Spatial Runoff Estimations based on the Isotopic Signal of an Upstream Lake

Master's Thesis GEO 511, 30 April 2014

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ACKNOWLEDGEMENTS

I feel very thankful and content having written this Master's Thesis. Without the help and assistance of friends and families, I would not have been able to produce this Master's Thesis. Thank you very much!

My special thanks go to:

Benjamin Fischer for being my tutor in the truest sense of the word. He kept me in suspense, so I learned a lot by my own. I would like to thank Benjamin for the interesting discussions and for his endless patience and support with "Alexa and Matlab". Furthermore he was babysitting *Picarro* and feeding it with my samples.

Eveline Braun, Helena Kühnle, Angela Maurer, Andrea Ruecker, Lea Reusser, Ronnie Schmit, Monika Sommer-Ruch, Claudia Widmer, Franz Widmer, Peter Widmer, Yvonne Widmer for supporting me in the field, carrying materials, taking samples, protocolling and even being interested in what I was doing there, in the *Reppisch* valley.

Angela Maurer for her support when installing the *WLPWS* while it was heavily raining and we were wetter than the *Reppisch*. Still then, we did our thing. She also helped me installing the *ISCO Samplers* and accompanied me on nice warm field days.

Eveline Braun for helping me on the longest field day ever, cleaning the material and helping me with her fundamental knowledge in *ArcGIS*.

Vreni Landert I would like to thank very much for proofreading my thesis and leading it to a more proper English style.

Lea Reusser for her hints at some confusing sentences.

Samuel Gygli for his invaluable inputs on scientific English writing.

Sandra Röthlisberger for also feeding *Picarro* with my samples and taking me to the Meerkats in the backyard of the Irchel-complex.

Bianca Lienert for helping me cleaning the *WLPWS*.

Ivan Woodhatch for helping me out with this and that in his workshop, for fruitful talks and for giving me tasters of his encyclopaedic brain concerning British sayings, also on this and that.

Jan Seibert for his refreshing inputs and ideas concerning the view onto my data. And I would also like to thank him and his wife Petra Seibert for letting me install the rain gauges in their garden and for emptying them for me.

Franz Widmer. Real love is patience. He was very persevering with me, taking me the way I am, encouraging me, giving me power during my whole studies and now, even marrying me.

I would like to especially thank my families for supporting me also financially throughout my entire studies.

Biberstein, March 2014 Alexandra Chevrolet

SUMMARY

As integral parts of water molecules stable water isotopes can be traced throughout the hydrological cycle. They are as well a valuable tool to identify and trace hydrological processes and flowpaths in small catchments. Modified by phase changes and mixing processes water molecules can be composed of different isotopic compositions. A comparison of the abundance ratio of the stable isotopes hydrogen D and oxygen ^{18}O of various samples to a standard or to each other, allows the researcher to draw conclusions on the water's flowpaths. The so-called d-excess provides additional information on the enrichment of D in relation to ^{18}O.
In order to characterise the Reppisch basin in the Swiss Plateau the isotopic signals, in particular the d-excess values of the main stream Reppisch, of surface tributaries, of the lake Türlersee and of precipitation in the area were determined and compared to each other. First water samples of the Reppisch, the Türlersee and some inflows were collected in the summers of 2010 and 2011. In the summer of 2013 the monitoring was extended to precipitation collection, discharge measurements and event sampling. Different geographical, meteorological and hydrometrical parameters of the sampled basin components were discussed as possible formers of a certain d-excess signal.
Induced by additional kinetic evaporation effects, the d-excess values of the small-sized lake Türlersee constantly decreased and reached 1.4 ‰ by September 2013. Furthermore, the lake's Evaporation Line showed a characteristic slope of 4.4 of open water bodies which had undergone strong evaporation. The other observed components provided clear fingerprints in their isotopic compositions as well and could be allocated to their sources.
The range of all d-excess values became bigger with the time lapse of monitoring period 2013. The precipitation's d-excess values (around 8 ‰) varied strongly, especially during events which were mainly sampled in September. The Türlersee signal of low d-excess values became weaker downstream the Reppisch the further away they were sampled. Thus the Reppisch's d-excess values approached the ones of the inflows (around 9 ‰). After 5.7 km the Türlersees's d-excess signal was diminished. Henceforward, the Reppisch's d-excess signal was dominated by the other tributaries. Observed discharge rates confirmed the Türlersee's domination of the Reppisch runoff until 5.7 km. The inclusion of hydrometric data into the analysis further revealed that the lake's d-excess signal in the Reppisch strongly depended on its portions in the Reppisch and not as previously assumed on base- and stormflow situations determined by one single threshold. Therefore, in the lower part of the basin lowest d-excess values in the Reppisch came together with highest Türlersee portions in the Reppisch, independently of actual runoff rates. In general over monitoring period 2013, falling and rising limbs of the Reppisch were accompanied by decreasing and increasing d-excess values. Furthermore, the observed Türlersee portions showed a clear hysteresis. At equal runoff rates in the Reppisch, the Türlersee portions were smaller on rising limbs and bigger on falling limbs.
Varying runoff proportions and the anomalous behaviour in combination with changing d-excess signals led to questions of antecedent condition settings; the Current Precipitation Index (CPI7) was applied. The monitoring days of summer 2013 were classified according to the modelled CPI7 settings into dry, humid and wet conditions. These determined different antecedent condition settings correlated with observed runoff rates, with rising and falling limbs and with d-excess signal's evolution over time. Moreover, highest Türlersee portions were all found in basin settings classified as being wet. Overall, beside daily and weekly runoff fluctuations, the basin was found to be in a special situation during monitoring period 2013. For three months the Reppisch was mainly draining its stores from the heavy precipitation events of the end of May.

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ABBREVIATIONS

acc	accumulated
API	Antecedent Precipitation Index [mm d^{-1}]
AWEL	Amt für Abfall, Wasser, Energie und Luft, Kanton Zürich, Baudirektion
BD	Birmensdorf
CPI	Current Precipitation Index [mm d^{-1}]
D (^{2}H)	Deuterium, Hydrogen Isotope
d	Deuterium Excess or d-excess [‰]
d^{-1}	per day
dm	daily mean
δ	Delta annotation in [‰] relative to a standard, here to GMWL
GMWL	Global Meteoric Water Line
^{1}H	Hydrogen Isotope
IHS	Isotopic Hydrograph Separation
ISS	Isotopic Source Separation
K	Recession Constant [1 d^{-1}]
LMWL	Local Meteoric Water Line
m^{-1}	per month
^{16}O	Oxygen Isotope
^{18}O	Oxygen Isotope
obs	observed
P	Precipitation [mm d^{-1}]
WLPWS	Water Level Proportional Water Sampler
Q	Discharge [m^3 s^{-1}]
Q347	Discharge rate which is reached for at least 347 days of the year [m^3 s^{-1}]
Q_{all}	Own discharge measurements [m^3 s^{-1}]
Q_{BD}	Discharge in Birmensdorf [m^3 s^{-1}]
ΔQ_{BD}	Discharge difference between Birmensdorf and Türlersee [m^3 s^{-1}]
Q_{TS}	Discharge at Türlersee [m^3 s^{-1}]
RE	Sample Point in Reppisch basin
RE_{ISCO}	Sample Point in Reppisch basin with ISCO Sampler
RE_{WLPWS}	Sample Point in Reppisch basin with WLPWS
RE_{RG}	Rain Gauge
RE_{RGTS}	Rain Gauge at the Türlersee
RE_{RGWE}	Rain Gauge in Wettswil
RH	Relative Humidity [%]
t	Time
T	Temperature [°C]
TS	Türlersee
sim	simulated
spec	specific
VSMOW	Vienna Standard Mean Ocean Water
w^{-1}	per week
wm	weekly mean

1 INTRODUCTION

1.1 Context

The *Knonauer Amt* region in the district of *Zurich* is an agricultural region with an attractive landscape. The lake *Türlersee* and the stream *Reppisch* help to make this valley an excellent local recreation area (Höhn, 2008). In recent years the *Knonauer Amt* region has become more and more popular as a residence for commuters working in the city of *Zurich* or *Zug* (Rühl, 2006). With a growing population there is an increasing desire for near-natural landscapes (Arnold et al., 2009). This growing anthropogenic pressure on sensitive biospheres has increased the need to obtain fuller information about the local water regime.

The hydrologic system of the Reppisch and Türlersee needs to be understood more profoundly. Some natural sciences studies that were carried out in the Reppisch valley were for biological purpose around questions of macrozoobenthos compositions in the Reppisch (Wolf, 1981), for the ecological and hydrological health of the entire Reppisch system (Känel et al., 2010), for investigations on phosphorous concentrations in the Türlersee (Elber et al., 2001) or for environmental problems such as hazardous behaviour of the Reppisch (concerning floods, Scherrer, 2006).

But for all that, there remains a lack of information on the Reppisch system, on its discharge proportions, whether the Reppisch is mainly fed by the lake, by surface inflows or by subsurface tributories. There is as well a more general lack of knowledge on compositions and isotopic signals of stream water which is influenced by lakes that have undergone strong evaporation. Hence, in the Reppisch area, hydrological and meteorological variabilities and influences on discharge amounts and proportions have not been subject to research until now.

For an enhanced understanding of reactions and variations in the water cycle of a specific catchment, the stable water isotopes (^{18}O and D) are very helpful in tracing moisture sources (McGuire & McDonnell, 2007). Each water sample has its own fingerprint formed by evaporation fractionation processes. Comparing the isotopic composition of a certain water body to the *Global Meteoric Water Line (GMWL)* enables the researcher to determine where the examined water samples might come from. $\delta D = 8 * \delta^{18}O + 10$ ‰ (Dangaard, 1964) is the equation expressing the *GMWL* as the mean composition of all the meteoric water on earth. By rearranging the *GMWL* formula to $d = \delta D - 8 * \delta^{18}O$, the so-called *Deuterium Excess* (d-excess) in per mille can be calculated. The d-excess expresses the shift of *GMWL,* or ones own water sample, from the axes intersection (Kendall & Caldwell, 1998). It quantifies the enrichment of hydrogen D in relation to oxygen ^{18}O.

Many researches have been undertaken by using stable water isotopes to determine runoff components especially during events. A discussion among hydrologists is whether storm runoff water is mainly built by event water, or by water previously stored in the catchment, pre-event water. Their determination is based on simple mass balance equations and called *Isotopic Hydrograph Separations* (*IHS*) (Sklash & Farvolden, 1979; Pearce et al., 1986). Other studies used stable water isotopes concentrations to determine water balances of lakes (Dinçer, 1968; Gat,1995; Payne, 1970). The d-excess has been used as information about a tropical lake's water balance and the local hydrological cycle (Vallet-Coulomb et al., 2008), in paleoclimatic lake sediment studies in the *Himalayas* (Yuan et al., 2011), in a survey around lake *Garda's* hydrological balance (Longinelli et al., 2008), in a model around high d-excess values in snowpack formations in polar regions (Jouzel & Merlivat, 1984) and in many other studies as additional information. The d-excess has rarely been used as a main information source.

Insofar as known, no study was using d-excess values to trace the evaporation signal of a lake downstream its outflow and thereby to estimate runoff proportions and behaviours. The ideal long narrow valley setting of the Reppisch basin straightforward invites a researcher to make use of the

advantageously simple overview of the inflows, Türlersee and Reppisch.
So far, no other researches with isotopes have been undertaken in the Reppisch valley although the historical data proved a clear distinction of the isotopic signals of the Türlersee, the inflows and the Reppisch. Payne's (1970) study in Kenya could as well clearly distinguish between the lakes, spring and precipitation waters' isotopic signals of the same area. Their clear signals were used to proof disconnections between the lake and springs. This thesis intends to prove connections between the sampled basin components in the Reppisch valley. Historical data of 2010 and 2011 showed that the isotopic composition was gradually changing, following downstream the Reppisch from the Türlersee on. This means that the d-excess values of the Reppisch approached the *GMWL* the further away from the Türlersee they were samples.
Open water bodies which have undergone evaporation show a so-called *Evaporation Line*, and thus characteristic slopes of 4 to 7 instead of 8 of the *GMWL* (Dansgaard, 1964). In 2011 data, the Türlersee showed clear evaporation effects, it achieved a slope value of 5.7. Hence, the strong signals of the Türlersee and the various clearly distinct signals of the other components will be traceable downstream the Reppisch valley. Nevertheless, it is not known how suitable the d-excess signals really are to estimate runoff variations along a stream discharging a lake. It is also not clear how d-excess signals will evolve over the monitoring period 2013 and what parameters will influence its values. Therefore, this study will bring more clarity on tracing d-excess signals and on the Reppisch system's characteristics.

1.2 Research Focus – Scope

Buttle (2006: 43) let arise the fundamental question "What is the spatial and temporal scale of variations in the isotope signature of water held in various stores in the hydrological system?".

This thesis focuses on the characteristic of the Reppisch basin especially on surface waters. Historical data showed that downstream the Reppisch the Türlersee's signals became weaker. The d-excess signals of the Reppisch approached the *GMWL* the further away from the Türlersee they were measured. Why did this altering happen? How big is the contribution of the Türlersee to the total Reppisch runoff during dry and wet periods, or even what happens when a rainstorm crosses the valley? How does the Türlersee contribution vary over time? Are there any other important contributors to the Reppisch? How do the basin components interact and build up the discharge of the Reppisch during hot summer weeks and during events?
The lowest pre-event contribution to a stormflow hydrograph has been noted to take part among others in urban and agricultural regions (Buttle, 2006). The Reppisch catchment has an agriculturally used area of 39.4% and a settlement area of 6% (Känel et al., 2010; AWEL, 2013). Are there any influences of mentioned landcover types detectable on the d-excess signals?
The increase in d-excess values downstream the Reppisch might mainly occur through small surface inflows from the hills aside and through near stream groundwater. Groundwater is said to be the main long-term component of total runoff (Ward & Robinson, 1990 in Buttle, 2006). In the case of the Reppisch, does the groundwater contribution overtop the one of the Türlersee after six to 14 km distance downstream as the d-excess values of grab samples from 2010 let assume?

The different contributors to total runoff of a stream are spatially and temporally variable, always depending on the antecedent conditions and on the rainfall duration and intensity (Beven, 2012). Variations in precipitation and antecedent conditions on the other hand, form the isotopic compositions and proportions of water discharging a catchment (Buttle, 2006). Additionally, the characteristic of a certain basin dictates drainage quantity and temporal dimensions of total runoff. As already mentioned, water isotopes are very helpful tracers in determining flowpaths, water compositions and proportions. In the Reppisch area no investigations with stable water isotopes have been undertaken so far. Therefore, this project aims to characterise the Reppisch basin by tracing the d-excess signals and determining discharge proportions of the Reppisch with the help of isotopic and hydrometric data. The d-excess signals are compared and mixing and phase changing processes interpreted.

On this account, the following hypotheses for this project are placed:

HYPOTHESES

1) **The further away from the Türlersee downstream the Reppisch, the more the d-excess values of the Reppisch approach the *GMWL*.**

2) **Due to the obvious Türlersee's d-excess signal in the Reppisch, the Reppisch's baseflow d-excess values are lower than its stormflow d-excess values.**

3) **During event situations, precipitation inputs cause quick and large tributaries to the Reppisch, whereas the lake contribution rises only slowly.**

4) **By combining isotopic with discharge data, a quantification of runoff proportions of the Reppisch will reveal that during baseflow situations the main component of the Reppisch runoff is the Türlersee portion.**

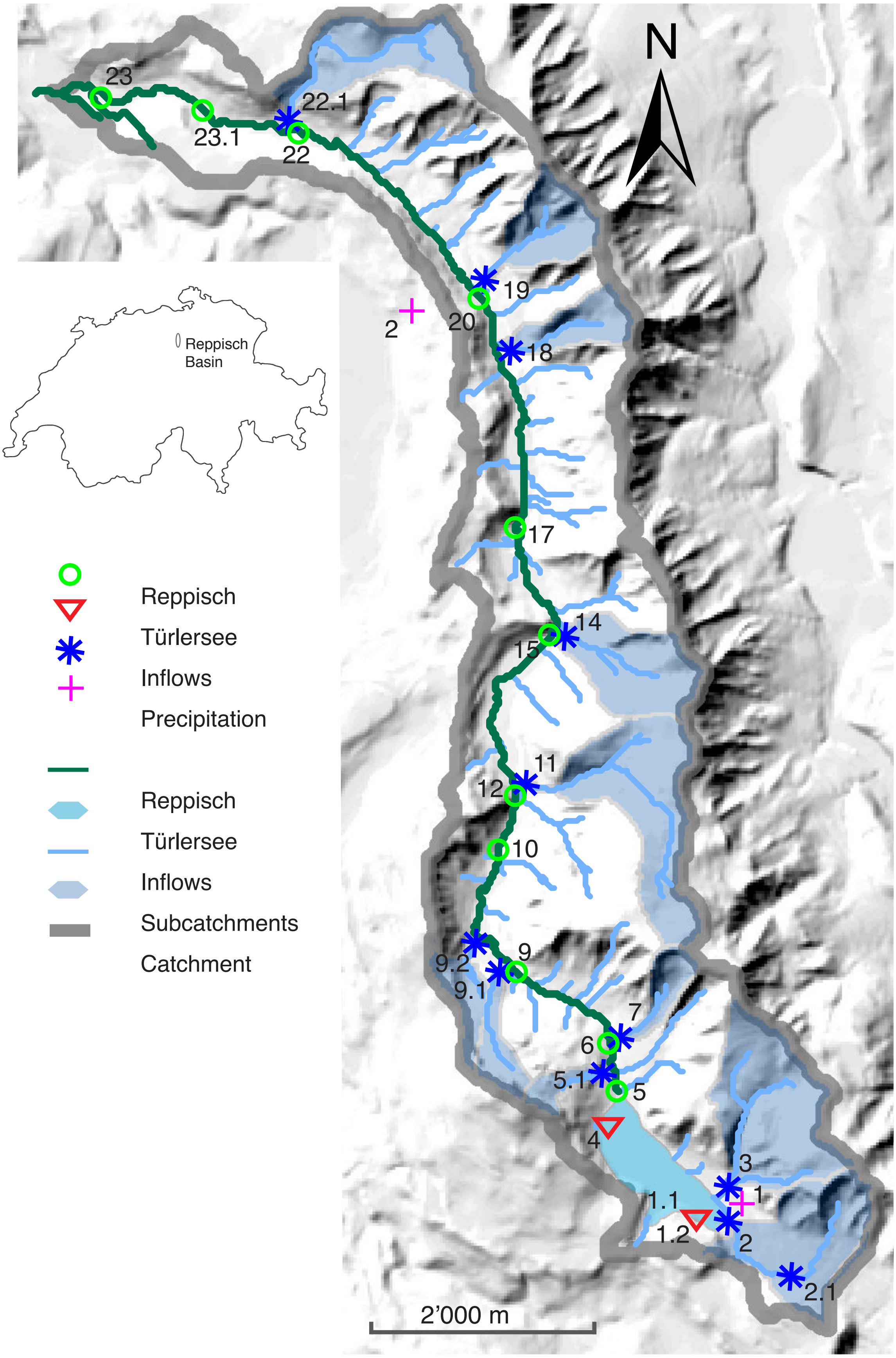

Figure 1 Reppisch basin with monitoring points of 2013 (data source of Digital elevation model swissALTI3D 2m: Swiss Federal Office of Topography, SWISSTOPO, 2002, own map; Switzerland insert map: WORLDATLAS, 2014).

