to the groundwater 3.70 m) yielded a $^{3}He_{trit}$ of 0.1 TU.

The non- detectable or very low concentrations of radiogenic $^{4}He$ ($^{4}He_{rad}$) are an additional indication for the absence of older water components. Exceptions are the slightly elevated $^{4}He_{rad}$ concentrations in Gries (KB 01/09 13 + 27 m) and close to Wildon (40102) which point to the influence of fracture zones in the basement of the recharge area.

The few monitoring sites with somewhat elevated $^{3}He_{trit}$ as the ones close to Wundschuh (No. 656342), Wildon (No. 40102), St. Georgen (No. 31082) and the spring close to St. Veit (No. 36032, Kralik et al., 2011) indicate an inflow of water from outside of the basin. Another reason for MRTs > 5 years are waters from deeper wells (Gries KB 01/09 27 m) in combination with relative thicker unsaturated zones (St. Veit, No. 36322, 13.5 m) (see Tab. 1, 3 and 4 as well as Fig. 9 and 10). The major ion chemistry of the groundwater at the South-Western part of the Grazer Feld suggests flow through the carbonate-free Upper Terraces west of the Grazer Feld. In a similar way, the hydrochemistry of groundwater in the South-East (South of the river Mur) of the Leibnitzer Feld, including the spring No. 36032, is influenced by waters derived from the adjacent remnants of the carbonate-free Upper Terraces (Fig. 5, Flügel and Neubauer, 1984).

The calculated $^{85}Kr$ tracer age of groundwater in the Südbeton well is only slightly different from a “zero-age” (Table 4) confirming the findings from $^{3}H/^{3}He$ data with ages generally younger than 5 years (Tab. 4 and 5).

## 6. Conclusions

Measuring monitoring wells for $^{18}O/^{2}H$-variation four times a year and $^{3}H/^{3}He$ isotopes one to two times a year provided a parsimonious strategy to investigate young groundwater and to significantly improve the hydrogeological conceptual model. $^{85}Kr$-analyses were applied in two monitoring sites as robust verification of other tracers and confirm their findings. Mean $^{18}O/^{2}H$ data showed that the majority of groundwater recharge is supplied by precipitation with a balanced contribution in the summer and winter. Some groundwater wells relatively close to rivers contain a high fraction of river water. Long term major ion chemistry, together with determinants including boron and nitrate indicate contamination from agricultural and urban sources. Concentrations of CFC-11 and CFC-12 considerably exceed the atmospheric equilibrium value in some monitoring wells and CFC-12 correlates to other sewage indicators such as $SO_4$, Na, Cl and B.

The majority of wells yielded MRTs of less than 5 years. Just a few wells showed longer MRTs either due to contributions from subsurface recharge from more distant areas or deeper (>20m) wells with thicker unsaturated zones.

Overall the study confirms that nitrate contamination occurs by diffuse or point sources from agricultural and/or urban activities mainly during the last five years. MRTs help to improve water management decisions and to set measures that all monitoring wells will reach a good status. From this work it is clear that measures need to be implemented quickly to mitigate against further deterioration of these waters and to achieve the goals within timescales defined by the EU Water Framework Directive.

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List of Tables:

**Table 1**

Well construction details Grazer and Leibnitzer Feld: No. Austrian Quality Monitoring System

| Well number | Well site | Elevation of land surface (m) | Diameter of well (cm) | Mean depth to water (m) | Total depth of well (m) below ground | Open interval (m) |
|---|---|---|---|---|---|---|
| | Grazer Feld | | | | | |
| 104472 | Lend Graz | 360 | 12.3 | 18.64 | 44.0 | 8.6-44.0 |
| 105462 | Gries Graz | 340 | 14.8 | 7.33 | 23.9 | 7.3-23.9 |
| 105482 | Gries Graz | 350 | 12.0 | 15.92 | 36.0 | |
| 107252 | Liebenau Graz | 320 | | 8.25 | 19.7 | |
| 107402 | Liebenau Graz | 325 | | 8.95 | 11.8 | |
| 112392 | Andritz Graz | 315 | 12.0 | 8.29 | 8.9 | |
| 116142 | Neuseiersbg. Graz | 325 | 100 | 11.24 | 12.4 | |
| 117282 | Puntigam Graz | 335 | 100 | 6.65 | 8.9 | |
| 608492 | Wagnitz | 357 | | 2.34 | 16.2 | |
| 611522 | Gössendorf | 330 | 20.0 | 2.32 | 11.7 | |
| 613162 | Andritz | 360 | 100 | 3.34 | 6.4 | |
| 624372 | Kalsdorf | 345 | 20 | 3.88 | 14.5 | |
| 652092 | Unterpremstätten | 315 | 100 | 6.89 | 10.3 | |
| 652532 | Oberpremstätten | 330 | 14.4 | 4.33 | 8.7 | |
| 655192 | Werndorf | 313 | 150 | 4.79 | 6.5 | |
| 655512 | Werndorf | 295 | 15 | 2.94 | 9.5 | |
| 656302 | Gradenfeld | 305 | 100 | 2.64 | 6.1 | |
| 656342 | Wundschuh | 310 | 100 | 14.0 | 16.1 | |
| KB01/09 13m | Gries Graz | 346.51 | 12.5 | 8.38 | 13.0 | |
| KB01/09 27m | Gries Graz | 346.51 | 12.5 | 8.38 | 29.0 | |
| Spring | Kalsdorf | 320.0 | spring | 0 | 0 | |
| Mur | Grieskai Graz | | river | 0 | 0 | |
| | Leibnitzer Feld | | | | | |
| 12022 | Tillmitsch | 273 | 160 | 1.88 | 4.0 | |
| 12292 | Gralla | 282 | 100 | 4.91 | 7.5 | |
| 20152 | Lang | 265 | 100 | 10.80 | 12.3 | |
| 25262 | St. Veit | 245 | 100 | 5.12 | 5.6 | |
| 27282 | Ragnitz | 270 | 100 | 4.87 | 7.0 | |
| 31082 | St. Georgen | 296 | 100 | 7.13 | 10.0 | |
| 31142 | St. Georgen | 275 | 100 | 5.22 | 8.0 | |
| 36322 | St. Veit | 260 | 12 | 13.29 | 18.9 | |
| 40102 | Wildon | 295 | 100 | 7.98 | 9.6 | |
| 45212 | Wagna | 245 | 100 | 3.31 | 4.2 | |
| 45242 | Wagna | 250 | 100 | 2.71 | 3.8 | |
| 36032 | St. Veit | 259 | spring | 0 | 0 | |
| Sd. II | Lysimeter Wagna | 266.8 | 12.6 | 4.02 | 11.0 | |
| S-beton | St. Veit | 260 | 150 | 4.77 | 7.3 | |
| Laßnitz | Stangersdorf | 284 | river | 0 | 0 | |
| Sulm | Leibnitz | 264 | river | 0 | 0 | |
| Gravel pit lake | Tillmitsch | 283 | lake | 0 | 0 | |

| | | | | | |
|---|---|---|---|---|---|
| Gravel pit lake | Gnaser | 257 | lake | 0 | 0 |

**Table 2**

Physical properties and concentrations of major ions of sampling sites not belonging to the Austrian Water Quality Monitoring System

| Site No. | Sampling date | Water temp. (° C) | Electric conduct. (µS/cm) | pH | Dissolv. Oxygen (mg/L) | Ca (mg/L) | Mg (mg/L) | Na (mg/L) | K (mg/L) | $HCO_3$ (mg/L) | $SO_4$ (mg/L) | Cl (mg/L) | $NO_3$ (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| KB01/09 13m | 22/04/2010 | 14.1 | 718 | 7.35 | 7.5 | 91.6 | 17.3 | 25.4 | 5.1 | 279 | 54.7 | 46.4 | 33.0 |
| KB01/09 27m | 22/04/2010 | | 669 | 7.47 | 6.9 | 88.4 | 17.1 | 21.2 | 4.8 | 283 | 50.9 | 38.2 | 25.2 |
| Kalsdorf Spring | 22/04/2010 | 10.1 | 879 | 7.22 | 8.4 | 120.1 | 26.0 | 16.9 | 2.5 | 385 | 58.1 | 39.5 | 53.8 |
| Wagna Sd. II Lysimeterst. | 26/08/2009 | 14.7 | 681 | 6.96 | 7.3 | 120.7 | 11.9 | 15.0 | 2.2 | 343 | 36.5 | 19.3 | 37.8 |
| Wagna Sd. II Lysimeterst. | 28/04/2011 | 10.3 | 726 | 7.15 | | | | | | | | | |
| Südbeton well | 28/04/2011 | 10.8 | 888 | 7.16 | 4.7 | | | | | | | | |
| Gnaser gravel pit lake | 28/04/2011 | 17.4 | 581 | 8.15 | 16.6 | | | | | | | | |

**Table 3**

Isotope data and concentration of dissolved gases in water as well as Mean Residence Times (MRTs) from the Grazer Feld

| Sample No. | Sampling period | $\delta^{18}O$ (‰)* | Std. Dev.* | $\delta^{2}H$ (‰)** | $^{3}H$ (TU) | $^{3}H$ 1σ uncer-tainty | CFC11 (pmol/kg) | CFC12 (pmol/kg) | $^{3}He$ ($10^{-11}$cc/kg) | $^{4}He$ ($10^{-5}$cc/kg) | Ne ($10^{-4}$cc/kg) | $^{4}He_{radio}$ ($10^{-6}$ cc/kg) | Tritiogenic $^{3}He$ (TU) | MRT (yr) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 104472 | 25/8/09 | -9.80 | 0.27 | -70.6 | 7.4 | 0.3 | 6.3 | 64.0 | 6.79 | 5.01 | 2.15 | 0.0 | 0.0 | < 5 |
| 105462 | 25/8/09 | -10.09 | 0.36 | -72.1 | 9.1 | 0.4 | 23.0 | 214 | 6.76 | 5.00 | 2.16 | 0.0 | 0.0 | < 5 |
| 105482 | 25/8/09 | -8.64 | 0.14 | -61.4 | 8.0 | 0.4 | 12.4 | 53.2 | 7.20 | 5.25 | 2.21 | 0.0 | 0.0 | < 5 |
| 107252 | 26/8/09 | -8.35 | 0.23 | -59.9 | 7.5 | 0.3 | 6.9 | 37.1 | 7.30 | 5.32 | 2.25 | 0.0 | 0.1 | < 5 |
| 107402 | 26/8/09 | -8.34 | 0.19 | -60.5 | 8.5 | 0.4 | 26.6 | 170 | 8.01 | 5.81 | 2.46 | 0.0 | 0.2 | < 5 |
| 112392 | 25/8/09 | -8.57 | 0.19 | -60.9 | 8.4 | 0.4 | 9.7 | 42.1 | 7.34 | 5.35 | 2.26 | 0.0 | 0.1 | < 5 |
| 116142 | 26/8/09 | -8.53 | 0.10 | -60.5 | 7.9 | 0.4 | 131 | 120 | 8.08 | 5.77 | 2.44 | 0.0 | 0.6 | < 5 |
| 117282 | 25/8/09 | -8.59 | 0.21 | -61.5 | 8.0 | 0.4 | 17.7 | 78.2 | 7.33 | 5.31 | 2.26 | 0.0 | 0.3 | < 5 |
| 608492 | 1/9/09 | -9.01 | 0.08 | -64.7 | 8.1 | 0.4 | 15.6 | 66.8 | 7.28 | 5.30 | 2.24 | 0.0 | 0.1 | <5 |
| 611522 | 1/9/09 | -8.30 | 0.13 | -58.9 | 7.8 | 0.3 | 45.7 | 83.2 | 6.82 | 4.98 | 2.13 | 0.0 | 0.0 | < 5 |
| 613162 | 25/8/09 | -10.72 | 0.21 | -72.4 | 8.4 | 0.4 | 0.9 | 1.3 | 7.06 | 5.20 | 2.24 | 0.0 | 0.0 | < 5 |
| 624372 | 1/9/09 | -7.03 | 0.19 | -56.1 | 8.2 | 0.4 | 4.6 | 73.6 | 7.65 | 5.57 | 2.40 | 0.0 | 0.0 | < 5 |
| 652092 | 26/8/09 | -8.38 | 0.23 | -60.1 | 7.8 | 0.3 | 7.1 | 23.5 | 8.24 | 5.92 | 2.56 | 0.0 | 0.5 | < 5 |
| 652532 | 25/8/09 | -8.20 | 0.34 | -58.8 | 8.7 | 0.4 | 23.2 | 36.2 | 7.88 | 5.69 | 2.40 | 0.0 | 0.3 | < 5 |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 655192 | 1/9/09 | -8.16 | 0.17 | -58.0 | 7.7 | 0.3 | 3.7 | 27.4 | 8.30 | 6.05 | 2.50 | 0.0 | 0.0 | < 5 |
| 655512 | 26/8/09 | -8.27 | 0.06 | -60.1 | 7.6 | 0.3 | 11.9 | 72.5 | 6.75 | 5.07 | 2.10 | 1.3 | 0.0 | < 5 |
| 656302 | 26/8/09 | -8.24 | 0.21 | -58.9 | 7.6 | 0.4 | 5.3 | 12.2 | 6.25 | 4.57 | 1.97 | 0.0 | 0.1 | < 5 |
| 656342 | 26/8/09 | -8.61 | 0.10 | -59.8 | 10.1 | 0.5 | 1.5 | 5.8 | 1.24 | 5.11 | 2.24 | 0.0 | 21.9 | 11–25 |
| KB01/09 13m | 22/4/10 | -9.90 | | -69.9 | 7.8 | 0.6 | 118.7 | 70.3 | 7.05 | 5.99 | 2.11 | 10.2 | 0.6 | < 5 |
| KB01/09 27m | 22/4/10 | -10.0 | | -69.6 | 6.0 | 0.5 | 89.5 | 78.6 | 7.52 | 6.05 | 2.17 | 8.9 | 1.4 | 6 - 10 |
| Kalser Spring | 22/4/10 | -8.72 | | -61.9 | 7.8 | 0.6 | 93.0 | 14.6 | 6.58 | 4.77 | 2.08 | 0.0 | 0.0 | < 5 |
| Mur | 22/4/10 | -11.10 | | -77.7 | | | | | | | | | | |