2 MATERIALS AND METHODS

2.1 Study Site Reppisch Catchment

2.1.1 Geographical Location

The *Reppisch* catchment is located southwest of Zurich in the *Knonauer Amt* region, a part of the canton of *Zurich*, in northeast Switzerland. The long narrow *Reppisch* valley with lake *Türlersee* on the top, is situated parallel to the *Sihl* valley and *Lake Zurich*.
The Reppisch valley shows a unique geomorphologic setting: its narrowness was formed by a glacial drainage channel of the *Linth Glacier*. Its steep flanks of slopes around 30° aside (own data) are the origins of the sampled inflows of maximum 20 l/s discharge (summer 2013) and lengths between 0.6 and 3 km. The Türlersee, lying in the uppermost part of the valley, was dammed up by a landslide from the *Aeugsterberg* on the west side (Hantke, 1967; Scherrer, 2006).
The study site includes the part of the Reppisch catchment from *Birmensdorf* (RE23) onwards, at 466 m above sea level, to the uppermost inflow (RE2.1) of the Türlersee at 643 m above sea level (Swisstopo, 2013). The Reppisch basin has a size of about 24 km^2, thus it belongs to the small catchments (0.01 to 100 km^2) according to the definition of catchment categories (Buttle, 1994).
The examined part of this basin is the origin of the entire Reppisch system. Today no glaciers are found in the area (Swisstopo, 2013). All the sample points and the examined subcatchments of this study are illustrated in *Figure 1*.

2.1.2 Geology

The Reppisch basin is embedded in the upper freshwater molasse. Thus the ground mainly consists of sandstone and clay. Especially the flanks still consist of these clastic sediments, whereas the valley bottom today is mostly built up of quaternary unconsolidated rock, morainic material of the *Würm Glacial Stage*. On the eastern flanks there are found some solifluction debris and solifluction soils. The Reppisch's flowpath is shaped by the quaternary settlements and landslips, by some sections with recent deposited crushed stones of the Reppisch itself and by the small alluvial fans of the small inflows (Swisstopo, 2013; Hantke, 1967; Scherrer, 2006; own observations).

2.1.3 Soils

In the Reppisch valley most soils are *Luvisols* (classification according to *World Reference Base for Soil Resources*, "Braunerde" and "Kalkbraunerde" according to KA5-classification (Schmidt et al., 2007)). *Luvisols* stand for a good water storage capacity and for a good hydraulic conductivity. Hence, the entire basin has predominantly good soil conditions for an agricultural treatment. Although, in some parts the soils are influenced by stagnant moisture due to the high annual precipitation amounts and seepage water of the Reppisch. These different types of *Gleysols* are located in the water meadow zones along the Reppisch and in depression zones. On the freshwater molasses of the steep slopes between *Üetliberg* and *Felsenegg* some shallow brown and slope soils can be found. On the bottom of these steep slopes *Regosols* have developed on the solifluidal material (Scherrer, 2006; Peyer et al., 1988).

2.1.4 Vegetation and Land Use

According to Odermatt & Wachter (2004) the Reppisch valley belongs to the colline zone and some parts higher than the Türlersee (643 m a.s.l.) belong to the montane zone. In both zones deciduous forests are the predominant flora. Mostly pastures lie in the valley bottom whilst the forests cover the steep flanks on the sides. The climatic conditions are ideal for wheat, root crop and pastures as well as for beeches and fir trees. The growing season for agriculture and forestry lies between 180 and 210 days. Additionally preserved wetland areas seam the Reppisch and the Türlersee (Peyer et al., 1988; Kanton Zürich Baudirektion, 2014). Due to its nativeness and great biodiversity the whole research site belongs to an inventory of landscapes with a national importance, the "Bundesinventar der Landschaften von Nationaler Bedeutung" (BLN object 1306) since 1983 (BLN/IFP, 1983 in BAFU, 2013).
Also situated in the valley bottom there are small villages, getting smaller and ending up in a conglomerate of a few houses the closer they are to Türlersee. Agricultural land use also becomes more dominant the more upstream it is located. In the "statistic of the area used" of 1992/97 the urban area was about 10.3 %. It has obviously grown since then. Many new buildings and construction sites are found especially close to the entrance of the valley. The forest area is about 47.4 %, the agricultural area 39.4 %, the waterbodies 2.1 % and unproductive areas make up 0.7 % of the total 24.7 km^2 of the Reppisch basin (Arealstatistik 92/97 Geostat in AWEL, 2009).

2.1.5 Climate

The Reppisch valley lies in the typical Swiss plateau climate region. Which is influenced by the oceanic climate of the Atlantic Ocean and by the continental climate of the east. As the predominant system, westerly winds bring humidity and mild maritime air from the Atlantic Ocean. This has a cooling effect in summer and a warming one in winter. Air temperatures in Switzerland mainly depend on the altitude (Meteoschweiz, 2008). The mean annual air temperature for *Stallikon* in the Reppisch valley has been 9 °C for the years 2010 to 2012. The mean air temperature for the sampling period of June to September 2013 in the Reppisch basin has been 14.6 °C (own calculations, data source: Meteocentrale). The Reppisch area is a moderately humid region. The total mean annual precipitation lies between 1'200 and 1'400 mm. In winter it sometimes snows (Meteoschweiz, 2008; Odermatt & Wachter, 2004; Spiess et al., 2002; Scherrer, 2006).
The three summers of research in the Reppisch basin took place in climatically special years. The summer of 2010 was very cool and rainy, interrupted by heat waves and ending with moderate temperatures (Meteoschweiz, 2010). The year 2011 included the third driest spring, temperatures broke records, July had been the coolest one since the year 2000, in the second half of August thermometers reached more than 30 °C, the area cooled down, then temperatures reached again more than 30 °C in September, ending with very cool air (Meteoschweiz, 2012).
The summer of 2013 again seemed to be willing to break records. It had been the seventh warmest summer since 1864. Whereas in June the meteorological situation was in a normal range, the second half of July and the first week of August were extremely hot and dry. For the months of June, July and August a precipitation deficit of 66 %, a plus of 124 % of solar radiation (of the standard value from 1981 – 2010) and a plus of 0.8 degrees of temperature deviation were reached. The next two sunnier summers were recorded in 2003 and in 1911 (Meteoschweiz, 2013a). September 2013 was of midsummer character in the beginning and continued to be in the means of the norms concerning temperatures and precipitation (Meteoschweiz, 2013b).

2.1.6 Hydrology

For the surface waters the rough hydrological overview is as follows: The mean discharge and Q347 of the Reppisch in Birmensdorf and at the outflow of Türlersee is 0.410 m^3/s and 0.0700 m^3/s (AWEL, 2009) and 0.105 m^3/s and 0.0057 m^3/s respectively (AWEL, 2013a). All of the sampled inflows of this project have a similar character concerning their discharge amounts. For the summer of 2013 the range of their weekly measured discharges was between 0 and 26 l/s, the mean discharge was 3.53 l/s (own data).
The mean water temperature in the Türlersee for June to September 2013 was 20.75 °C, whereas its minimum of 11.6 °C was measured in June and its maximum of 27.1 °C in July. The annual mean temperature of the lake is 12.2 °C (AWEL, 2013b). The mean temperature of the Reppisch in Landikon (sample point RE22, 1.5 km upstream from Birmensdorf) for the sampling period in 2013 was 15.4 °C (weekly samples, own data).
The overall slope of the Reppisch down to Birmensdorf is 0.9 %. Within the study area no inflow of cleaned waste water or up- and downsurge influences the water quality or the runoff ratio (AWEL, 2009).
According to Scherrer's (2006) sprinkling experiments in the whole Reppisch catchment the following runoff process types could be distinguished: *Hortonian Overland Flow (HOF), Saturation Overland Flow (SOF), Sub-Surface Flow (SSF)* and *Deep Percolation (DP)*. While *HOF* processes take place on soils of low permeability or in urban areas, *SOF* was found to be quite rare in the area except for saturated (with a low gradient) and thin soils and it is very dominant related to agriculturally treated fields. *Quick SSF* is also rare, whereas *slow SSF* takes place especially on the steep forested flanks aside the Reppisch and very slow *SSF* in less steep forest soils. *DP* should not affect the study site, it is more pronounced in the southeast of Birmensdorf where there are more moraines or crushed stones.
Scherrer (2006) divided the discharge types of the Reppisch catchment into five categories. The third category "delayed contributory area" ("verzögert beitragende Fläche") makes up the greatest part, namely 41.3 % of the whole Reppisch catchment. It makes up probably even more than 41.3 % in this study site.

2.2 Monitoring Strategy

The processes and reservoirs as contributors and important parts of the Reppisch basin described in the *INTRODUCTION,* should be captured as well as in any way possible within this thesis' timespan for field work. Water samples of three main contributors to the Reppisch runoff, namely the Türlersee, the inflows and precipitation and, of course, of the Reppisch itself were taken weekly. Soil-, ground- or pondwater were not taken into the examination. Evaporation rates or amounts from any surfaces nor transpiration by any plants, have been taken into account either. For determining Reppisch proportions (see also *APPENDIX A)*), discharge measurements of the Reppisch and the sampled inflows were conducted weekly. Additionally, continuous discharge data of the Reppisch at the lake outflow (RE6) and at the basin outlet in Birmensdorf (RE23) have been taken into account and continuous meteorological data was added to the analysis of the isotopic data and to estimate the rainfall-runoff behaviour of the Reppisch basin. Discharge and meteorological data have been provided generously by the *AWEL* and *Meteocentrale* respectively.

The following chapters introduce the historical and actual monitoring strategies and give an overview of all monitoring points and methods in the field, laboratory and during data processing.

2.2.1 Sampling Periods

In 2010 grab samples were taken in July and August, in 2011 they were taken from June to September, which was the same sampling period for the summer 2013 (see *Table 2*). In all summers grab samples were taken weekly. Additional three sampling days with discharge measurements were conducted in the summers of 2011 and in a weekly interval in 2013. The monitoring of the summer 2013 was further extended with continuous stream water collecting *Water Level Proportional Water Sampler (WLPWS)* and *Totalisators* (rain collectors). For a deeper understanding, event-sampling with continuous sampling of *ISCO Samplers* of the type *6712* and *Sequential Rain Collectors* (*Tipping Buckets*) were also undertaken.
The areal distribution of all monitoring points are depicted in *Figure 1* and *Table 1* gives a detailed overview of them.

Table 1 All monitoring points of monitoring period 2013. Data source of lake's area by AWEL (2013a), data source of own calculations of geometries: Digital elevation model swissALTI3D 2m: Swiss Federal Office of Topography, SWISSTOPO, 2002.

ID	Situation	E	N	Distance [km]	Stream Length [km]	Catchment Area [km²]
RE_{RGTS}	Totalisator	681 234	235 647	2.18		
RE_{RGWE}	Totalisator	678 510	243 629	13.76		
RE1.1 RE1.2	Lake	680 976	235 397	2.13		Lake's Area 0.50
RE2.1 $RE_{WLPWS2.1}$ $RE_{ISCO2.1}$	Inflow	681 839	234 808	0.83	0.83	0.48
RE2	Inflow	681 158	235 393	1.91	1.91	1.05
RE3	Inflow	681 206	235 614	2.20	3.27	1.30
RE4	Lake	680 191	236 401	4.14		
RE5	Reppisch	680 214	236 506	4.25	0.04	4.09
RE5.1	Inflow	680 185	236 687	4.38	0.61	0.15
RE6	Reppisch	680 182	236 914	4.69	0.48	5.16
RE7 RE_{WLPWS7} RE_{ISCO7}	Inflow	680 182	236 914	4.70	0.87	0.24

Table 1 (Continued)

RE9 RE$_{WLPWS9}$	Reppisch	679 318	237 534	5.90	1.68	6.76
RE9.1	Inflow	679 278	237 524	5.92	1.23	0.26
RE9.2	Inflow	678 912	237 813	6.46	0.72	0.26
RE10	Reppisch	679 173	238 691	7.43	3.22	8.63
RE11	Inflow	679 311	239 181	8.07	3.83	1.27
RE12 RE$_{WLPWS12}$ RE$_{ISCO12}$	Reppisch	679 311	239 181	8.05	3.83	8.96
RE13	Reppisch	679 180	239 531	8.53	4.31	11.20
RE14 RE$_{WLPWS14}$	Inflow	679 640	240 643	9.91	2.04	0.80
RE15 RE$_{WLPWS15}$	Reppisch	679 640	240 643	9.89	5.67	12.66
RE17	Reppisch	679 292	242 094	11.65	7.43	15.64
RE18	Inflow	679 378	243 070	12.77	1.17	0.40
RE19 RE$_{WLPWS19}$	Inflow	678 987	243 629	13.46	1.58	0.55
RE20 RE$_{WLPWS20}$ RE$_{ISCO20}$	Reppisch	678 974	243 611	13.44	9.23	18.30
RE22	Reppisch	677 291	245 141	16.15	11.93	21.53
RE22.1	Inflow	677 291	245 141	16.17	2.77	0.87
RE$_{WLPWS23.1}$ RE$_{ISCO23.1}$	Reppisch	676 702	245 190	16.84	12.60	22.84
RE23	Reppisch	675 660	245 430	18.21	14.00	23.82

2.2.2 Field Methods

The aim in the field was to capture different signals in their isotopic composition. Therefore the monitoring was divided into three parts as summed up in *Figure 2*.

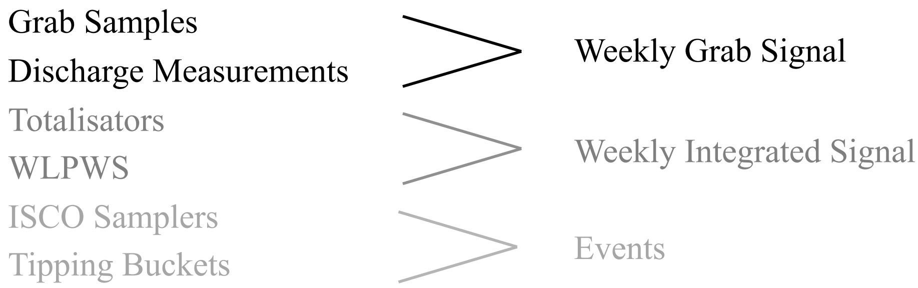

Figure 2 The data collection divided into various sampling instrumentations with different time intervals.

2.2.2.1 Weekly Grab Signal

To capture the isotopic weekly grab signal and to be able to derive where the Reppisch runoff mainly comes from, weekly water grab samples were taken. Water of inflows to the Türlersee, of the lake itself, of the outflow of the lake, of different stages downstream the Reppisch and water of inflows into the Reppisch were sampled by hand. After washing the bottles with the water of the sampling location three times, a sample was taken, where possible, in a depth of about 20 cm below water surface. Like this, capturing of superficial contaminations could be avoided.
Discharge measurements with the salt dilution method were also carried out where possible in a weekly interval. Discharges were measured and calculated by using the system of *Sommer* (Sommer, 2012). For more information on the salt dilution method see Moore (2005). Otherwise the bucket method was used to measure the discharges of the very small inflows (around 0.5 to 7 l/s).

2.2.2.2 Weekly Integrated Signal

To capture a weekly integrated signal, so-called *Water Level Proportional Water Samplers* (*WLPWS*) were installed at nine sample points of the Reppisch and of the inflows. These *WLPWS* were installed on 13/08/13, henceforward on they were emptied weekly. A sensitivity analysis and a discussion on the here used *WLPWS* is provided in the *APPENDIX C)* of this thesis.
For the whole monitoring period of 2013 precipitation samples were gathered in two *Totalisators*, which were also emptied weekly. These collectors are constructed to surely prevent the collected water from evaporation and the associated fractionation. The water can be stored in the 3 L plastic bottle for several weeks or months without undergoing evaporation. The *Totalisators* were manufactured by the Croatian company *Palmex d.o.o.* in *Zagreb* (Palmex, 2013).
One precipitation collector was installed close to the lake (RE_{RGTS}) and one in Wettswil (RE_{RGWE}) on the west side of the Reppisch valley. In this way continuous data of the isotopic input signal of the precipitation could be obtained. The variations in the isotopic composition of rain in time and space was accounted for.

2.2.2.3 Events

Moreover, for a deeper understanding of the Reppisch system some events were captured as well. For that purpose five automatic samplers *ISCO* of the type *6712* (24 samples (ISCO, 2012)) were installed at the monitoring locations on 21/08/13 (see map in *Figure 1*).
Rising water levels during storm runoff activated the sampling of the *ISCO Samplers*. After the completion of programme A, when the first six bottles were filled in a 30 minutes interval, programme B with filling the remaining 18 bottles in a 1-hour time step was started. The *ISCOs* took 200 ml and 500 ml per sample for the inflows and the Reppisch respectively.
During the same on-going event, precipitation was also sampled continuously with two *Sequential Rain Collectors* (*Odyssey Tipping Bucket Rain Gauge Logger*) located next to RE_{RGTS} and RE_{RGWE}.

2.2.3 Laboratory Methods

While sampling in the field, it was always tried to avoid evaporation by closing the glass bottles immediately and hermetically. All water samples of this study were filled into the 20 ml glass bottles and stored in cardboard boxes until their examination in the laboratory. In the laboratory of the *Department of Geography, University of Zurich*, firstly the samples were filtered with a 0.45 µm filter (25 mm PTFE Syringe Filter, *Simplepure* USA) and filled in new 20 ml glass bottles. Secondly, 1 ml of the filtered samples were pipetted into vials closed with a PTFE/silicone/PTFE septa cap. The pipetted samples were stored in a refrigerator at 5 to 7 °C until their final analysis. The final analysis was undertaken with a Cavity Ring-Down Spectroscope-Picarro Liquid Analyser (*WS-CRDS Picarro L1102-i,* manufacturers precision is < 0.5 ‰ for δD and < 0.1 ‰ for $\delta^{18}O$ (Picarro Inc., 2008 in Fischer et al., 2014 in submission)) and the analysis scheme of Penna et al. (2010) . Gained values are specified as δ-values in per mille (‰) relative to *Vienna Standard Mean Ocean Water* (*VSMOW*) (Fischer et al., 2014 in submission; Gupta et al., 2009).
Measured samples were generally accepted until deviations of 0.8 ‰ for δD and 0.08 ‰ for $\delta^{18}O$. Even though, some measured samples with lower deviations could result in variations of the d-excess of more than one per mill. If this was the case, a sample was remeasured as well.

2.3 Theories

This chapter gives a detailed overview of the theories supporting this Master's Thesis. The following chapter *Tracers in Hydrology* outlines the utilisation of tracers in hydrology in general. *Stable Water Isotopes as Tracers* explains the fundamentals of referencing hydrological standards (*Vienna Standard Mean Ocean Water*) and of stable water isotopes (*Fractionation*). The following chapter highlights how the measurements of stable water isotopes are determined and referred to a global average (*The Global Meteoric Waterline and Deuterium-Excess*). The final subchapter elucidates the applied ideas and data processing steps.
APPENDIX A) presents the model of *Isotopic Source Separation* that was used for quantifying discharge portions of the Reppisch. The method did not perform well and the generated results were useless. Therefore, the entire topic including its discussion with critical reflections was placed in the *APPENDIX*.

2.3.1 Tracers in Hydrology

Tracers are tools to help understanding a certain phenomenon by following its paths. In hydrology tracers are mainly used as tools to understand transport processes, to quantify their parameters, to identify and quantify phase changes, to reconstruct paleoclimatic conditions, to assess surface water - groundwater interactions and to evaluate the vulnerability of water resources and for many topics more, especially concerning the modelling part in hydrology for example to calibrate and test models (Leibundgut et al., 2009; Buttle, 2006).
The different types of tracers that are used in hydrology can be split up into two groups: *a) Environmental tracers* are the ones that already exist in nature or that already are a part of a certain flow system. They can be treated as an inherent component of the water cycle. If a tracer is passively injected to the system by any human activity, for example tritium release to the atmosphere by nuclear bomb tests, this tracer is still treated as an environmental one. Hence, anthropogenic and natural environmental tracers are environmental isotopes, hydrochemical substances, pollution tracers. They are put spatially into the system via precipitation or geogenic sources. *b) Artificial tracers* are actively, punctually injected to the system by the researcher. So the boundaries in time and space and the hydrological situations are defined by the context of the hydrological experiment. Artificial tracers are chemicals, biological and drift substances as for examples spores (Leibundgut et al., 2009).
Drift substances already lead to a first difficulty; they may get stuck somewhere and could reside in the system for a longer time span than the traced water actually does. A next difficulty may appear with chemicals; they might be prone to reacting with substances in the examined system, for example with soil components. To avoid such situations the used tracer should be and behave characteristically like water itself.
In this project the utilised tracers fit both above delineated types of tracers: Namely as the *environmental tracers* the stable water isotopes deuterium (denoted as D or ^{2}H) and oxygen ^{18}O and as the *artificial tracer* salt was used for the salt dilution method for discharge measurements with salt tracers.