* VSMOW = Vienna Standard Mean Ocean Water; mean and standard deviation of four measurements between 2009/2-2009/12, ** mean of three measurements between 2009/2-2009/12; TU =Tritium Unit ([$^3$H/$^1$H] = ~10-18 = 0,119 Bq/kg); STP = Standard condition for Temperature and Pressure (273,15° Kelvin and 101,325 kPa)

**Table 4**

Isotope data and concentration of dissolved gases in water as well as Mean Residence Times (MRTs) from the Leibnitzer Feld

| Sample No. | Sampling period | $\delta^{18}O$ (‰) * | Std. Dev. | $\delta^{2}H$ (‰) ** | $^{3}H$ (TU) | $^{3}H$ 1σ uncertainty | CFC11 (pmol/kg) | CFC12 (pmol/kg) | $^{3}He$ ($10^{-11}$cc/kg) | $^{4}He$ ($10^{-5}$cc/kg) | Ne ($10^{-4}$cc/kg) | $^{4}He_{radio}$ ($10^{-6}$ cc/kg) | Tritiogenic $^{3}He$ (TU) | MRT (yr) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12022 | 27/08/09 | -5.43 | 0.23 | -47.3 | 7.2 | 0.5 | 68.1 | 36.1 | 7.33 | 5.43 | 2.26 | 0.0 | 0.0 | < 5 |
| 12292 | 27/08/09 | -9.36 | 0.16 | -66.4 | 9.0 | 0.4 | 2.4 | 5.8 | 6.20 | 4.55 | 1.98 | 0.0 | 0.0 | < 5 |
| 20152 | 27/08/09 | -8.73 | 0.11 | -62.3 | 7.5 | 0.3 | 2.6 | 23.1 | 6.58 | 4.92 | 2.08 | 0.0 | 0.0 | < 5 |
| 25262 | 27/08/09 | -8.35 | 0.23 | -59.9 | 11.7 | 0.5 | 1.4 | 7.5 | 6.55 | 4.87 | 2.08 | 0.0 | 0.0 | < 5 |
| 27282 | 26/08/09 | -8.71 | 0.08 | -61.9 | 7.5 | 0.4 | 2.3 | 7.9 | 7.92 | 6.06 | 2.45 | 1.1 | 0.0 | < 5 |
| 31082 | 26/08/09 | -8.57 | 0.19 | -60.9 | 7.1 | 0.3 | 2.4 | 6.4 | 8.75 | 6.96 | 2.76 | 1.3 | 0.0 | 6 – 10 |
| 31142 | 26/08/09 | -8.33 | 0.56 | -59.4 | 8.4 | 0.4 | 3.3 | 10.5 | 7.92 | 6.05 | 2.44 | 1.2 | 0.0 | < 5 |
| 36322 | 27/08/09 | -8.79 | 0.08 | -61.1 | 7.5 | 0.4 | 2.4 | 8.8 | 11.9 | 8.71 | 3.47 | 0.0 | 0.0 | 6 – 10 |
| 40102 | 27/08/09 | -8.77 | 0.19 | -62.6 | 7.8 | 0.4 | 3.1 | 9.5 | 9.04 | 11.5 | 2.36 | 58.0 | 4.6 | 6 – 10 |
| 45212 | 27/08/09 | -9.17 | 0.30 | -65.2 | 8.1 | 0.4 | 7.2 | 32.4 | 7.17 | 5.45 | 2.16 | 3.3 | 0.7 | < 5 |
| 45242 | 27/08/09 | -8.94 | 0.19 | -63.3 | 9.1 | 0.4 | 2.2 | 0.1 | 7.88 | 5.72 | 2.43 | 0.0 | 0.2 | < 5 |
| 36032 | 1/9/09 | -7.03 | 0.19 | -56.1 | 8.2 | 0.4 | 4.6 | 73.6 | | | | | | 6 – 10 |
| Sd. II Lysim. | 26/08/09 | -8,99 | 0.18 | -64,5 | | | 12.3 | 30.3 | 7.18 | 5.39 | 2.20 | 1.1 | 0.0 | < 5 |
| Sd. II Lysim. | 28/04/11 | -8.81 | | -62.0 | 8.8 | 0.4 | | | 7.06 | 5.35 | 2.18 | 1.9 | 0.1 | < 5 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| S-beton | 28/04/11 | -8.44 | -58.6 | 9.8 | 0.4 | 6.47 | 6.17 | 2.20 | 9.7 | 0.0 | < 5 |
| Laßnitz | 17/06/09 | -8.18 | | | | | | | | | |
| Sulm | 17/06/09 | -8.76 | | | | | | | | | |
| Tillmitsch lake | 17/06/09 | -4.24 | | | | | | | | | |
| Gnaser lake | 28/04/11 | -7.79 | -55.9 | 8.5 | 0.4 | 6.99 | 4.52 | 1.88 | 2.2 | 0.0 | < 5 |

See abbreviations and comments Table 3

**Table 5**

Krypton-85 activities and related water residence times for a piston flow (PF) and exponential model (EM) scenario.

| Site | $^{85}Kr$ (dpm/cc Kr) | PF age (years) | | | EM age (years) | | |
|---|---|---|---|---|---|---|---|
| | | mean | min | max | mean | min | max |
| Wagna lys. Sd. II | 71.7±2.7 | 0.8 | 0.2 | 1.9 | 0.9 | 0.2 | 1.7 |
| Südbeton well | 67.7±2.6 | 2.1 | 1.6 | 2.5 | 2.0 | 1.3 | 2.8 |
| Gnaser gravel l. | 75.5±3.6 | 0.4 | 0.0 | 0.8 | 0.4 | 0.0 | 0.9 |
| Atmosphere | 72.6±2.8 | 0.6 | 0.0 | 1.8 | 0.7 | 0.0 | 1.4 |

**Figures:**

**Fig. 1**. Position of the Grazer Feld and Leibnitzer Feld groundwater bodies in the South-East (Province Styria) of Austria.

**Fig. 2**. Mean $^{18}O$ values of selected quality monitoring wells and springs (large symbols), other monitoring wells (Harum et al. 2011; small symbols), estimated groundwater flow and surface water discharge and infiltration to the Grazer Feld.

**Fig. 3**. Mean $^{18}O$ values of selected quality monitoring wells (large symbols), domestic wells (Papesch and Rank 1995; small symbols), estimated groundwater flow and surface water discharge and infiltration to the Leibnitzer Feld.

**Fig. 4.** Delta $^{18}O$ *vs.* $^{2}H$ values of selected quality monitoring wells, springs, rivers and gravel pit lakes in the Grazer Feld and Leibnitzer Feld.

**Fig. 5**. Major Ion chemistry of the groundwater samples in the Grazer Feld and Leibnitzer Feld ($H_2O$ Fachdatenbank 2009) and the mean river Mur-water at Kalsdorf (Grazer Feld).

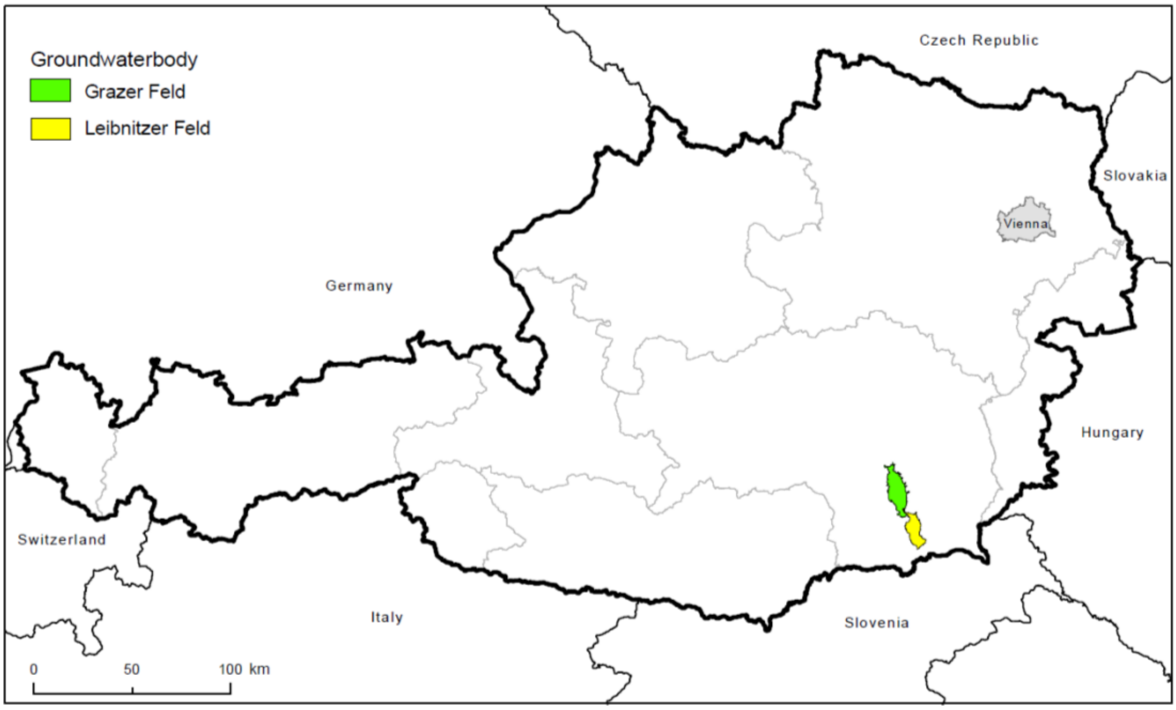
**Fig. 6.** Mean nitrate *vs.* boron content of groundwater samples in the Grazer and Leibnitzer Feld ($H_2O$ Fachdatenbank 2009) and their indicated likely origin.

**Fig. 7.** CFC-11 *vs.* CFC-12 concentrations in groundwater of the Grazer Feld and Leibnitzer Feld with oxygen contents above and below 1 mg/L. The concentrations of other groundwater bodies in Austria are shown for comparison. The development of equilibrium concentration in water (10°C) over time is shown as black diamonds. Values above and in the centre of Graz are indicated with numbers of the monitoring wells.

**Fig. 8.** Tritium content of precipitation (Univ.Graz; ANIP 2012), groundwater (Grazer + Leibnitzer Feld) and the river Mur *vs.* time.

**Fig. 9.** Mean Residence Times (MRTs) of selected quality monitoring wells, estimated groundwater flow and surface water discharge and infiltration in the Grazer Feld.

**Fig. 10.** Mean Residence Times (MRTs) of selected quality monitoring wells (large symbols), domestic wells (Papesch and Rank 1995; small symbols), estimated groundwater flow and surface water discharge and infiltration in the Leibnitzer Feld.

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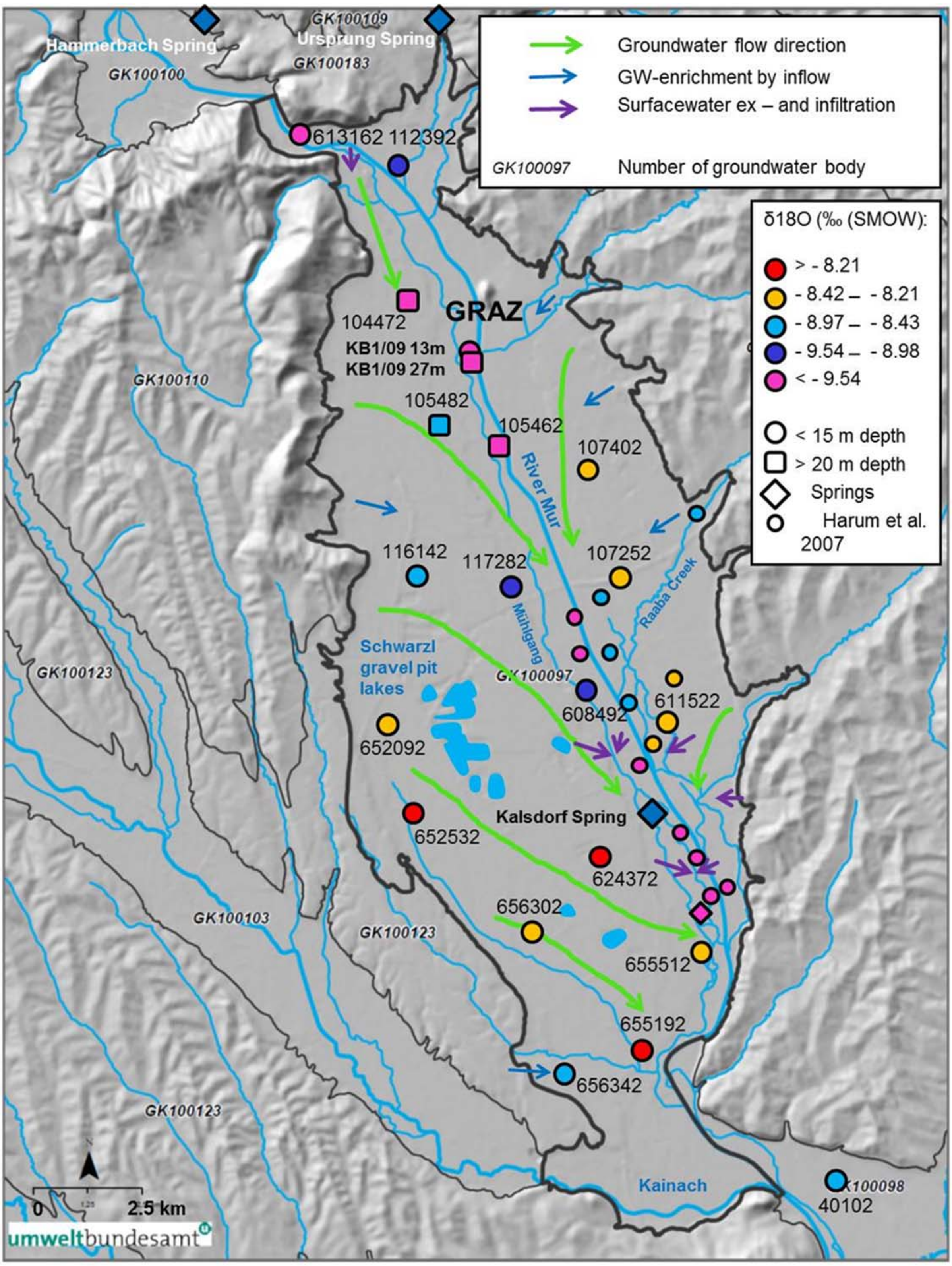