2.3.1.1 Stable Water Isotopes as Tracers

A useful stable isotope tracer *a)* should have a large mass difference between the rare and abundant isotope, *b)* should generally have low atomic masses, *c)* the rare isotope should be a small fraction of the overall elemental occurrence and *d)* it should have more than one oxidation state (Sulzman, 2007). Stable water isotopes fulfil these constraints. The use of them according to standards are outlined in the following paragraphs.

2.3.1.2 Vienna Standard Mean Ocean Water

The stable water isotopes like D and ^{18}O are relatively ideal conservative tracers. "Relatively" because they can still become modified when undergoing phase changes. Nevertheless, they are ideal, hence they are not just dissolved, they are an integral constituent of water. To identify the ways of water, D and ^{18}O can be traced by determining their abundance ratio in a water sample (McGuire & McDonnell, 2007).
Abundance ratios are calculated as follows:

$$\delta\ [‰] = (R_{sample}/R_{standard} - 1) * 1000 \quad (1)$$

where R is the heavy-to-light ratio and δ in parts per mille deviation from the standard (because of the very small numbers) (Craig, 1961; Sulzman, 2007). The ratio of the stable water isotope D to ^{1}H is $1.5575 * 10^{-4}$ and the one of ^{18}O to ^{16}O is $2.0052 * 10^{-3}$. These measured ratios are expressed as the *Vienna Standard Mean Ocean Water (VSMOW)*. The light-stable isotopic composition of hydrogen and oxygen of a certain water sample can be described by always referring to the *VSMOW* (Craig, 1961; Kendall & Caldwell, 1998).

2.3.1.3 Fractionation

The abundance ratio of δD and $\delta^{18}O$ relative to *VSMOW* can be used as a "fingerprint". This fingerprint provides information about the origin or the pathways of a certain water sample. The different ways that waters have travelled also induced differently pronounced processes which the waters have undergone. This means that waters that have undergone phase changes like evaporation, condensation or melt have also undergone fractionation. Therefore, waters that have undergone different processes result in different isotopic compositions (McGuire & McDonnell, 2007).
Fractionation appears due to the distinct neutron numbers inducing different masses that isotopes of the same element have. For example, hydrogen exists as protium (^{1}H), deuterium (^{2}H) or tritium (^{3}H). Protium has one proton. Deuterium has one proton and one neutron, which gives it a mass number of two, hence deuterium has twice the mass of protium. Tritium has 2 neutrons and one proton which makes it already three times heavier than protium. A similar situation is found for oxygen. Oxygen is always built up by eight protons and it can have from 13 up to 20 neutrons (Kendall & Caldwell, 1998).
These mass-dependant, slightly different behaviours during phase changes lead to isotopic fractionation. Molecules with heavy isotopes are more stable than lighter ones. D-D-bonds are stronger than H-H-bonds. Hence, for dissociation of D-D-bonds more energy must be available (McGuire & McDonnell, 2007; Kendall & Caldwell, 1998).
The two different fractionation processes are of interest in the context of this thesis just as background knowledge concerning the *Global Meteoric Water Line* and the *Deuterium Excess* which are described further down:

- *Equilibrium fractionation* (reversible) → reaction rates forward and backward are parallel and proportional. For example during condensation, the heavier isotopes preferentially become enriched in the remaining liquid phase whilst the lighter ones preferentially get evaporated (Kendall & Caldwell, 1998).
- *Kinetic fractionation* (irreversible unidirectional) → dependent on isotopic mass ratio and their bond energies (Sulzman, 2007).

2.3.1.4 The *Global Meteoric Water Line* and *Deuterium Excess*

Air masses moving from above the sea to continents and across the continents lose water by precipitation. Previous to the rainout, condensation of water vapour induces fractionation. With the rainout the remaining air masses become depleted in the heavy isotopic species like $H_2^{18}O$ and HDO and the liquid phase relatively enriched in the heavy isotopic species (McGuire & McDonnell, 2007; Kendall & Caldwell, 1998).
This condensation of atmospheric water vapour under equilibrium conditions (about 100 % humidity) is described by the gradient of 8 in the *Global Meteoric Water Line (GMWL).* The *GMWL* is a linear correlation between δD and $\delta^{18}O$ in per mille (Dansgaard, 1964).

$$\delta D = 8 * \delta^{18}O + 10 \text{ [‰]} \quad (2)$$

A plotted *GMWL* illustrates a globally averaged relation of $\delta^{18}O$ versus δD and is determined by approximately 400 samples of meteoric waters as rain, snow and hail and waters of rivers and lakes (McGuire & McDonnell, 2007).

Relative humidity induces additionally kinetic processes that prefer the lighter molecule (e.g. $^{1}HD^{16}O$). The above-mentioned parallelism is now disturbed, the deviation from equilibrium fractionation results in a *Deuterium Excess* (d-excess or d), a 10 ‰ offset. Therefore the axes does not intersect at 0, it crosses at 10 and is still always referring to the slope of 8 (Dansgaard, 1964).

$$d = \delta D - 8 * \delta^{18}O \text{ [‰]} \quad (3)$$

If the axes intercept was at 0 ($\delta^{18}O = \delta D = 0$), the *GMWL* would describe a composition of a sample of the *VSMOW* (Kendall & Caldwell, 1998).

Thus different conditions affect the isotopic compositions of waters. For instance, samples depleted in heavy isotopic species tend to be associated to colder regions or periods, samples enriched in heavy isotopic species are associated to warm regions or periods (*Figure 3*). So the isotopic composition of local water samples is a complex reflection of their source, of variations in climate, of rainfall seasonality and of the local geography. The main controllers of the isotopic signature of precipitation according to the summary of McGuire & McDonnell (2007) are the

- source water vapour
- and ambient temperature.

In combination with geographic and temporal variations, they result in various effects, namely *Continental, Elevation, Amount* and *Latitude effects*.

The *VSMOW, GMWL* and d-excess are illustrated in *Figure 3*. The figure also shows that different regions or seasons will be placed in different areas of the *GMWL* space according to their $\delta^{18}O$ - δD relationship.

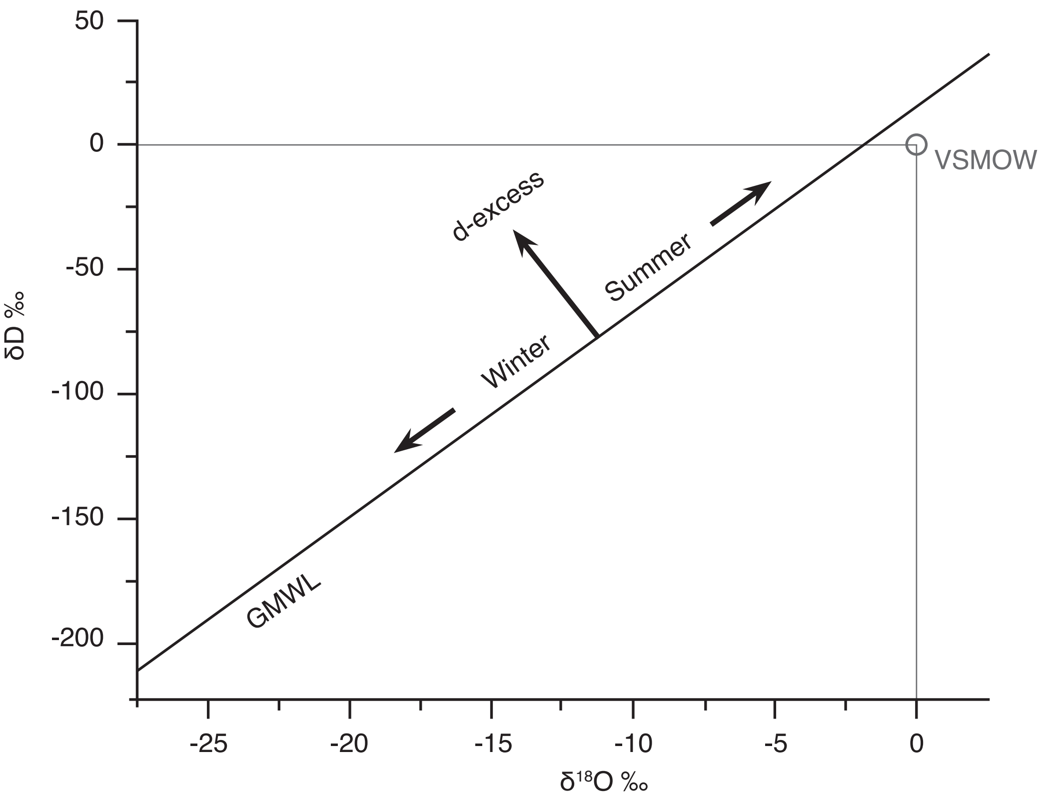

Figure 3 *Global Meteoric Water Line* (*GMWL*), d-excess and *Vienna Standard Mean Ocean Water* (*VSMOW*) (own sketch modified after McGuire & McDonnell, 2007 and Sahra, 2005).

For this study I'll bear in mind all these effects that may have influenced the isotopic composition of the collected water samples. Some variations of their isotopic signals might not only be explained by mixing and local evaporation effects, but also by the water liquid and vapour origins. To capture these signals, additionally rainwater was collected.

2.3.2 Antecedent Conditions

2.3.2.1 Concept of Antecedent and Current Precipitation Index

For a later placing of the isotopic samples in a wider context than just snapshots of the actual weather and discharge on the sampling day, it is important to look at weather and runoff conditions prior to the sampling days. To estimate whether the taken samples of the Reppisch, Türlersee and their inflows fall into a dry or a wet period, the *Antecedent* and *Current Precipitation Indexes* (*API* and *CPI*) were calculated for the monitoring period in summer 2013. These indexes are the theoretical precipitation memory of a measured basin. They are used to characterise a catchment for a certain time span. They introduce the processes that a catchment has undergone during the days or weeks before the event of interest. Hence, they reflect the soil moisture evolution which then influences storm runoff generation and groundwater recharge (Smakhtin & Masse, 2000). The basin's reaction to an on-going event will be different, depending on the antecedent conditions. The *API* describes for a certain point in time how wet the basin of interest is. *CPI* includes the current precipitation into this calculation, it combines the latest added precipitation with the wetness already available in the catchment.

2.3.2.2 Derivation of Baseflow Recession Coefficient K for API and CPI

The baseflow recession coefficient K characterises the catchment of interest. It describes how long it takes until a certain reservoir has drained. It quantifies the rate at which streamflow decreases when recharging is only given by groundwater (and surface inflows in the Reppisch basin) (Vogel & Kroll, 1996).

K was determined in a semilogarithmic plot, where time steps t of discharge measurements was plotted versus the Log of recession limbs $\log Q_t$ during times of no rain (Tallaksen, 1995). The determination of the slope and the following raise to the power of the time steps used, led to K of the Reppisch basin in summer 2013.

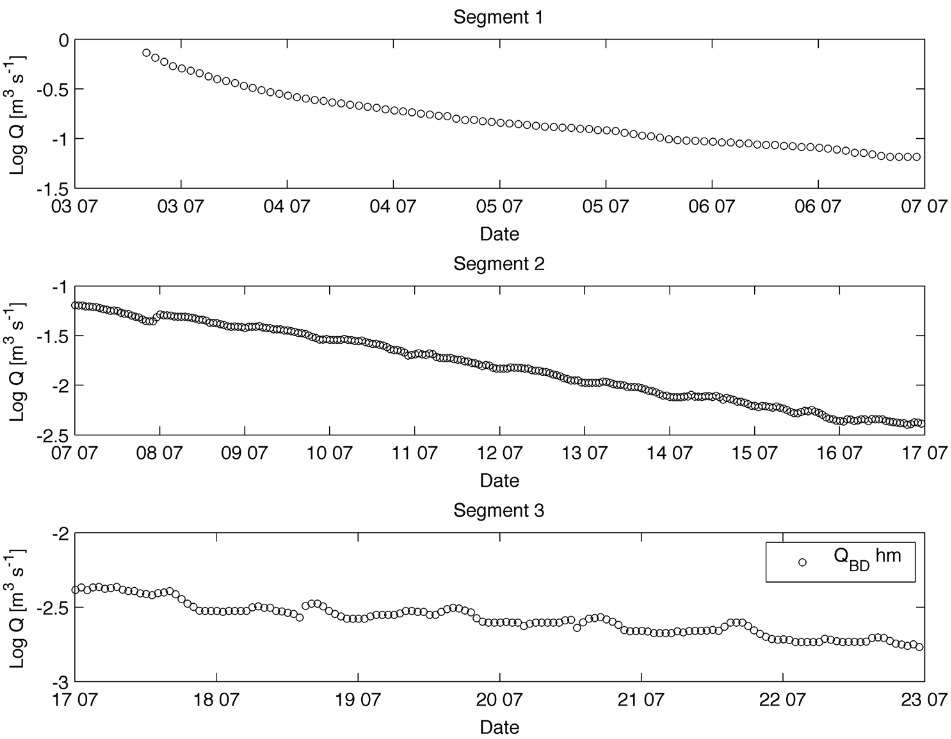

Figure 4 Log of hourly mean discharges in Birmensdorf [$m^3 s^{-1}$] (data source: AWEL) with on-going time during July 2013. The three plots represent three segments which are simply distinguishable by a bend of the recession curve during a dry spell. The mean of the three slopes was used to determine the recession constant K.

The derivation of K is shown in *Figure 4* with data of the timespan 04 – 23/07/13. During that time the hourly mean discharge rates decreased from 0.95 to 0.064 m^3/s. The slope (C) was determined by the mean of the three slopes of the segmented overall recession limb (data source: AWEL):

$$C = (0.25 + 0.13 + 0.058) / 3 = 0.146 \quad [-]$$

By raising to the power of the time step which was used for derivation of the slope (24) and the time step which was used for precipitation measurements (1) in further *API* and *CPI* modelling, K for the monitoring period 2013 becomes

K = C^t^ = 0.146^(1/24) = **0.923** $[1\ d^{-1}]$

After modelling *CPI* with different Ks, the K of 0.923 seemed to be the most realistic for the monitoring period 2013. For a comparison, differently derived Ks for the Reppisch valley are elucidated in the *APPENDIX C)*.
The upcoming paragraph introduces the *API/CPI* calculations, which mainly follow the instructions of Fedora (1987).

2.3.2.3 Calculation of API and CPI

"There are nearly as many methods as there are works on recession analysis, ..." (Tallaksen, 1995: 353). For this project it was decided to follow the methods which were used by Fedora (1987) and Smakhtin & Masse (2000). *API* describes the exponential decay of residual effects of precipitation through time. *CPI* adds the actual precipitation to *API*. After Smakhtin & Masse (2000) and Fedora (1987) (where it was still called *API*) it is expressed as:

$$CPI_t = API_{t-\Delta t} * K + P_t \qquad [mm\ d^{-1}] \qquad (4)$$

Where CPI_t is the index in $[mm\ d^{-1}]$ at time t ($API_{t-\Delta t}$ = index in [mm] (own calculations)), Δ = time interval at precipitation observations (days), K = Recession Coefficient $[1\ d^{-1}]$ and P = catchment precipitation in $[mm\ d^{-1}]$ for day t. *API* and *CPI* at time t have a memory of all precipitation that has fallen prior to time t. Previously fallen precipitation and time t always decay. *CPI* fully adds newly fallen precipitation during time interval Δt to the actual situation (Smakhtin & Masse, 2000; Fedora, 1987). "API at any time has a complete "memory" of precipitation that has fallen during the most recent time interval, a partial "memory" of rain that fell a short time ago, and only a vague "memory" of rain that fell a long time ago." (Fedora, 1987: 70).
API and *CPI* "memories" time durations are arbitrarily chosen by the researcher. In this thesis, *CPI* conditions are chosen to include a moving window of 7 days and then called *CPI7*. *CPI7* at time t includes the actual day and the last 7 days (*API* would then ignore the actual day).

2.4 Applied Ideas – Data Processing

This chapter is a short guideline through the underlying assumptions and expectations of the behaviours in the Reppisch basin. It also provides an overview of data processing steps which are later presented in the part *RESULTS*.

Overview

Firstly, the signals of the Türlersee, the inflows, precipitation and the Reppisch are compared to each other along the *GMWL* and among the three monitoring periods. According to the distribution of the water samples in the *GMWL* space, first assumptions on isotopic modifications within the Reppisch basin can be made.

If a surface water body like the Türlersee has undergone strong evaporation, its d-excess values will change dramatically below 10 ‰ of the *GMWL* (Dansgaard, 1964). Therefore the Türlersee's d-excess signal shows a detectable difference to the one of other water's signals, and thus will be traceable through time and space until the signal was modified again by mixing or phase changes. Because of this clearly traceable and strong d-excess signal of the Türlersee, the following comparisons will mainly take d-excess signals into account.

Meteorology

In chapter 3.1 the meteorological and hydrological background of the monitoring period 2013 are elucidated. The meteorological conditions are known to strongly influence a water components isotopic signal (Ingraham, 2006). Therefore collecting precipitation (chapter 3.3.1) already reveals an idea of how much "new" water of what kind of fingerprint has entered the basin and could be mixed with water which has already been in the basin. Phase changes which induce a modification of the isotopic composition, depend on certain air temperature (chapter 3.3.1) and relative humidity (chapter 3.3.2) developments and media interactions (Kendall & Caldwell, 1998).

Runoff

Considering the discharge situation in the Reppisch delivers a first impression of the hydrological setting during the monitoring period 2013 (chapter 3.1).

The d-excess distribution of the inflows, Türlersee, precipitation and Reppisch water samples of 2013 are shown in *Figure 7* as box plots. They illustrate that the isotopic signals of the examined water components significantly differ from each other. They can be further distinguished quite clearly and hence their signals can be followed by examining different other possible influences on isotopic signals (chapter 3.2).

How d-excess signals evolve over time (*Figure 9*), incorporates as well runoff situations, space and meteorology. Chapter 3.2.2 sums up the behaviours of d-excess signals over time with different discharge amounts in the Reppisch and in the inflows.

As noticed on field days in the Reppisch basin, during rain events the discharges increase. Hence I assumed that with increasing discharge amounts, relatively less water which has undergone evaporation (lower d-excess values) contributes to the total runoff. Therefore, higher discharge amounts are assumed to elevate d-excess values in the sampled streams in the Reppisch basin. Possible correlations between discharge amounts and d-excess values of the different observed surface water components are illustrated in chapter 3.2.3.

Space
Space as a trigger of possible d-excess changes is illustrated as distances of sample points in the Reppisch from the Türlersee, as stream lengths and subcatchment areas. Downstream distances (chapter 3.2.4) from the Türlersee are at the same time connected to increasing influences of other components to a Türlersee signal in the Reppisch. These influences, like phase change effects and admixture with different waters, are increasing with increasing distance and thus with increasing time lapses.
Possible correlations between stream lengths (chapter 3.2.5), subcatchment areas (chapter 3.2.6) and d-excess signals lead into the same topic as with distances though not for all components in connection with the Türlersee signal. Stream lengths and subcatchment areas correlating with decreasing d-excess values are especially assumed for the inflows. With an increasing flowpath as far as their inflow into the Reppisch or Türlersee, the inflows might undergo more evaporation.
For the Reppisch sample points increasing d-excess signals with increasing stream lengths and subcatchment areas seem more likely because in the Reppisch, Türlersee portions should decrease with increasing distance from the lake. Therefore, area-dependant mixing ratios of Türlersee and inflow waters in the Reppisch are calculated in chapter 3.2.8. Additionally in chapter 3.2.9 Türlersee and inflow fractions in the Reppisch are quantified from observed discharges at the lake's outflow and at the catchment's outlet in Birmensdorf.