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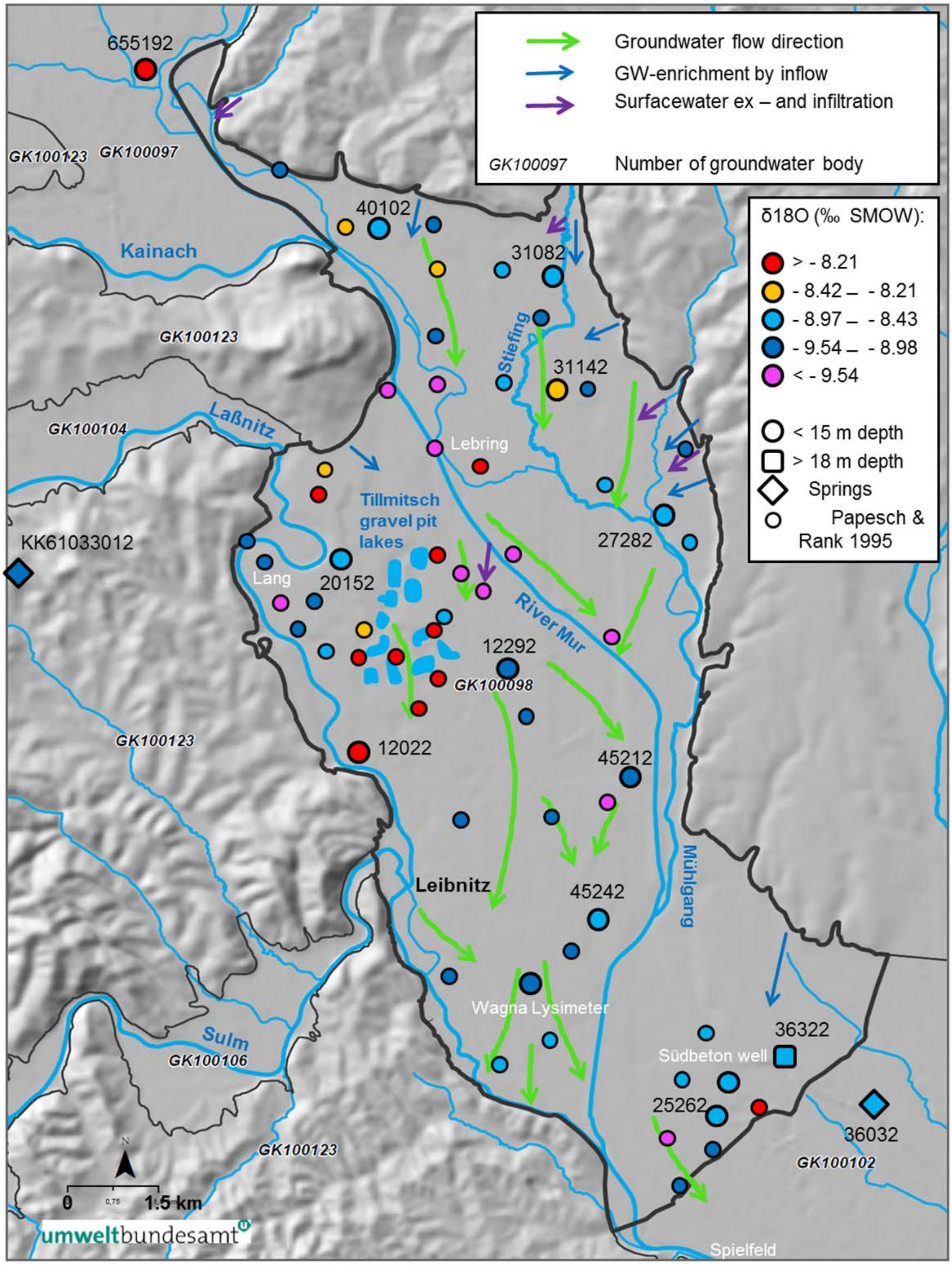



**Fig. 3**. Mean $^{18}$O values of selected quality monitoring wells (large symbols), domestic wells (Papesch and Rank 1995; small symbols), estimated groundwater flow and surface water discharge and infiltration to the Leibnitzer Feld.