Specific Discharge
Specific discharges per subcatchment add a third dimension to the above discussed geographic quantities. Calculated for different subcatchments but for the same point in time (chapter 3.2.7), specific discharges characterise the actual behaviour of a subcatchment. If they differ from each other, interpretations on diverse surface and subsurface stores, flowpath and rainfall-runoff reactions can be made.

Antecedent Conditions
As a third dimension specific discharges include the characteristics of a subcatchment which govern processes as storing and draining water. Time as a fourth dimension also takes delayed or quick reactions of a subcatchment into account. Therefore, in chapter 3.4 the monitoring days of summer 2013 are attributed to *CPI7* classes. Including the antecedent conditions into the analysis of the isotopic signals reveals more information about correlations of d-excess signals versus the various above discussed situations.

Events
Events as well give an insight into the characteristic of a catchment (chapter 3.5). The discharge rates and d-excess signal's changes with a sudden input or with a long-lasting phase of precipitation elucidate information on the water mixture in a stream. Comparing the d-excess values and rainfall rate of the actual precipitation with the emergence of the d-excess values of the streams during the same event, could confirm or reject the before made estimations and interpretations on stream behaviours and discharge proportions.

Uncertainties
Finally, sampling activities always reveal some uncertainties and sensitivities. Therefore, in chapter 3.6, the d-excess values of the precipitation samples collected as weekly integrated signals are compared to the ones collected during events and to the accumulated precipitation amounts.
Additionally, other appeared uncertainties are elucidated in the *APPENDIX C)*.

2.5 Data Acquisition and Depiction

Table 2 provides an overview on the overall data collection of the three monitoring periods 2010, 2011 and 2013. The isotopic compositions of 1233 water samples in total were determined.

Table 2 Overall data collection of the summers 2010, 2011 and 2013.

	Monitoring Points in Reppisch, Türlersee, inflows	Water Grab Samples	Discharge Measurements
Historical Data			
July - August *2010*	± 23	188	
June - September *2011*	± 23	348	27
Actual Data			
June - September *2013*	± 24	362	184
Total		*898*	*211*

Extensions 2013	Streamwater		Rainwater	
	9 WLPWS	5 ISCO Samplers	2 Rain Collectors	2 Sequential Samplers
Additional Water Samples	56	211	23	45
Overall analysed Water Samples	*898 + 335 = **1233***			

Table 3 gives an overview of colours and symbols used in the following figures. Some colours or marks are used to depict several different data, depending on the topic.

Table 3 Symbols and colours used in all figures.

Subject	Marks	According Description	Colours
Türlersee	▼	Triangle	Red
Inflows	*	Star	Blue
Reppisch	o	Circle	Green
Precipitation	+	Plus	Magenta
Swamps	□	Square	Cyan
WLPWS	◊	Diamond	
GMWL	-	Line	Grey
d of GMWL	-	Line	Grey
June	o		Green
July	*		Blue
August	▼		Magenta
September	□		Cyan
Dry			Red
Humid			Green
Wet			Blue
2010			Red
2011			Green
2013			Blue
Baseflow	o	Circle	
Stormflow	•	Dot	

3 RESULTS

In the following chapters the isotopic and discharge data of the summers 2010, 2011 and 2013 are analysed with different plots. The main analysis is pronounced on the data of summer 2013. The summers 2010 and 2011 will sometimes be included for the purpose of comparison. Discharge data of the *AWEL* from the gauging stations in Birmensdorf (RE23), at the outflow of the Türlersee (RE6) and meteorological data of *Meteocentrale* of the recording station in Stallikon were as well incorporated into the analysis.

3.1 Overview on Monitoring Period 2013

3.1.1 Hydrology and Meteorology of June to September 2013

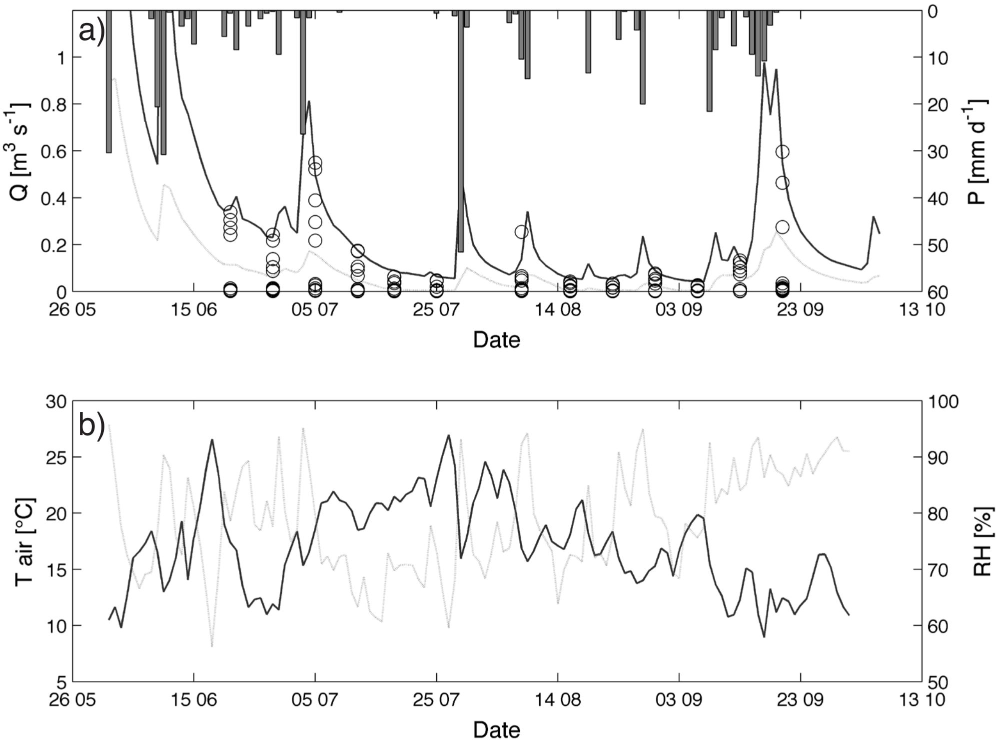

Figure 5 *a)* Daily mean Q_{BD} is depicted with a dark line, daily mean Q_{TS} with the grey line (data source: AWEL) and Q_{all} are the circles indicating discharge point measurements of the Reppisch and the inflows [$m^3 s^{-1}$] (own data). One vertical row of marks represents one sampling day. Bars display daily mean precipitation [mm d^{-1}] (data source: Meteocentrale). *b)* Mean daily temperatures [°C] are depicted by the dark curve and mean daily relative humidity [%] by the light curve (data source: Meteocentrale).

Table 4 Meteorological (data source: METEOCENTRALE) and hydrological (data source: AWEL) conditions during monitoring period 2013.

2013	P_{acc} [mm m^{-1}]	Mean Monthly T [°C]	Mean Q_{BD} dm [m^{3} s^{-1}]	Mean Q_{TS} dm [m^{3} s^{-1}]
June	126.4	15.7	0.945	0.285
July	87	20.6	0.219	0.053
August	72.4	18.1	0.103	0.025
September	78.4	14	0.248	0.079
Total	*364.2*	*17.1*	*0.379*	*0.111*

The sampling period of summer 2013 started in June when the Reppisch's discharge in Birmensdorf was decreasing from a peak of 9.5 m^3/s (outside graph in *Figure 5 a)*; data source: AWEL). These unusual high discharges even induced some floods in the area. Hence, the first sampling day on 07/06/13 took place while very high discharge rates occurred as well. The decreasing runoff during the whole summer was only interrupted significantly once in mid-July and at the beginning of August. Thereafter hardly any rain fell until 17/09/13 when discharges peaked again at 1.7 m^3/s. However, the entire summer was marked by a recession of the Reppisch's discharges reaching the absolute minimum of the whole year 2013 at a discharge of 0.038 m^3/s on 7 - 8/09/13 (*Figure 5 a)*; data source: AWEL). By that time, even two of the nine measured inflows fell dry.
Besides high discharge rates, June was also a period of slowly rising mean daily air temperatures reaching a first peak of more than 25 °C at the beginning of July, just about to drop back to daily means around 12 °C (*Figure 5 b)*). By the end of July, mean daily air temperatures reached heights of more than 20 °C again, whereas the relative humidity was decreasing to a level of about 60 %. Mean daily air temperatures and relative humidity showed movements into the opposite direction throughout the whole summer.

3.2 Signal Description

3.2.1 Isotopic Composition of Reppisch, Inflows, Türlersee and Precipitation

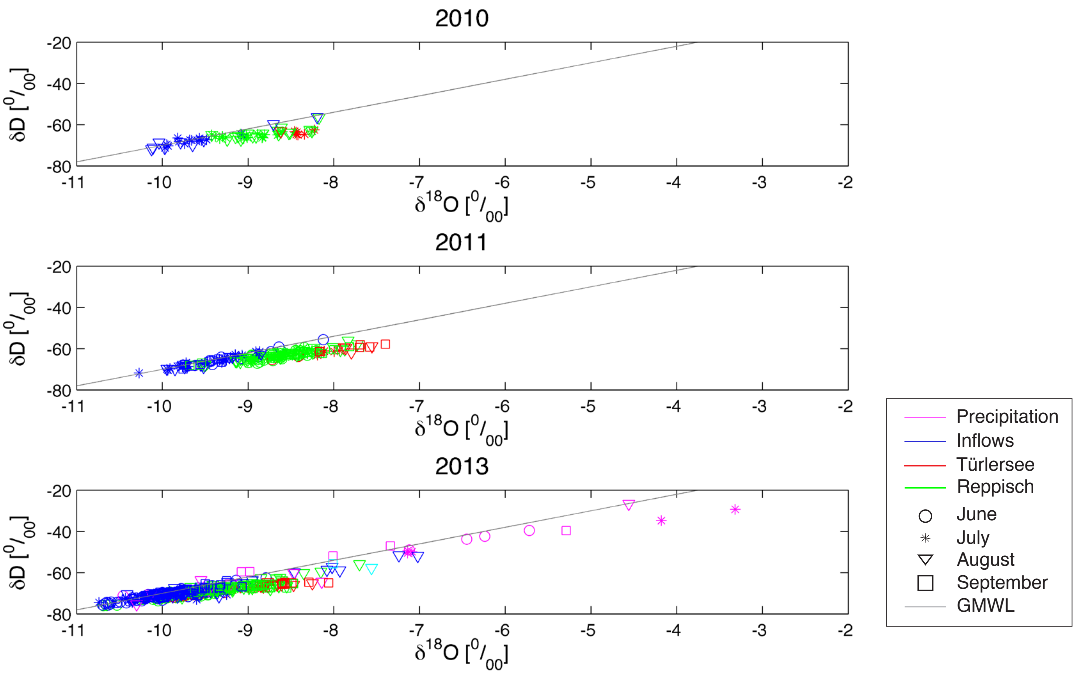

Figure 6 Isotopic compositions [‰] of all water samples of the summers 2010, 2011 and 2013 in the *GMWL* space. In 2013 the rain samples (RE_{RG}) and *WLPWS* (RE_{WLPWS}) are included.

Figure 6 presents the *GMWL* and the distributions of the isotopic compositions in $\delta^{18}O$ and δD of all samples taken in the summers of 2010, 2011 and 2013. Throughout all the three years of sampling the Reppisch basin, the three main observed components are distinguishable in their isotopic signals. Depicted in blue are the isotopic data of the inflows. They are distributed within the closest proximity of the *GMWL*. The red marks, which show the compositions of the lake's samples, are the furthest away from the *GMWL*. Between the blue and the red marks are the green signs of the Reppisch. They represent the mixing waters of the inflows and the Türlersee. In the *GMWL* space of 2013, collected rain waters (magenta) are also mostly found around the *GMWL*. However, it is noteworthy that their isotopic composition was often quite different to the one of the observed surface waters.

3.2.2 D-excess Distribution

The box plots in *Figure 7* provide a first overview of all the generated d-excess values during monitoring period 2013. They depict that the d-excess values of the four observed components obviously differ and that the Reppisch's median d-excess value of 6.75 ‰ lays in between the median of the inflows (9.04 ‰), Türlersee (4.68 ‰) and precipitation (7.76 ‰).

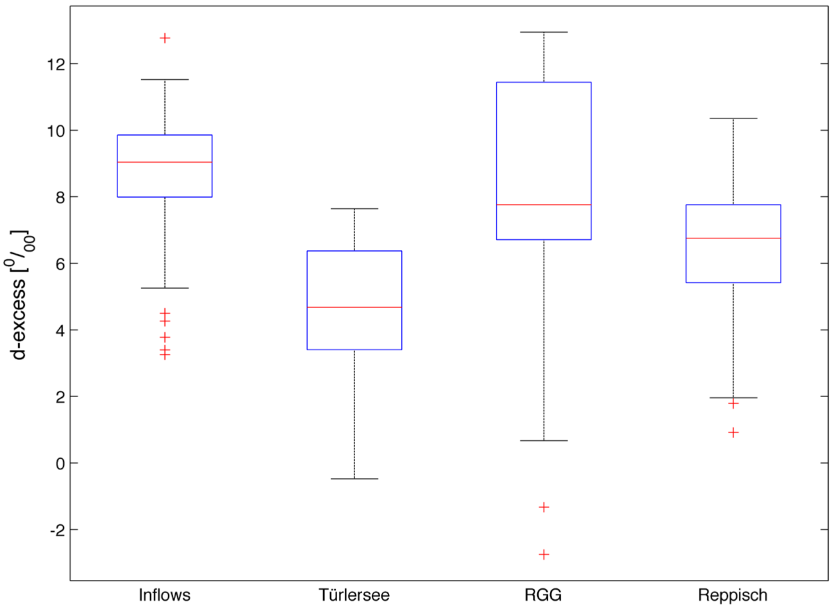

Figure 7 Variations in d-excess [‰] of all water samples, except for event and series samples, per observed component of the Reppisch basin in summer 2013. Box plot from inflows consists of 187 values, from Türlersee of 45 values, from RE_{RG} of 23 values and the Reppisch box plot consists of 184 values. The red line in the box depicts the median d-excess value. The upper border of the box is the 75th percentile, the lower one is the 25th percentile. Black endings show the upper and lower adjacent and red crosses depict outliers.

In *Figure 8* the inflow's d-excess variations are illustrated separately since they differ among each other. Their signals oscillate around a d-excess value of 9 ‰. Median d-excess values decrease downwards the valley. RE9.1, -9.2 and -11 show a stabilisation of the downwards trend, henceforward the previous decrease can be observed again.

RE2, discharging into the lake, shows the greatest variations of d-excess values, whereas RE2.1 which is located in the same inflow more upstream, shows one of the smallest variations.

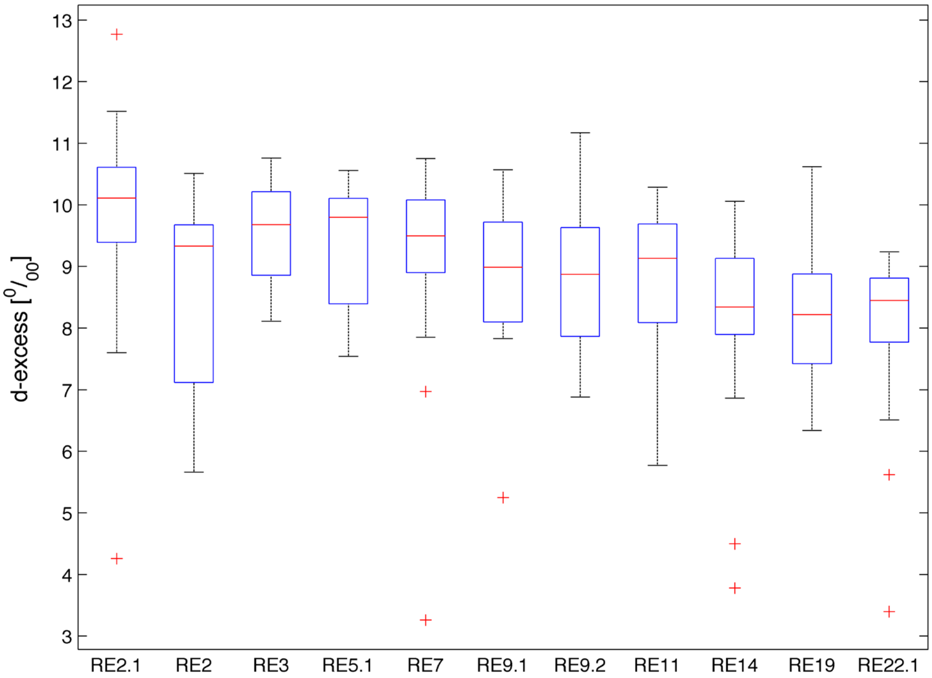

Figure 8 Variations in d-excess [‰] of all water samples, except for event data, of all inflows in summer 2013. Box plot of RE2.1 consists of 18 values, RE2 of 15, RE3 of 15, RE5.1 of 12, RE7 of 22, RE9.1 of 14, RE9.2 of 15, RE11 of 15, RE14 of 21, RE19 of 21 and RE22.1 consists of 15 values. The red line in the box depicts the median d-excess value. The upper border of the box is the 75th percentile, the lower one is the 25th percentile. Black endings show the upper and lower adjacent and red crosses depict outliers.

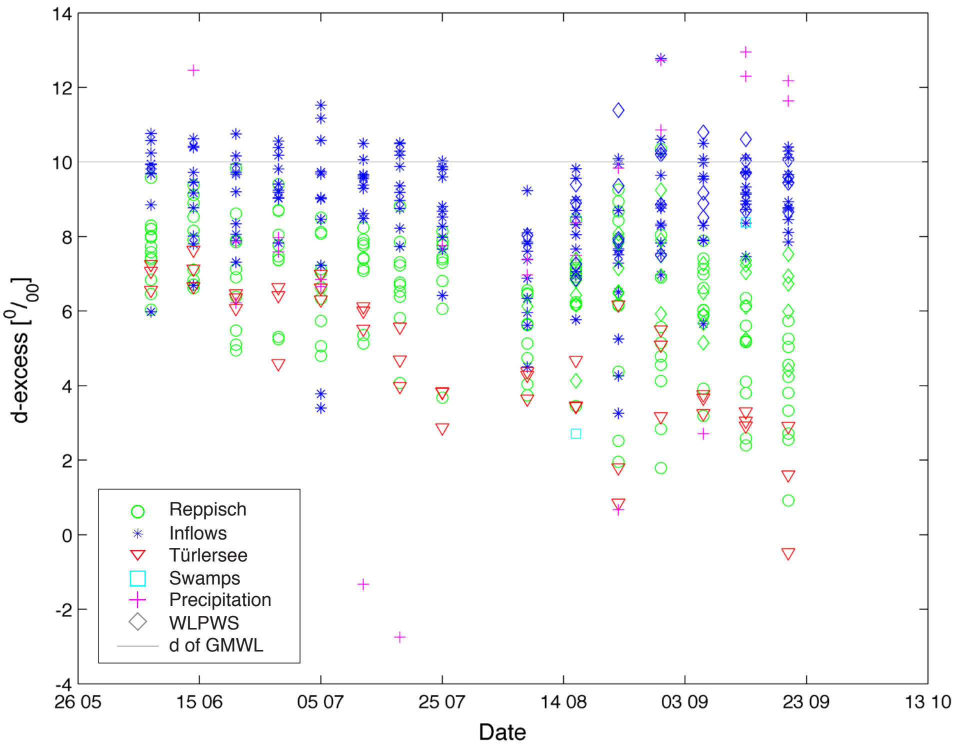

Figure 9 Time versus d-excess [‰] of all weekly water samples in summer 2013. A vertical sequence of marks indicates all samples collected during one monitoring day. Blue diamonds depict inflow samples collected with *WLPWS* and green diamonds Reppisch *WLPWS* samples.

Another overview of all weekly samples such as grab samples, RE_{RG} samples and RE_{WLPWS} samples of the monitoring period 2013 is represented in *Figure 9*. The marks depict the evolution and distribution over time. They illustrate a wave-like distribution for this time frame of the year. All the marks together show an increased spread from 16/08/13 onwards compared to 07/06/13 when the first samples were taken.

The highest d-excess values are mainly marked by the inflow- and rainwater. The lowest are mostly marked by the Türlersee, swamps and Reppisch and in three occasions by inflow- and rainwater. Typically in between, mostly there are found marks of the Reppisch samples like in *Figures 6* and *9*. In June, July and the beginning of August d-excess values of precipitation lay firstly in the range of the Türlersee and Reppisch signals. Afterwards they slightly increased into the ranges of the inflows to finally overtop all the surface water components in September.

3.2.2 D-excess and Discharge

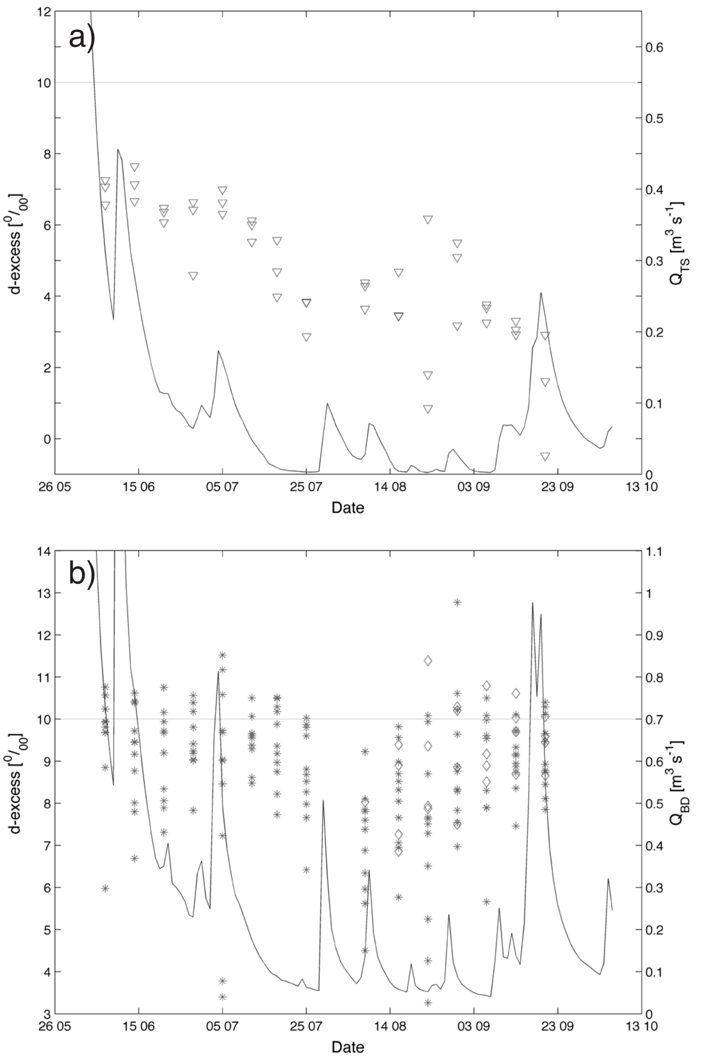

Figure 10 (Continued)

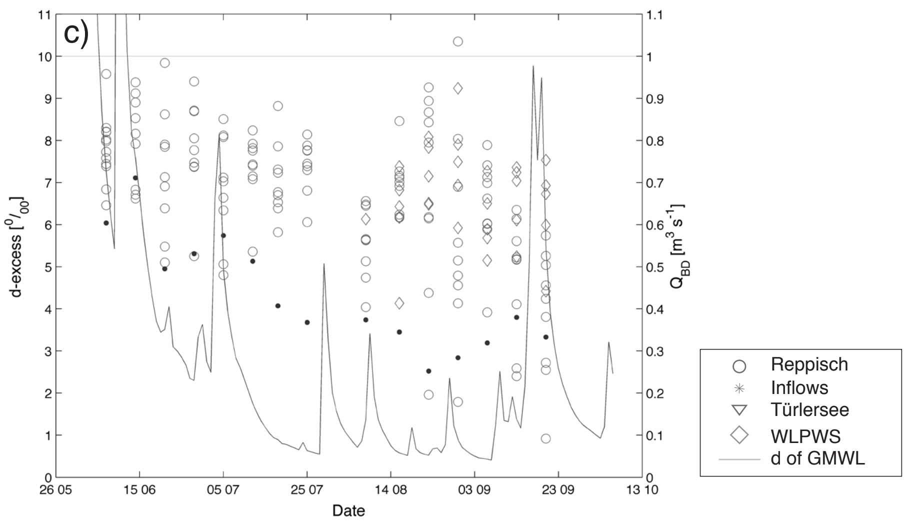

Figure 10 Time versus d-excess [‰] of all grab and *WLPWS* samples and Q_{TS} or Q_{BD} [m^3 s^{-1}] (data source: AWEL) in 2013. *a)* D-excess values of the Türlersee surface water, *b)* of the inflows, *c)* of the Reppisch, black dots mark d-excess values of RE5 at the outflow of the lake.

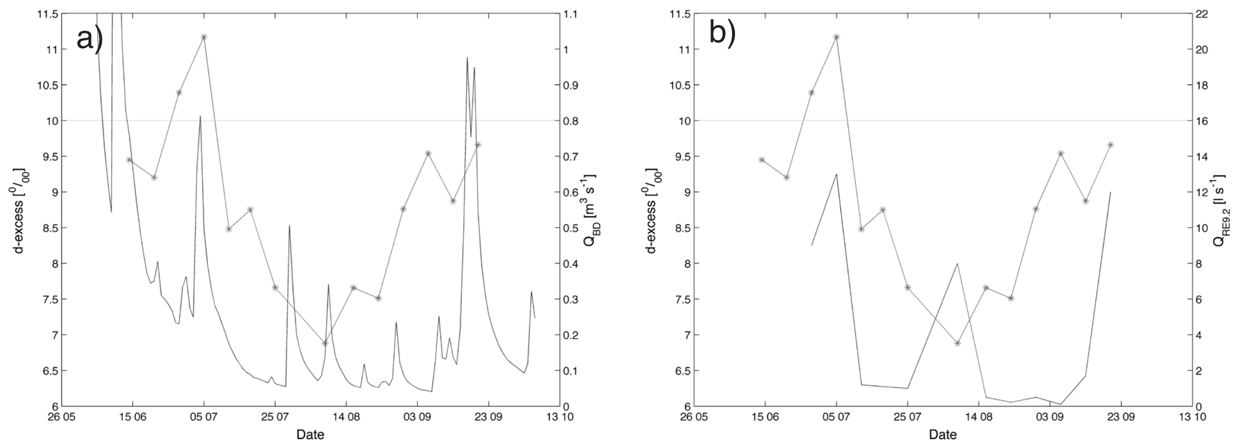

Figure 11 *a)* Time versus d-excess [‰] at RE9.2 (inflow to Reppisch) and Q_{BD} [m^3 s^{-1}] (data source: AWEL). *b)* Time versus d-excess [‰] at RE9.2 and $Q_{RE9.2}$ [l s^{-1}] (own weekly measurements).

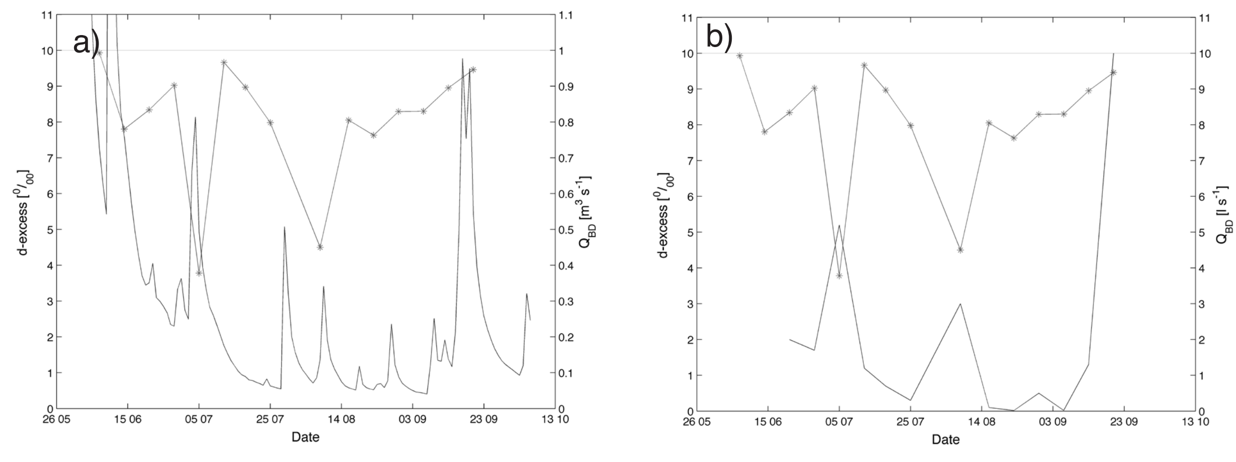

Figure 12 *a)* Time versus d-excess [‰] at RE14 (inflow to Reppisch) and Q_{BD} [m^3 s^{-1}] (data source: AWEL). *b)* Time versus d-excess [‰] at RE14 and Q_{RE14} [m^3 s^{-1}] (own weekly measurements).

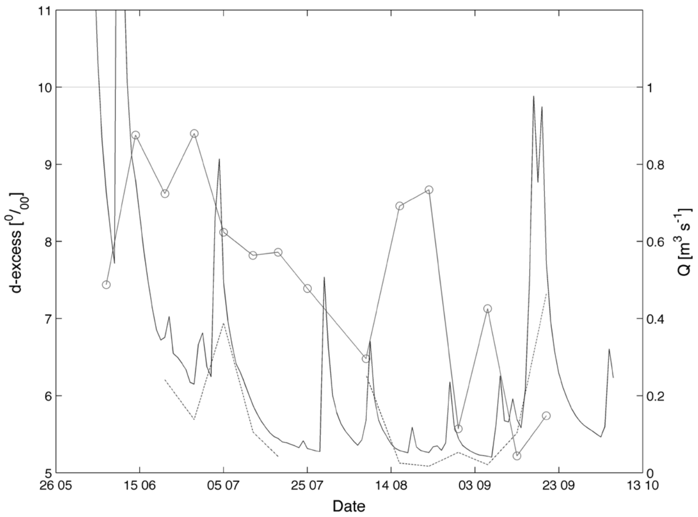

Figure 13 Time versus d-excess [‰] at RE15 (Reppisch) and Q_{BD} respectively Q_{RE15} [m^3 s^{-1}] (data source: AWEL and own measurements).

Figure 10 shows the evolution of d-excess over time for each examined surface water component during monitoring period 2013. Additionally discharges of the outflow at the Türlersee or the Reppisch are illustrated. In all the three plots, d-excess values show parallel or opposite increases and decreases with discharge rates.
To better split up d-excess values behaviours with runoff amounts, the *Figures 11* to *13* show picked out illustrations of RE9.2 and RE14 (inflows to the Reppisch) and of RE15 (Reppisch). A special situation occurred at the end of June and at the beginning of July: During a phase of high discharge, RE5 and RE15 display a rise of the d-excess whereas RE14 shows a low d-excess. At RE9.2, another inflow, d-excess values though rose as well.
The situation is different at the beginning of August when d-excess values not only from the inflows but also from RE15 decreased while the discharge rose. This decrease of the d-excess on 12/08/13 is shown at many inflow locations. However, RE5 keeps on showing parallel behaviour of discharge and d-excess.

3.2.3 Discharge Rates versus d-excess

Following the sometimes parallel course of discharge and d-excess values (*Figures 10* to *13*), one would assume a correlation between those two sets of values. To see if such correlations exist in each of the examined surface water components, *Figure 14* illustrates each Reppisch sample point separately comparing discharge amounts with d-excess values.

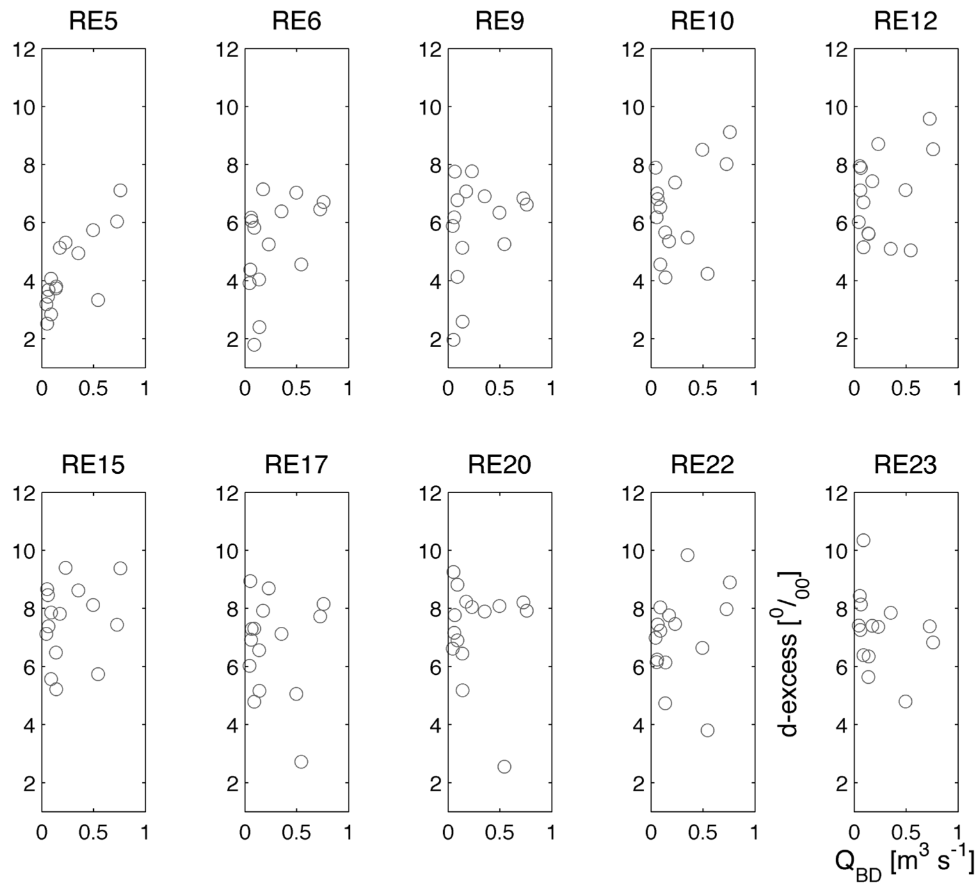

Figure 14 Discharge amounts [m^3 s^{-1}] (Q_{BD}, data source: AWEL) versus d-excess [‰] for each sample point of the Reppisch.

In *Figure 14* the entire d-excess values scatters from RE5 to RE15 move to higher magnitudes downstream the Reppisch. From RE15 to RE23 this elevating stagnates. More on these patterns will be shown in the next paragraph 3.2.4.
Figure 14 additionally shows a weak tendency of slightly increasing d-excess values with increasing discharge at the sample points RE5 (correlation with Q_{BD} 0.77 or 0.81 with ΔQ_{BD}), RE6 (0.45), RE9 (0.21) and also at RE10 (0.39). For these sample points, especially in the zones of higher discharge there are no d-excess values below 4 ‰ anymore. For the data locations from RE10 to RE23 such a correlation cannot be made.

Not all of the inflows show clear correlations between their d-excess values and rising discharges in the Reppisch either. The only exception is found at RE2 during the monitoring period of summer 2011 (*Figure 15*). This sample point is located at an inflow to the Türlersee which is very close to the lake. The correlation between its d-excess values and the added discharge amounts between the Türlersee and Birmensdorf ($\Delta Q_{BD} = Q_{BD} - Q_{TS}$) is 0.67.

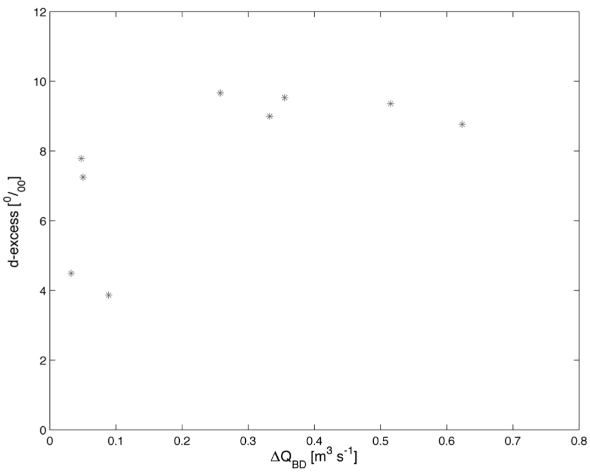

Figure 15 Discharge amount [m^3 s^{-1}] (data source: AWEL) versus d-excess [‰] for RE2 at the inflow to the Türlersee in 2011. ΔQ_{BD} is calculated as Q_{BD} - Q_{TS}, thus it represents all tributaries to the Reppisch between the Türlersee and Birmensdorf.

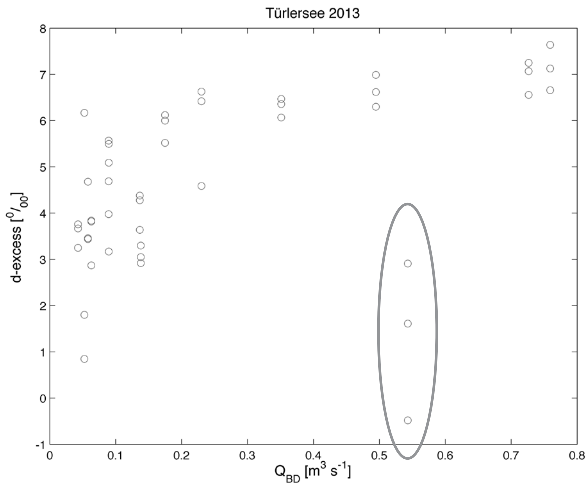

Figure 16 Discharge amount [m^3 s^{-1}] (Q_{BD}, data source: AWEL) versus d-excess [‰] of the Türlersee (all the three sample points are illustrated).

Visually the most evident correlation can be found between the discharge data and the d-excess of the Türlersee in 2013. The correlation was 0.54 including the outliers at 0.543 m^3/s of 20/09/13 (grey ellipse). Without this sampling day the correlation would be 0.78. Nevertheless, this dataset needs to be included because all the three sample points in the Türlersee showed such low d-excess values. They can hardly be ascribed to a measurement error.

3.2.4 Distance versus d-excess

As denoted by *Figure 14* from sample point RE5 to RE15 the d-excess values increase with increasing distance from the lake downstream the Reppisch. This observation was made indeed for the sample points in the Reppisch. On a distance of 14 km mean d-excess values are increasing from 4.33 ‰ at RE5 to 7.55 ‰ at RE15 from there on they oscillate around 6 to 7 ‰ (data of 2013, means are not shown in figures). *Figures 17* to *19* represent this lifting of the d-excess scatters for each of the three monitoring years separately.

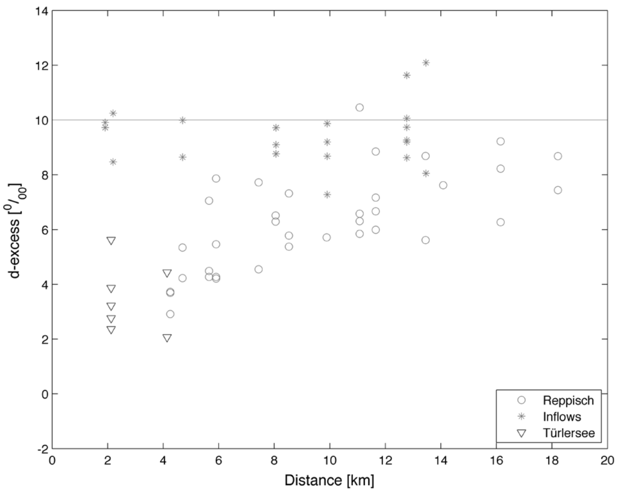

Figure 17 Distance [km] from the uppermost (not highest) part of the Reppisch valley (close to RE2.1) versus d-excess [‰] for all samples from the monitoring period **2010**. The vertical distribution shows all the samples taken at the same sample point (e.g. RE1.1 at 0.1 km). The grey line at d-excess of 10 ‰ depicts d-excess of *GMWL*.