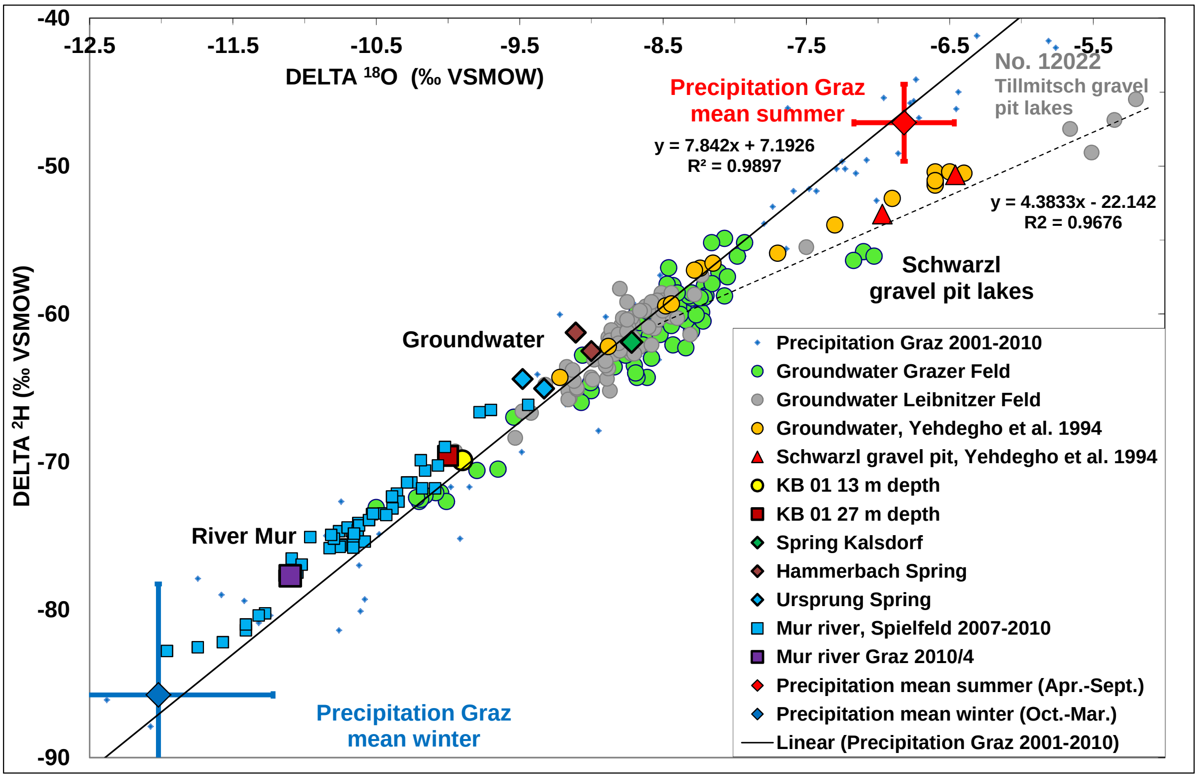
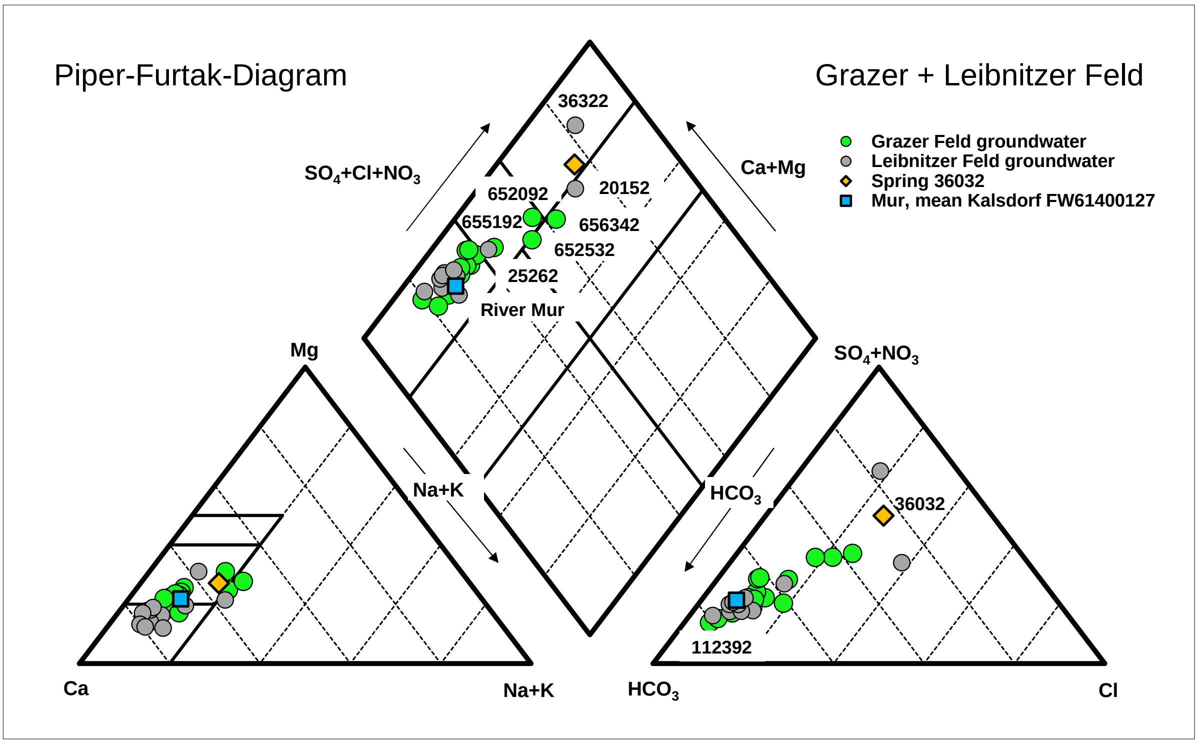



**Fig. 4.** Delta oxygen-18 *vs.* Hydrogen-2 values of selected quality monitoring wells, springs, rivers and gravel pit lakes in the groundwater bodies Grazer Feld and Leibnitzer Feld.

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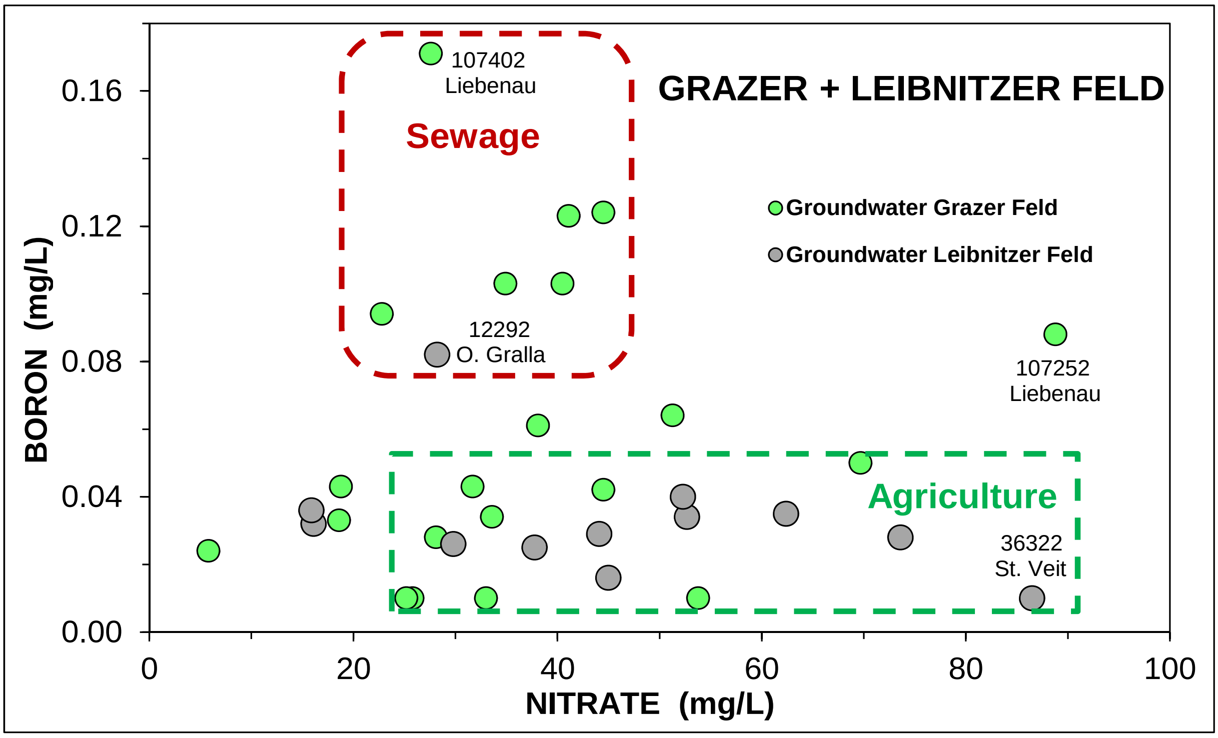