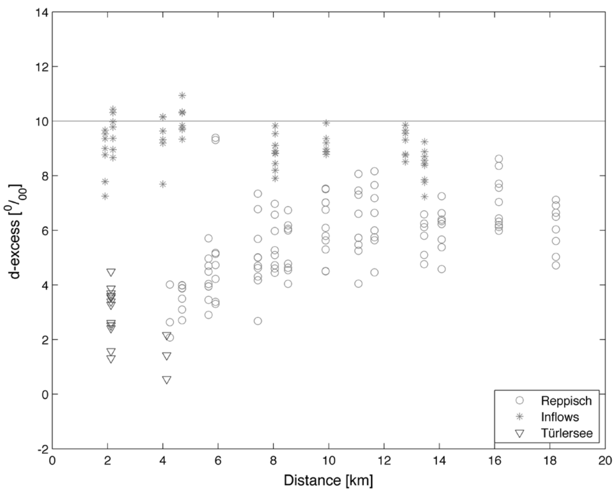

Figure 18 Distance [km] from the uppermost (not highest) part of the Reppisch valley (close to RE2.1) versus d-excess [‰] for all samples from the monitoring period **2011**. The vertical distribution shows all the samples taken at the same sample point (e.g. RE1.1 at 0.1 km). The grey line at d-excess of 10 ‰ depicts d-excess of *GMWL*.

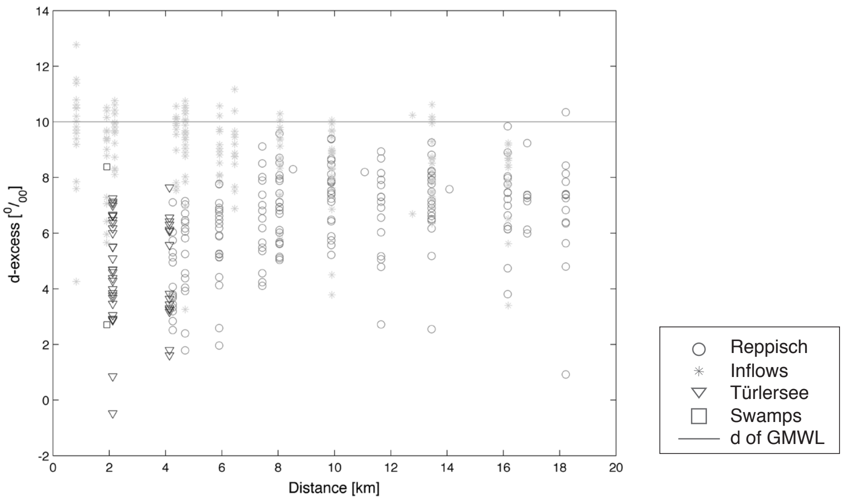

Figure 19 Distance [km] from the uppermost (not highest) part of the Reppisch valley (close to RE2.1) versus d-excess [‰] for all surface water samples (inclusive data from *WLPWS*, except data from event samples) from the monitoring period **2013**. The vertical distribution shows all the samples taken at the same sample point (e.g. RE2.1 at 0.1 km).

During all the three monitoring years the different surface water components of the Reppisch basin show similar d-excess values. The Türlersee mostly provided the lowest d-excess values and the inflows the highest. The Reppisch lay between the two others and came closer to the inflow values with increasing distance from the lake.

3.2.5 Stream Lengths versus d-excess

Figure 20 depicts the stream lengths versus d-excess from all samples of the Reppisch and the inflows. Again the signals of the Reppisch and the ones of the inflows are clearly distinguishable. By eliminating the outliers of the inflows their range would be much smaller than the ranges of the Reppisch samples.

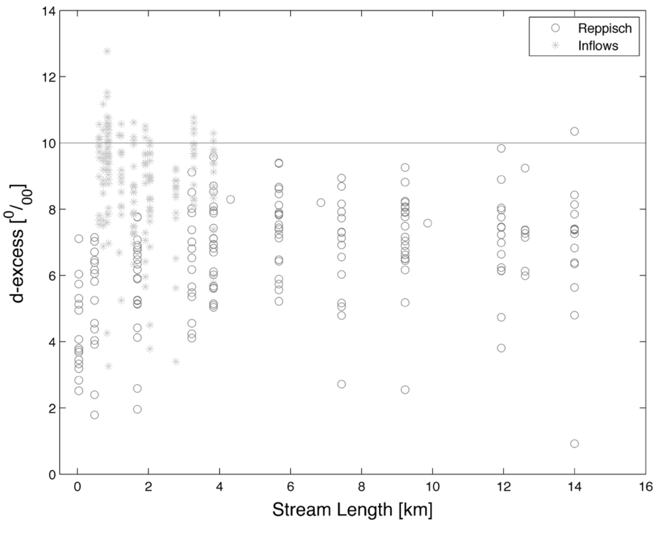

Figure 20 Stream lengths [km] of the Reppisch and the inflows versus their d-excess [‰] from the monitoring period 2013. The vertical distribution shows all the samples taken at the same sample point (e.g. RE23 with a length of 14 km). The grey line at depicts d-excess of 10 ‰ of *GMWL*.

3.2.6 Area versus d-excess

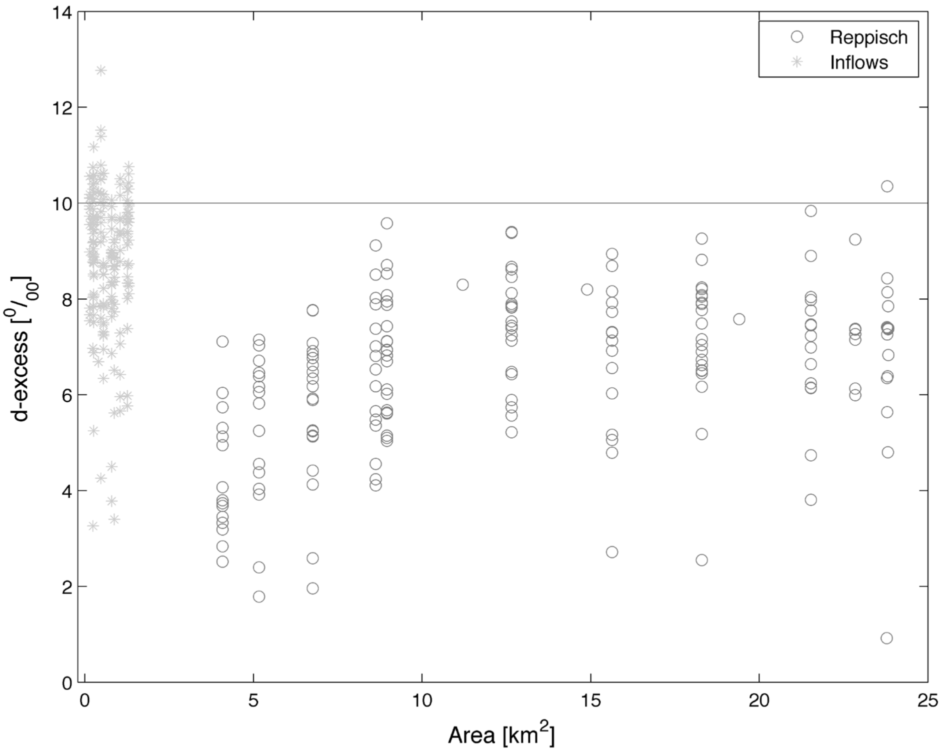

Figure 21 Subcatchment areas [km²] of the Reppisch and the inflows versus their d-excess [‰] from the monitoring period 2013. The vertical distribution shows all the samples taken at the same sample point (e.g. RE23 with an area of 23.78 km²). The grey line at depicts d-excess of 10 ‰ of *GMWL*.

The clear signal of an enlarging subcatchment area resulting in a higher d-excess of the Reppisch is the same signal as shown in *Figures 17* to *19.* The means of Reppisch d-excess values are the lowest at the closest sample points to the lake, this is also where Reppisch subcatchment areas are the smallest. These increasing means of Reppisch d-excess values stabilise between RE12 at 9 km² and RE15 at 13 km².

3.2.7 Observed Discharge Rates

Figures 22 and *23* provide an overview of discharge rates in the Reppisch and the inflows during monitoring period 2013. The start and ending points of the discharge curves in *Figure 22* are data of the *AWEL* gauging stations, the values in between are own discharge measurements at the Reppisch sample points. Due to these two different data aquisitions some curves might not be of total consistence.
Nevertheless, the various curves representing different monitoring days show an increase in runoff with increasing distance downwards the valley. Between 12 and 14 km many monitoring days show an intensified increase of runoff rates.

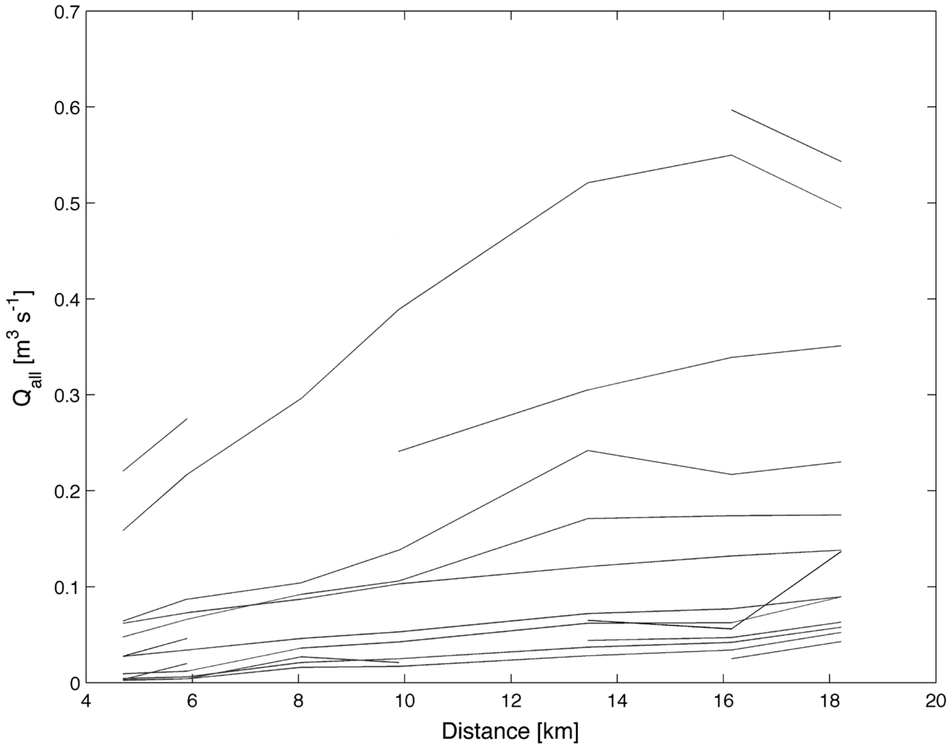

Figure 22 Distance [km] from the uppermost part in the Reppisch basin onwards versus discharge [$m^3 s^{-1}$] of the Reppisch measured at different sample points (own data). Discharge data of the outflow of the lake (Q_{TS}) and in Birmensdorf (Q_{BD}) are the first and the last data row respectively (data source: AWEL). One curve depicts one monitoring day (e.g. uppermost continuous curve is of 05/07/13), bends are discharge data per monitoring point (e.g. RE22 at 16 km with 0.55 m^3/s (own data)).

In *Figure 23* each dot represents discharge rates of the inflows. The connections between the dots are just for illustrating which measurements belong to the same monitoring day. Hence a curve represents one monitoring day.
At eight kilometres distance from the uppermost part in the valley there is RE11 located. This inflow delivered the highest measured water amounts to the Reppisch during monitoring period 2013. At a distance of 2.1 km RE3 also delivered very high rates, though this is an inflow to the Türlersee.

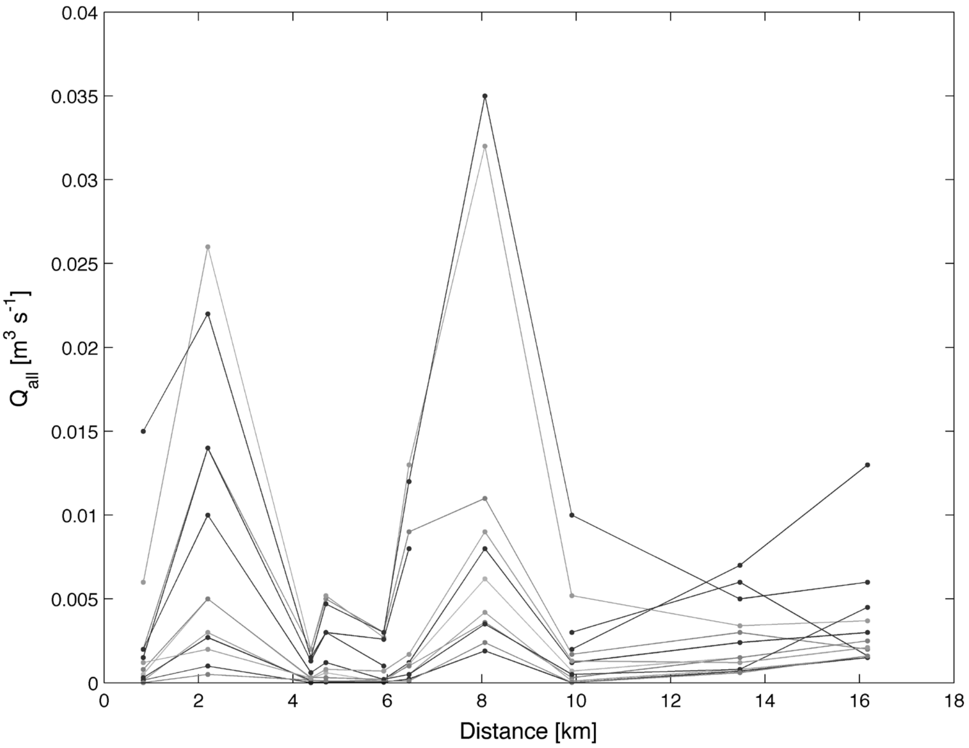

Figure 23 Distance [km] from the uppermost part in the Reppisch basin onwards versus discharge [m^3 s^{-1}] of the inflows measured at different sample points (own data). One curve is representative for one monitoring day, inflexion points are sample points with their according inflows (e.g. RE11 at 8 km).

3.2.7 Specific Discharges

Solely measured discharge rates do only provide few information on subcatchments behind a certain inflow. Hence, specific discharges in combination with d-excess values reveal more on the characteristics of a certain subcatchment. *Figure 24* elucidates the specific discharges of the monitoring points and *Figure 25* connects them to their d-excess signals.

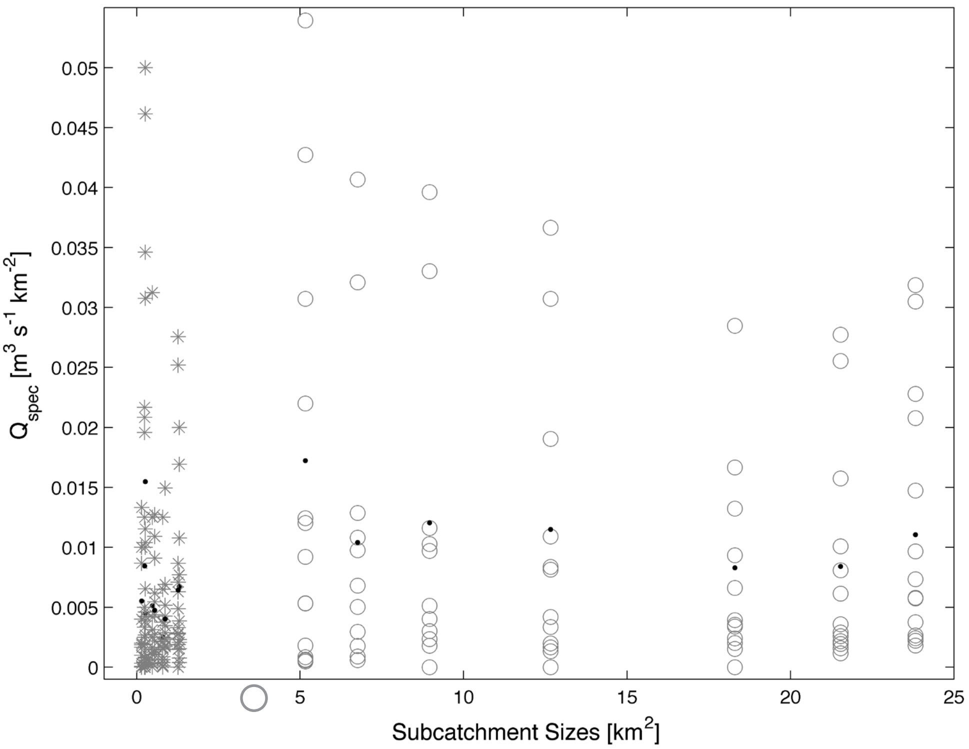

Figure 24 Subcatchment areas [km^2] of all Reppisch and inflow sample points versus their Q_{spec} [m^3 s^{-1} km^{-2}] for the monitoring period 2013. One vertical distribution of marks represents different monitoring days, hence Q_{spec} of one sample point. Stars indicate inflow samples' and circles Reppisch's Q_{spec}, black dots depict the according means. The outflow of the Türlersee is located at 4.3 km^2 (grey circle on x-axis).

Figure 24 shows subcatchment areas versus means of the specific discharges (Q_{spec}) per subcatchment of the inflows and the Reppisch where discharges were measured.
The mean Q_{spec} do not show any obvious tendency with subcatchment areas.

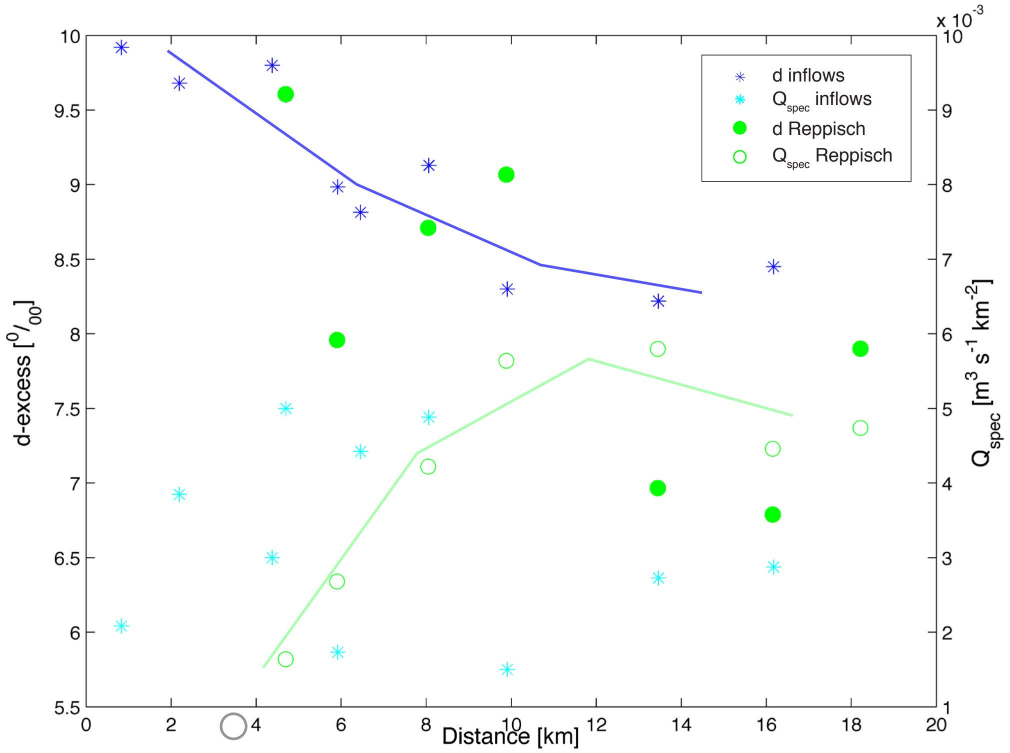

Figure 25 Distance [km] from the uppermost part in the Reppisch basin versus median d-excess [‰] and median Q_{spec} of all the sample points where discharge data were available for the entire monitoring period in summer 2013. Two marks of the same flowtype, vertically positioned at the same distance are values of the same monitoring point. The Türlersee is situated between 3 and 4 km (grey circle on x-axis).

The blue star and the green circle marks in *Figure 25* illustrate the medians of the d-excess from all the sample points where discharge measurement data were available throughout the entire monitoring period 2013.
The medians of the inflows' d-excess values (blue stars, blue line) apparently decrease downwards the Reppisch basin. The medians of the d-excess of the Reppisch samples increase from 4 to 14 km (green circles, green line). From RE20 onwards, at 13.4 km, the median d-excess values of the inflows and the Reppisch seem to stabilise between 7.5 and 8.2 ‰.
The cyan star and green dot marks are the corresponding specific discharges of each d-excess mark. There are no trends in the medians of the specific discharges.

3.2.8 Calculated Mixing Ratios Türlersee - Inflows

The discharge amounts of the inflows to the Reppisch between the Türlersee and Birmensdorf are in the same range up to a measured maximum of 35 l/s (own data). Hence, no bigger inflows of bigger subcatchments tribute to the Reppisch along the monitoring points. Therefore an estimation of the total runoff and its proportions in the Reppisch was undertaken by linking subcatchment areas to discharge amounts.
The Reppisch discharge proportions were calculated according to subcatchment sizes of each sample point in the Reppisch. Water portions at a specific sample point depend on its areal portion of the entire catchment. Hence, the percentage of Türlersee water which should be found in the total Reppisch runoff amount shrinks from 100 % at the lake outflow to 21.66 % in Birmensdorf. *Table 5* lists the subcatchment areas, their accordingly calculated water portions and determined mixing

ratios.

Table 5 Mixing ratios at specific sample points in the Reppisch. Ratios are determined by the subcatchment area ratios of the specific sample points.

Sample Point	Area [km^2]	Türlersee Water [%]	Tributary Water [%]	Mixing Ratio
RE6	5.16	100.00	0.00	
RE9	6.76	76.33	23.67	3.23
RE10	8.63	59.79	40.21	1.49
RE12	8.96	57.59	42.41	1.36
RE15	12.66	40.76	59.24	0.69
RE17	15.64	32.99	67.01	0.49
RE20	18.3	28.20	71.80	0.39
RE22	21.53	23.97	76.03	0.32
RE23	23.82	21.66	78.34	0.28

Area proportions were further used to calculate discharges at the specific sample points respectively (*Table 6*). Observed discharge at the lake outflow was used as initial runoff amount (data source: AWEL).
As already shown with specific discharges per subcatchment, a simple upscaling of discharge at the lake outflow to the catchment outlet in Birmensdorf does not work in all cases. This is because the different zones are not equally active in storing or draining water (Q_{spec}). Therefore, the last column in *Table 6* shows the deviations in percent of each monitoring day.

Table 6 Total Reppisch discharge at specific sample points (Q_{TS}, Q_{BD} or own measurements). Deviations are calculated with Q_{BD} as the observed discharge in Birmensdorf (data source: AWEL) which equals 100 %.

Date	Sample Point RE	Q_{TS} [m^3 s^{-1}]	Q_{sim} Area Proportional [m^3 s^{-1}]	Q_{BD} [m^3 s^{-1}]	Deviations Q_{sim} to Q_{BD} [%]
07/06/13	6	0.311			
	23		1.436	0.726	97.75
14/06/13	6	0.278			
	23		1.283	0.759	69.08
21/06/13	6	0.113			
	23		0.522	0.351	48.62
28/06/13	6	0.064			
	23		0.296	0.230	28.66
05/07/13	6	0.159			
	23		0.734	0.495	48.28

Table 6 (Continued)

12/07/13	6	0.048			
	23		0.219	0.175	25.51
18/07/13	6	0.009			
	23		0.042	0.089	-53.32
25/07/13	6	0.003			
	23		0.014	0.063	-78.02
08/08/13	6	0.028			
	9		0.037		
	10		0.047		
	12		0.049		
	15		0.069		
	17		0.085		
	20		0.099		
	22		0.117		
	23		0.129	0.137	-5.65
16/08/13	6	0.004			
	23		0.018	0.058	-68.16
23/08/13	6	0.002			
	23		0.009	0.053	-82.58
30/08/13	6	0.027			
	23		0.125	0.089	40.04
06/09/13	6	0.003			
	23		0.014	0.043	-67.79
13/09/13	6	0.062			
	23		0.286	0.138	107.40
20/09/13	6	0.220			
	23		1.016	0.543	87.03

For the monitoring day of 08/08/13 runoff upscaling worked best. Deviation of calculated to observed discharge in Birmensdorf (RE23) was -5.65 %. The other calculated discharges reached up to double amount of the observed one. The mean deviation was 60.53 %, calculated with positive deviations, or 13.12 % when calculating the mean with minus deviations as well.

3.2.9 Observed Türlersee Fractions in 2013

Not all of the inflows to the Reppisch were measured and sampled. In order to get an idea of the Türlersee and inflow portions in the Reppisch between the lake outflow and the catchment outlet in Birmensdorf, the upcoming paragraph highlights the fractions of discharge amounts in Birmensdorf. The portions were calculated with discharge measurements at the lake's outflow (Q_{TS}) and in Birmensdorf (Q_{BD}) (data source: AWEL). Their characteristics over time, specifically during the monitoring period of summer 2013, were compared to each other.
Table 7 sums up the data statistics of the Türlersee fractions of Q_{BD} (in % = 100 - ((Q_{BD} - Q_{TS})/ (Q_{BD} * 100)) compared to Q_{BD} for the timespan of 01/01/13 until 23/10/13. Accordingly, *Figure 26 a)* illustrates the daily Türlersee portions in the Reppisch in Birmensdorf. *Figure 26 b)* additionally presents daily mean discharge amounts for the same time span (data source: AWEL). Like this discharge portions can be compared to the according runoff situation per month.
For the discharges between January and October 2013 the range of the Türlersee fractions was 47.58 % or 0.907 m^3/s (*Table 7*). The mean was 27 % or 0.124 m^3/s. Generally, there are no great outliers in the fractions except for September when the mean Türlersee fraction is 31.59 % and the median is 38.32 %.
The monitoring period of 2013 shows an interesting setting in the ranges of the Türlersee fractions, they increased from June with 29.26 % to September with 46.68 %. The minimum fraction was in July with 4.3 % when daily mean discharge in Birmensdorf was 0.055 m^3/s. The maximum fraction was in September at 51.88 % when daily mean discharge was 0.977 m^3/s. This denotes that the according fractions of the inflows were between 48 % (0.038 m^3/s) and 96 % (4.938 m^3/s) of the discharge in Birmensdorf (Q_{BD} = 100 %).

Table 7 Türlersee fractions in Birmensdorf from January to October 2013. Grey values do not belong to monitoring period 2013, they are displayed for comparison.

	Range		Min.		Max.		Mean		Median	
	Q_{TS} of Q_{BD} [%]	Q_{BD} [$m^3 s^{-1}$]	Q_{TS} of Q_{BD} [%]	Q_{BD} [$m^3 s^{-1}$]	Q_{TS} of Q_{BD} [%]	Q_{BD} [$m^3 s^{-1}$]	Q_{TS} of Q_{BD} [%]	Q_{BD} [$m^3 s^{-1}$]	Q_{TS} of Q_{BD} [%]	Q_{BD} [$m^3 s^{-1}$]
Jan - May	25.55	2.193	12.10	0.236	37.65	2.429	26.70	0.565	26.72	0.444
June	29.26	5.603	15.34	0.230	44.60	5.833	33.55	0.945	34.43	0.559
July	38.06	0.759	4.30	0.055	42.36	0.814	19.79	0.219	20.73	0.154
August	40.26	0.290	4.74	0.052	45.00	0.342	21.80	0.103	20.89	0.082
September	46.68	0.937	5.21	0.041	51.88	0.977	31.59	0.248	38.32	0.143
October	23.18	0.373	17.87	0.093	41.05	0.466	31.20	0.219	32.41	0.196
Jan - Oct	*47.58*	*5.793* *Q_{TS} 0.907*	*4.30*	*0.041* *Q_{TS} 0.002*	*51.88*	*5.833* *Q_{TS} 0.910*	*27.00*	*0.460* *Q_{TS} 0.124*	*27.85*	*0.351* *Q_{TS} 0.100*

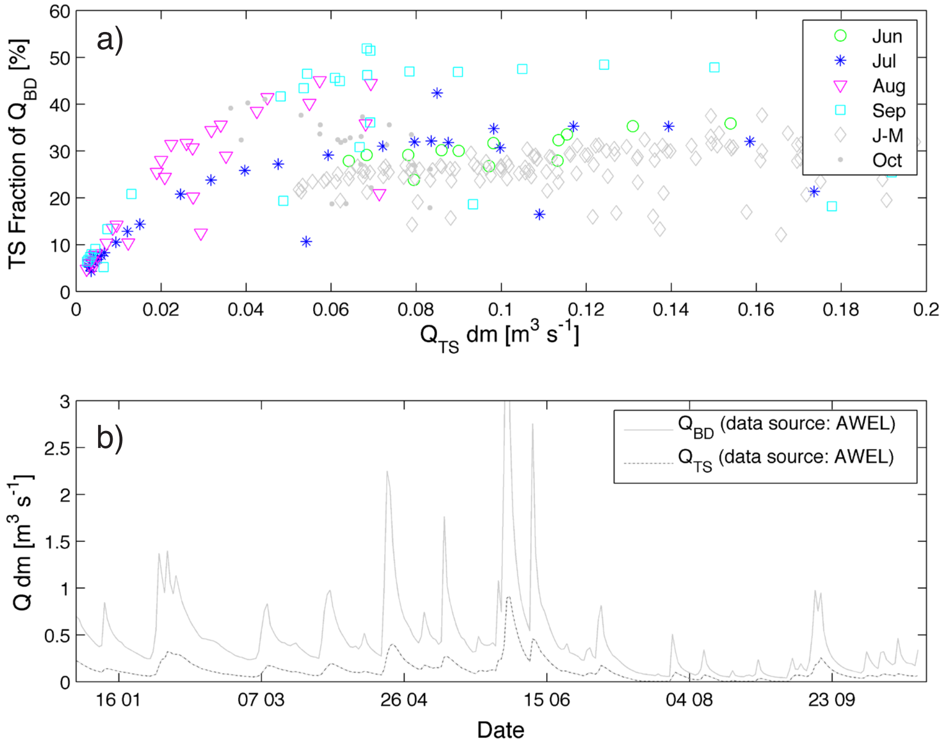

Figure 26 *a)* Türlersee fractions in [%] (= 100 - ((Q_{BD} - Q_{TS}) / (Q_{BD} * 100))) in a window of daily mean discharges from 0 to 0.2 m^3/s at the outflow of the Türlersee (data source: AWEL). *b)* Daily mean discharges of the outflow of the Türlersee and in Birmensdorf from January to October 2013.

In *Figure 26 a)* the coloured marks of the Türlersee portions indicate with increasing discharges at the lake's outflow (hence as well in Birmensdorf), the Türlersee fractions will relatively increase as well or vice versa. And thus, the inflow fractions are relatively getting smaller. This relationship stabilised at Q_{TS} of 0.1 m^3/s.
The data of June (green circles) shows mean daily discharges which were decreasing. The mean of the Türlersee fractions was consequently 33.55 % (*Table 7*).
In July (blue stars) discharges were decreasing and Türlersee fractions as well. The mean Türlersee fraction was 19.79 %. The blue stars depicting an obvious curve between 0.05 and 0.5 m^3/s are mostly of consecutive days. They show all the days from 06/07 to 25/07/13, when Q_{TS} was declining from 0.139 to 0.033 m^3/s, Q_{BD} from 0.4 to 0.06 m^3/s and the Türlersee fraction from 35.23 to 5.2 %. The two blue star marks at 0.5 m^3/s are values from 05/07/13 (higher Türlersee portion) and from 29/07/13. They indicate two different trends or two different settings of runoff behaviour in the basin.
Besides some spread marks in August and September, these months depict a similar curve as the one in July. The August and September curve is just lifted up to higher Türlersee portions. In August the marks are distributed between 0.05 and 0.200 m^3/s, in September they are in the range of 0 to 0.16 m^3/s.

Figure 27 demonstrates again runoff at the lake outflow versus Türlersee fractions, this time the marks are connected according to the time lapse of days. For time span of 01/01/13 until 23/10/13 the mean Türlersee fraction was 27 % or 0.124 m^3/s. The minimum fraction was in July with 4.3 % and the maximum in September with 51.88 %.
The curve of July (blue stars) belongs to the tail of the data series of June (green circles). Their connection is indicated with the lower red circle. Türlersee fractions of June and July are the char-

acterisation of the Reppisch and the Türlersee emptying the reservoirs of the Reppisch valley after the heavy rain events in May and June. Türlersee fractions decreased from 35.23 to 5.2 %. Hence, the marks forming the obvious curve represent the recession curve (decreasing discharges) of the Reppisch for June and July 2013.
The upper red circle in *Figure 27* shows the connecting day between July and August (magenta triangles). The last days of July are marked with rising stages in the Reppisch and rising portions of the Türlersee. The following nine days mark a recession in the Reppisch discharges and a decrease in Türlersee fractions, which drag behind by one day. Then the magenta curve of August again turns to higher discharges and higher Türlersee portions. In a loop it turns back to the behaviour of ten days before. It falls again in the same manner into the direction of zero.
In September (cyan rectangles) the recession curve depicts again the previously shown shape at higher Türlersee portions. Marks that are outliers indicate a change of the runoff regime to suddenly higher discharges in the Reppisch. These are often delayed at the lake's outflow. So the calculation of Türlersee portions of the total runoff amount in Birmensdorf leads then to very small percentages on the initial day, but rises abruptly on the second day.

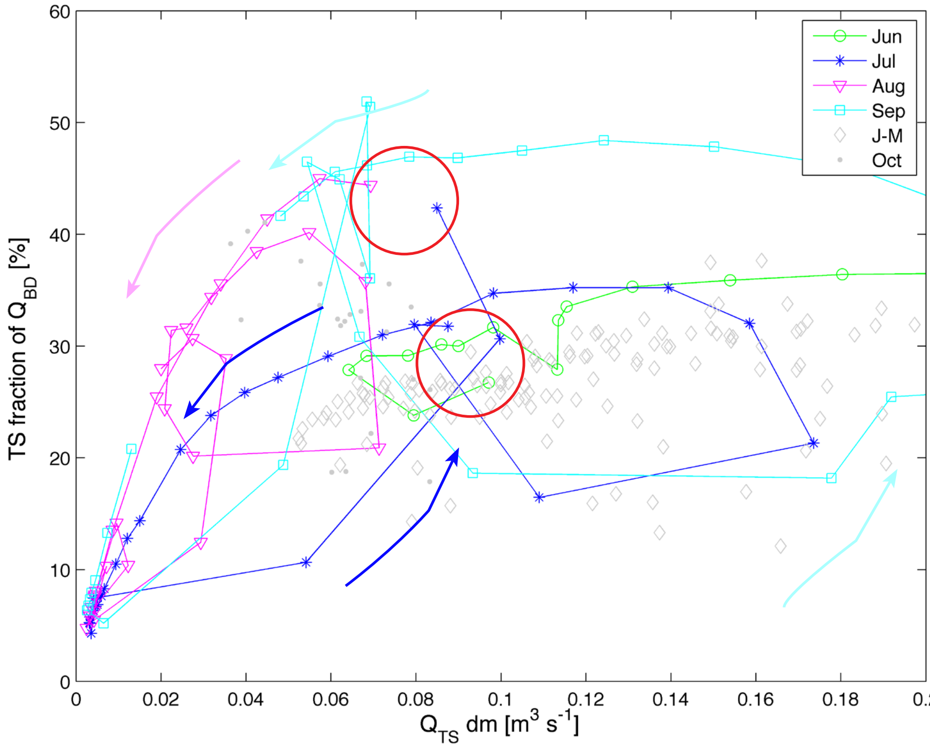

Figure 27 Daily mean discharge [m^3 s^{-1}] at the lake's outflow versus Türlersee fraction of total daily mean discharge in Birmensdorf [m^3 s^{-1}] in 2013 (data source: AWEL). Red circles point out connecting days between June, July and August. Arrows are standing for time lapse of the colour-coordinated curve.

3.3 Meteorology

Discharge rate and d-excess variations over time lead to questions of other influences than just distance-, area-, stream lengths- and amount-dependencies. It is the nature of isotopic signatures to be an integral mixture of all the different aspects that build up isotopic compositions and ratios. A very important part, or even t h e part which let arise the isotopic composition of waters that enters the Reppisch basin from outside, are the climatic or meteorological conditions. They influence the emergence of the initial water vapour in the sea, the transportation and conditioning of the vapour on its journey over the continents to Switzerland and the conditions while precipitation formation and achievement of reaching the ground in whatever form of water (Ingraham, 2006). These treatments form the initial isotopic conditions of the examined moisture in the Reppisch basin. The climate and the meteorological setting before and during the monitoring periods in the Reppisch valley added a vast amount of further treatment to the water samples before they entered the sampling bottles.
The following paragraphs describe meteorological conditions during the sampling period of 2013 and investigate for potential correlations between actual meteorological aspects like temperature, relative humidity and precipitation and the generated d-excess values of all taken samples.