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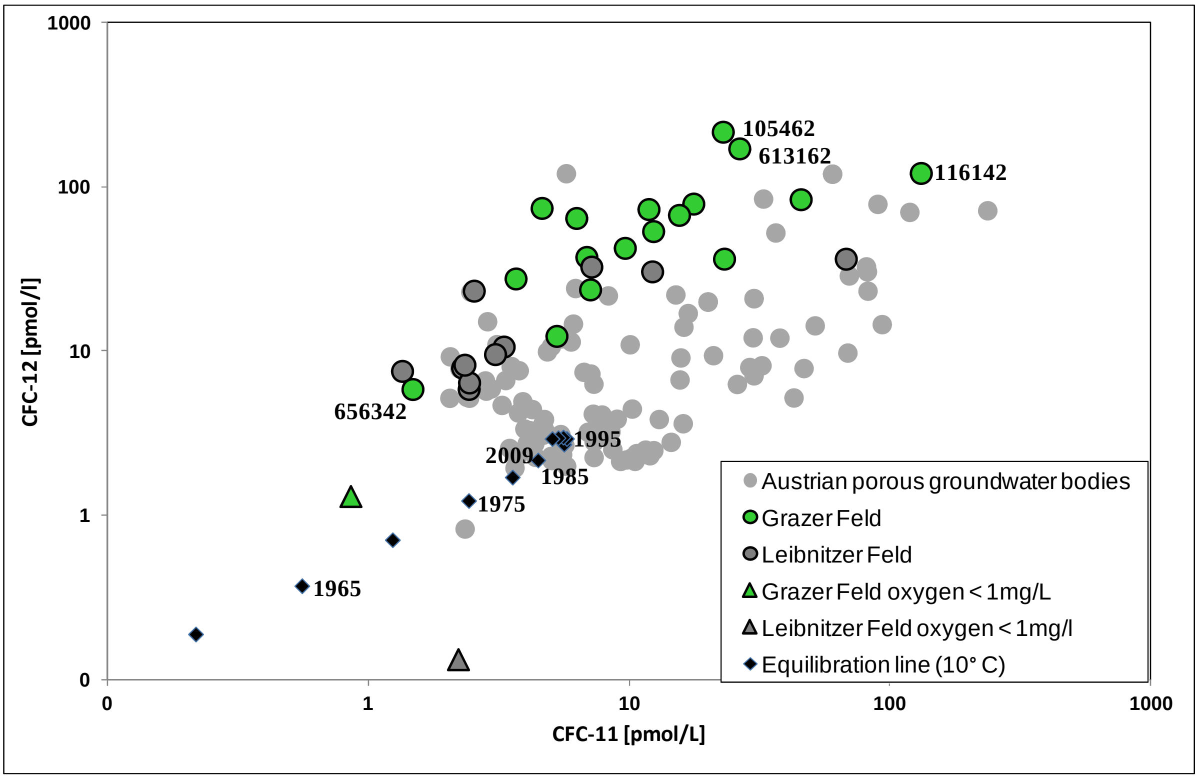


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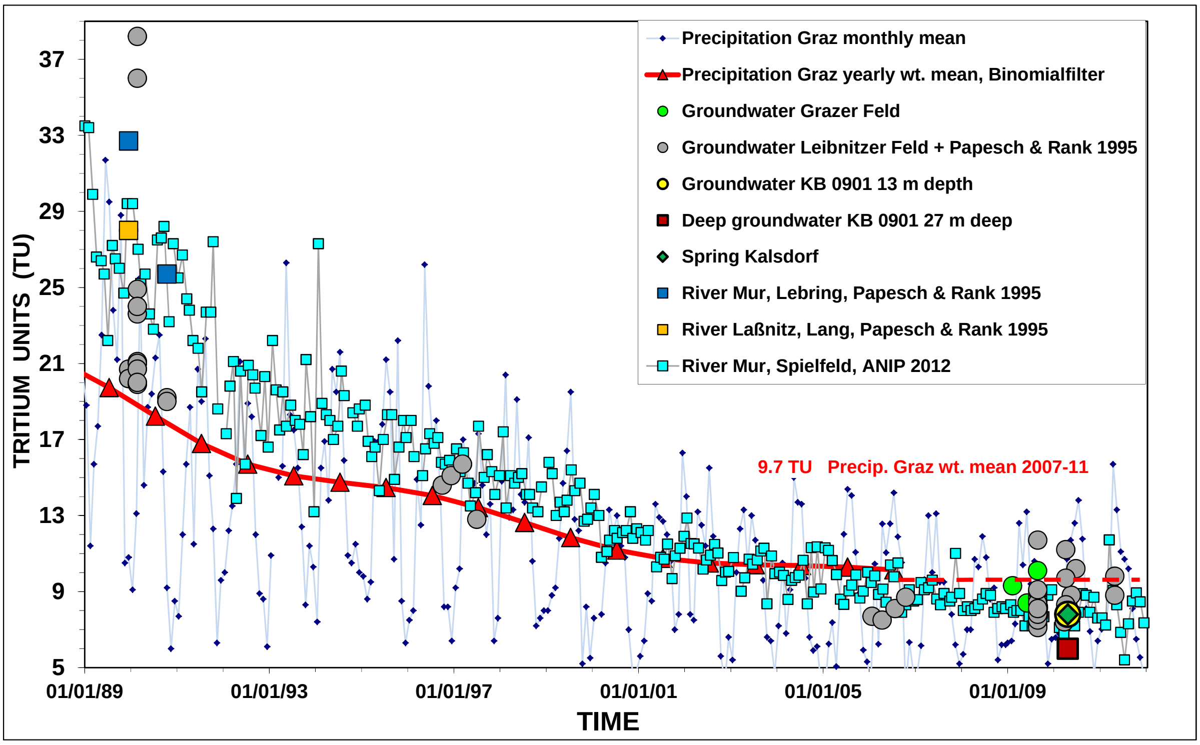


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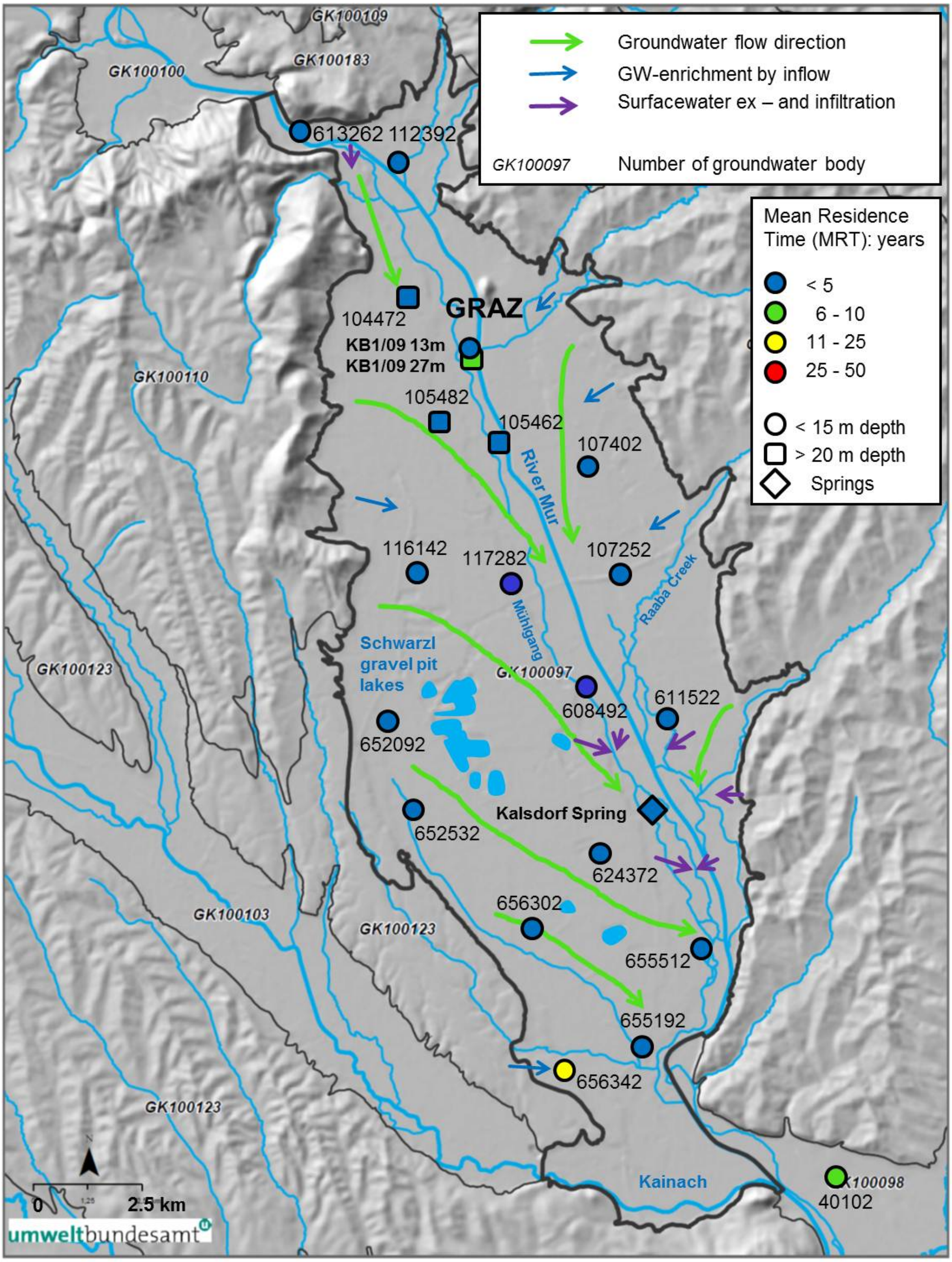


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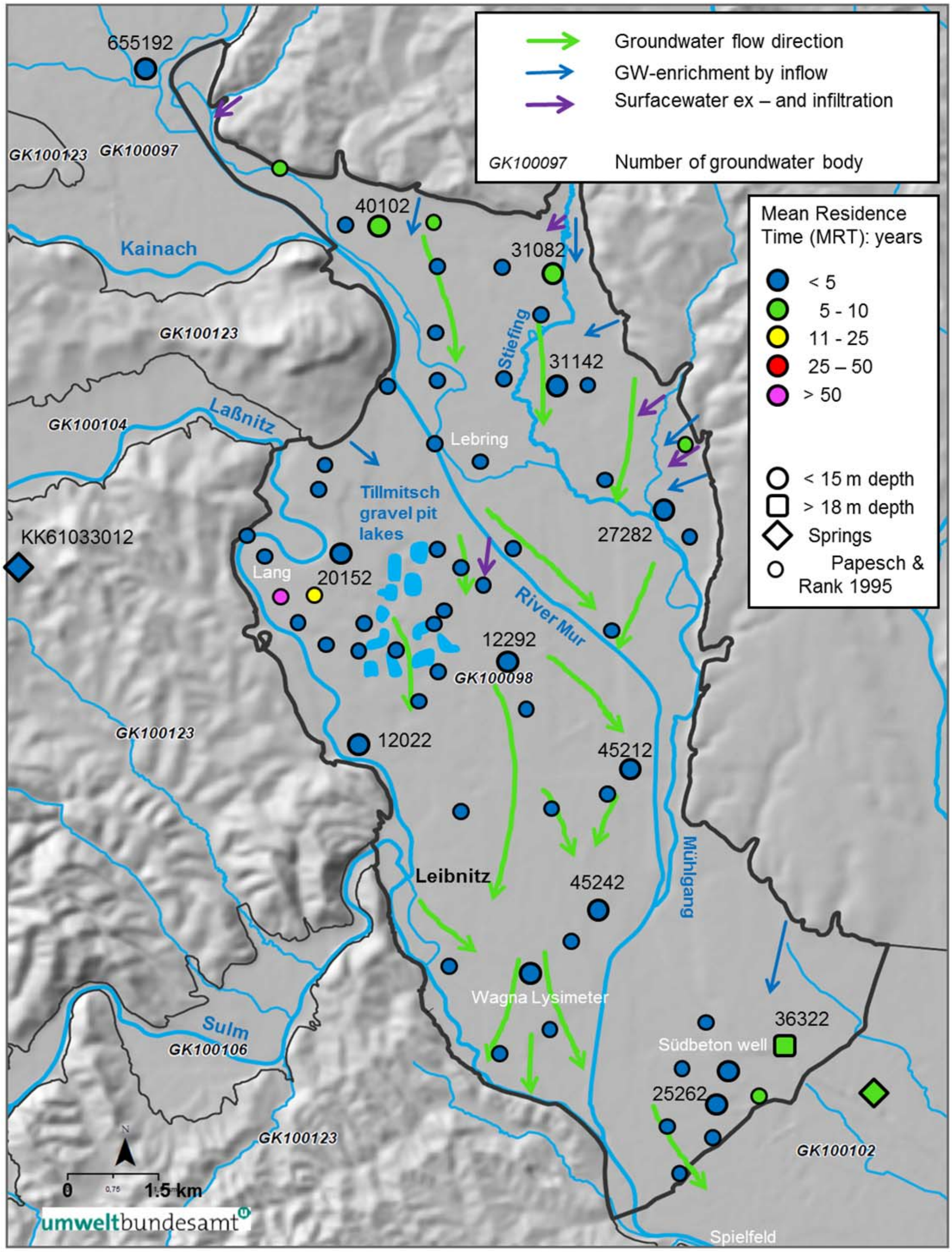


**Fig. 10.** Mean Residence Times (MRTs) of selected quality monitoring wells (large symbols), domestic wells (Papesch and Rank 1995; small symbols), estimated groundwater flow and surface water discharge and infiltration in the Leibnitzer Feld.