3.3.1 Precipitation, Temperatures and d-excess

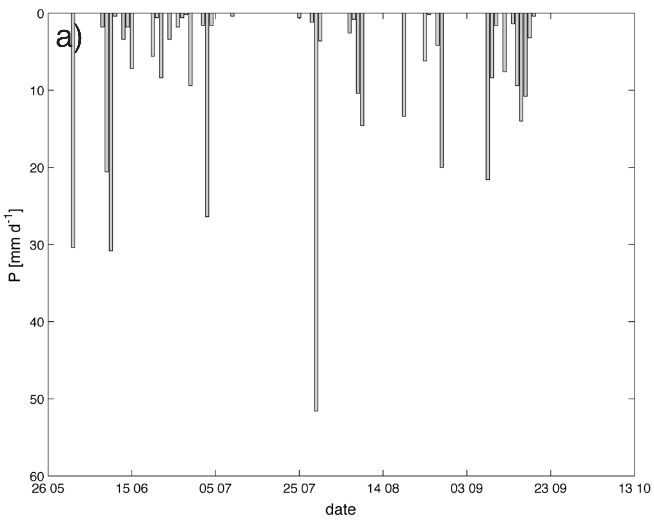

Figure 28 (Continued)

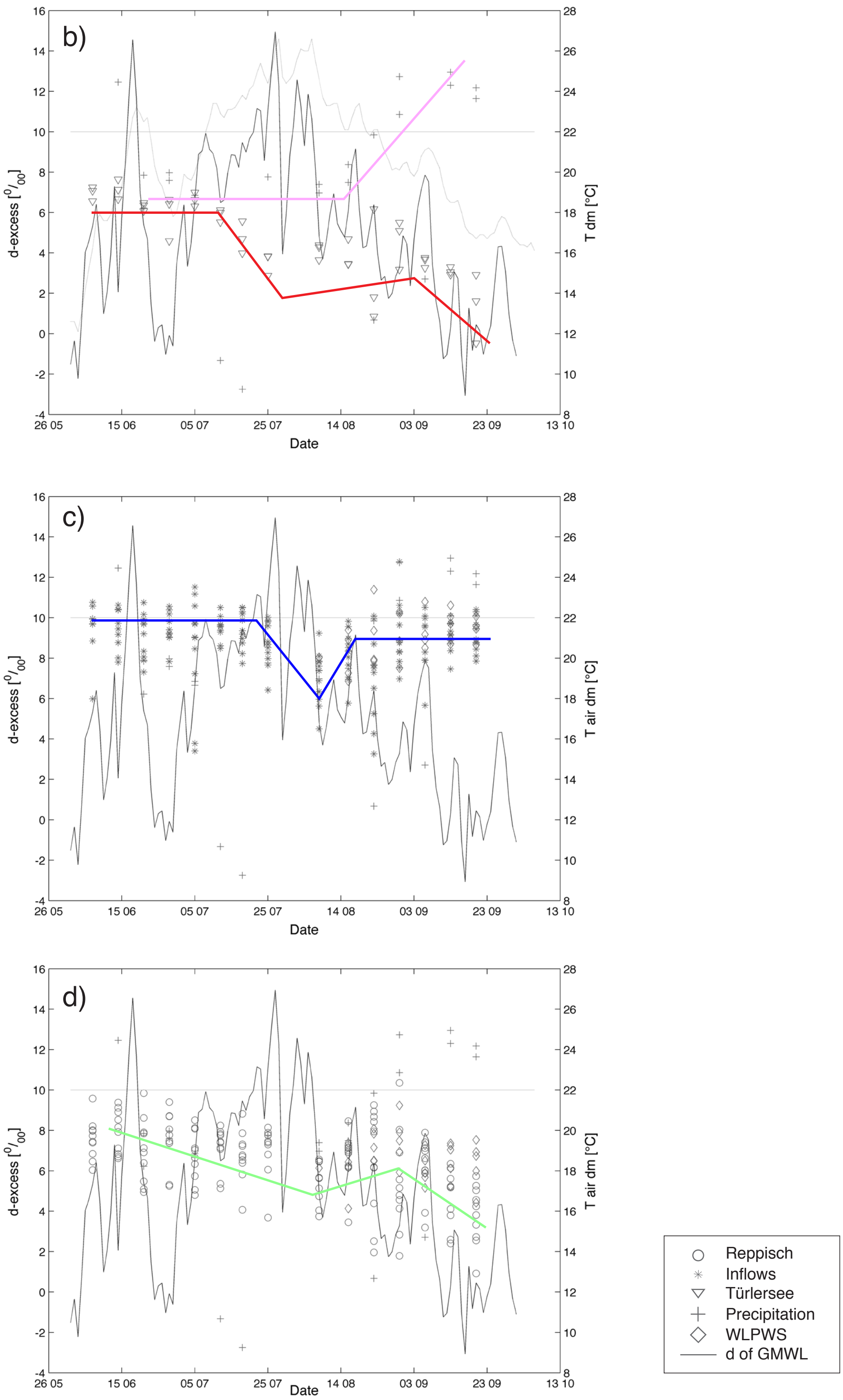

Figure 28 *a)* Daily precipitation sums in Stallikon [mm d⁻¹] (data source: METEOCENTRALE). *b)* D-excess of the Türlersee surface water and precipitation with daily mean lake (provisional data, source: AWEL) and air temperature. *c)* D-excess of the inflows and precipitation with daily mean air temperature. *d)* D-excess of the Reppisch and precipitation with daily mean air temperature (data source: METEOCENTRALE). One vertical accumulation of marks stands for one sampling day.

Figures 28 b) to *d)* show the d-excess values of each grab sample separately split up by the examined basin components with on-going time versus mean daily air and lake temperatures. *Figure 28 a)* depicts the daily precipitation sums as well for the monitoring period of summer 2013.
Bigger rain events are often followed by a drop of the curve of air temperatures. Lake temperatures in *Figure 28 b)* form a damped curve of the air temperatures. Whilst mean daily air temperature reached their first peak in June, mean daily lake temperatures followed only in July when they reached three peaks together with the air temperature by the end of July until the beginning of August. Mean daily lake temperatures were constantly higher than mean daily air temperatures, except for the 05 - 08/06, 16 - 19/06 and 27/07/13. On these days mean daily air temperature reached a peak of 27 °C and the one of the lake 26.6 °C, just one day later.
The calculated mean d-excess values of the Türlersee ranged between 7.14 ‰ on 14/06/13 and -0.48 ‰ on 20/09/13. In opposition to rising daily mean air and lake temperatures between 05/07/13 and 07/08/13, the d-excess values of the lake's surface water dropped. When temperatures shortly sank by the end of July, d-excess values were decelerating their dropping tendency.
At the same time, the d-excess values of precipitation rose from their distribution between 6 to 9 ‰ during June to mid-August into heights of 10 to 13 ‰ at the beginning of September.
Parallel to the rising d-excess values of the precipitation samples, the ones of the inflows were increasing too. After the big precipitation event of 29/07/13 with a sum of 51.6 mm, the inflows and the Reppisch's d-excess values increased and continued so until the end of August (Reppisch) and the beginning of September (inflows) when the next bigger rain events took place.
At the beginning of September, the Reppisch's and Türlersee's d-excess values showed a tendency of a decrease, whereas the d-excess values of the precipitation and the inflows increased. Altogether they appear like opening scissors.

The graphs *a)* to *d)* of *Figure 28* deliver an overview of the setting of precipitation and temperatures in summer 2013. They do not clarify if either precipitation or temperatures are the main trigger to changing d-excess values. Therefore *Figure 29 a)* to *d)* displays the water types separately where possible trends in d-excess with belonging to certain temperatures become more clear.

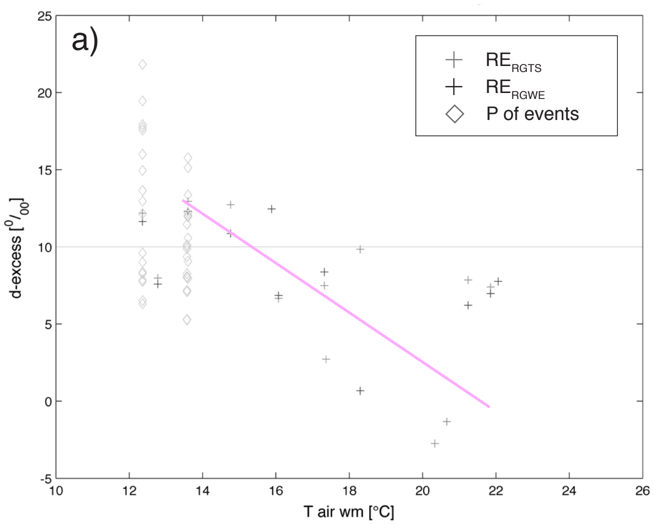

Figure 29 (Continued)

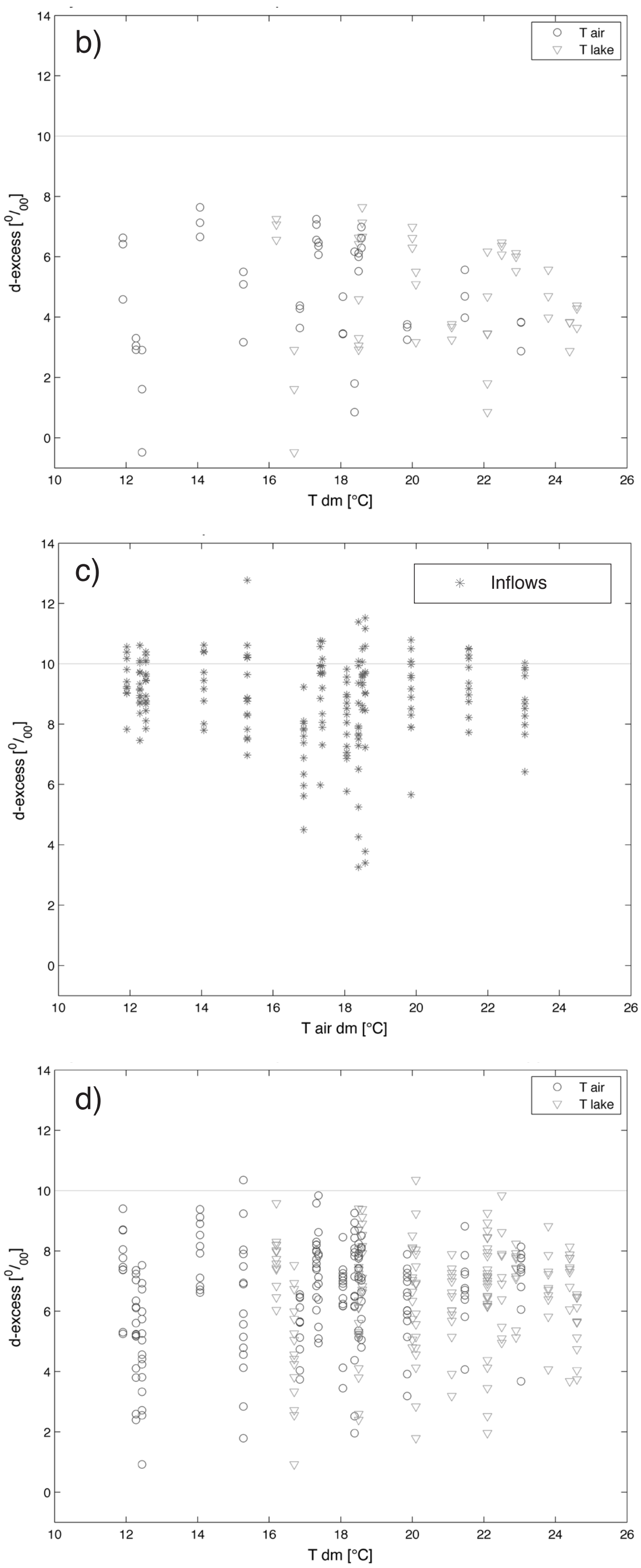

Figure 29 *a)* Weekly mean air temperature versus d-excess of weekly integrated (+, light grey RE_{RGTS}) and event precipitation water. *b)* Daily mean lake and air temperature versus d-excess of the Türlersee surface water. *c)* Daily mean air temperature versus d-excess of the inflows including *WLPWS*. *d)* Daily mean lake (provisional data, source: AWEL) and air temperature (data source: METEOCENTRALE) versus d-excess of the Reppisch including *WLPWS*. Straight line depicts d-excess of 10 ‰ of the *GMWL*.

The d-excess of rainwater samples is mostly positioned around 10 ‰, whereof it is higher seven times and lower 15 times (weekly integrated signals). 14 rainwater samples lie within the range of 15.9 to 23 °C weekly mean air temperatures and they all show d-excess values of -2.75 to 12.46 ‰. Eight rainwater samples lay between 12 and 15 °C and have d-excess values of 7.59 to 12.95 ‰. These two scatters indicate a slight trend of decreasing d-excess values with increasing weekly mean air temperatures. Albeit some outliers of negative d-excess values, a trend from d-excess values bigger than 10 ‰ at lower temperatures to values smaller than 10 ‰ at higher temperatures can be made out.
Precipitation water samples of events are also distributed within the weekly mean air temperature of the according week (*Figure 29 a)*) despite that they were emptied right after the event. Like this they were collected on different time ranges than the weekly integrated samples, hence, their signal is not imperatively connected to the mean weekly air temperature. Even so, they fit into the trend of all weekly integrated signals of increasing d-excess values with decreasing mean weekly air temperatures.
As seen in temperature time series, the lake temperatures have a damped signal compared to the air temperatures. Therefore the isotopic signals compared to lake temperatures (for *Figure 29 b)* and *d)*) are just a shifted image of higher mean temperatures and a more compact scatter than when they are compared to air temperature. Thus there is no evident trend in the Türlersee, but kind of a curve downwards to lower d-excess values with increasing temperatures. However, this curve is only detectable on the upper edge of the scatter. Very low d-excess values are also found at lower temperatures, around 12.5 °C for mean daily air and 16.5 °C for lake temperatures.
Following the air and lake temperature signals down the Reppisch, no evident trend could be found, not even the distribution of the Türlersee could be recognised. Except for a smaller scatter at higher temperatures, though this image has emerged due to less measurements at very high temperature conditions (*Figure 30*).
The d-excess distribution of the inflows show the widest range around mean daily air temperatures between 16 and 19 °C. This temperature range is the same as when most samples were taken in the Reppisch valley during the monitoring period of summer 2013.

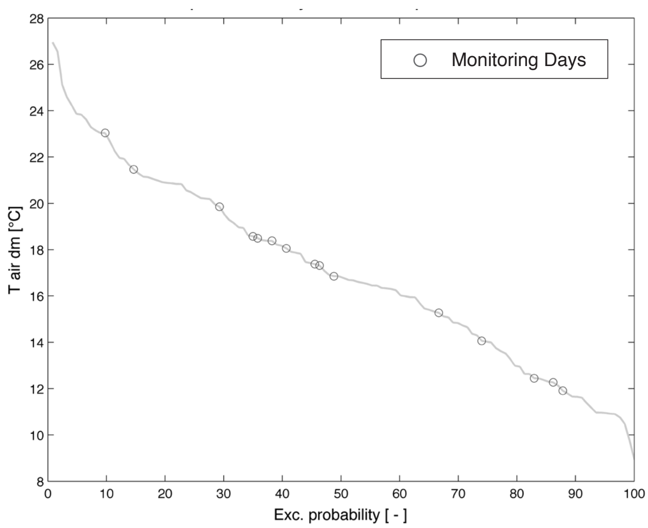

Figure 30 Exceedance probability of daily mean air temperature [°C] (data source: METEOCENTRALE) for the monitoring period of 2013.

The isolated look at temperature versus d-excess graphs does not bring up clear trends. The sampling days were not distributed evenly enough within the temperature span of summer 2013 in or-

der to make some statements about significant trends in the d-excess data. For instance, to state that in the inflows the narrowest distribution of d-excess between 8 and 11 ‰ is found at temperatures between 12 and 13 °C.
The following paragraphs take a closer look at another meteorological parameter, the relative humidity.

3.3.2 Relative Humidity and d-excess

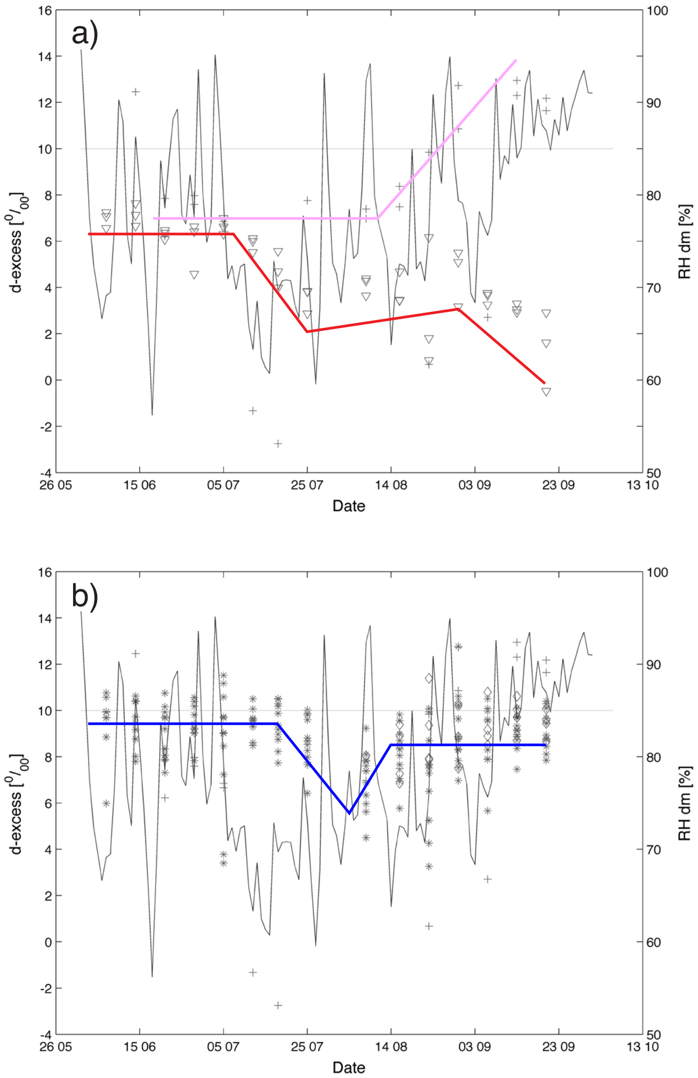

Figure 31 (Continued)

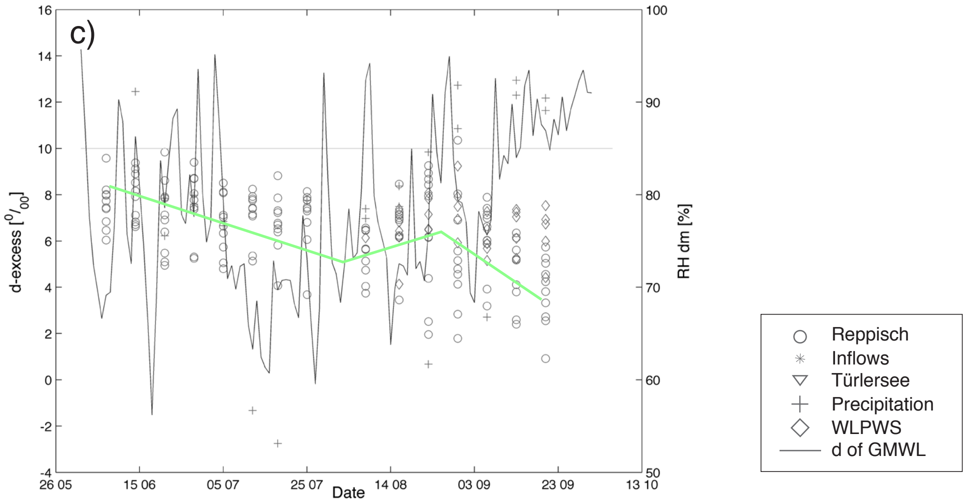

Figure 31 D-excess with daily mean relative humidity (RH) [%] (data source: METEOCENTRALE) *a)* of the Türlersee surface water and precipitation, *b)* of the inflows and precipitation and *c)* of the Reppisch and precipitation. One vertical accumulation of marks represents one sampling day.

During the monitoring period of 2013 the d-excess values of the Türlersee declined constantly (*Figure 31 a)*). From 05/07/13 to 25/07/13, d-excess values of the Türlersee sank parallel to the relative humidity. They decelerated by the end of July and beginning of August. This time span was marked several times by extreme and changing weather conditions, which are also reflected by the relative humidity. It rose to two peaks during the same weeks. On 14/08/13 it reached one of the lowest points of 65 %, from there on it increased again with some indentations. The d-excess values of the Türlersee were not interrupted in their trend as they decreased until the end of the monitoring period.
The precipitation sample's d-excess values (*Figure 31 a)*) sank as well within the first weeks of the monitoring period 2013. In July when relative humidity and the lake d-excess values dropped, no precipitation samples could be measured. With increasing relative humidity the rainwater's d-excess values constantly rose back to values between 10 and 13 ‰ like at the beginning of this monitoring period.
The inflows were oscillating most of the time within their preferred d-excess ranges of 8 to 12 ‰. In July when relative humidity decreased, the inflow's d-excess values decreased as well and reached their minima in August. With an increasing relative humidity from August to September, like precipitation events showed, the d-excess values of the inflows were rising as well, back close to the *GMWL*.
The Reppisch finally (*Figure 31 c)*), shows a similar, although more smooth d-excess curve like the Türlersee. From mid August to the beginning of September, the Reppisch d-excess values behaved more like precipitation and inflow values: with increasing relative humidity d-excess values rose as well. September was still marked by increasing relative humidity, while the Reppisch d-excess values sank again.

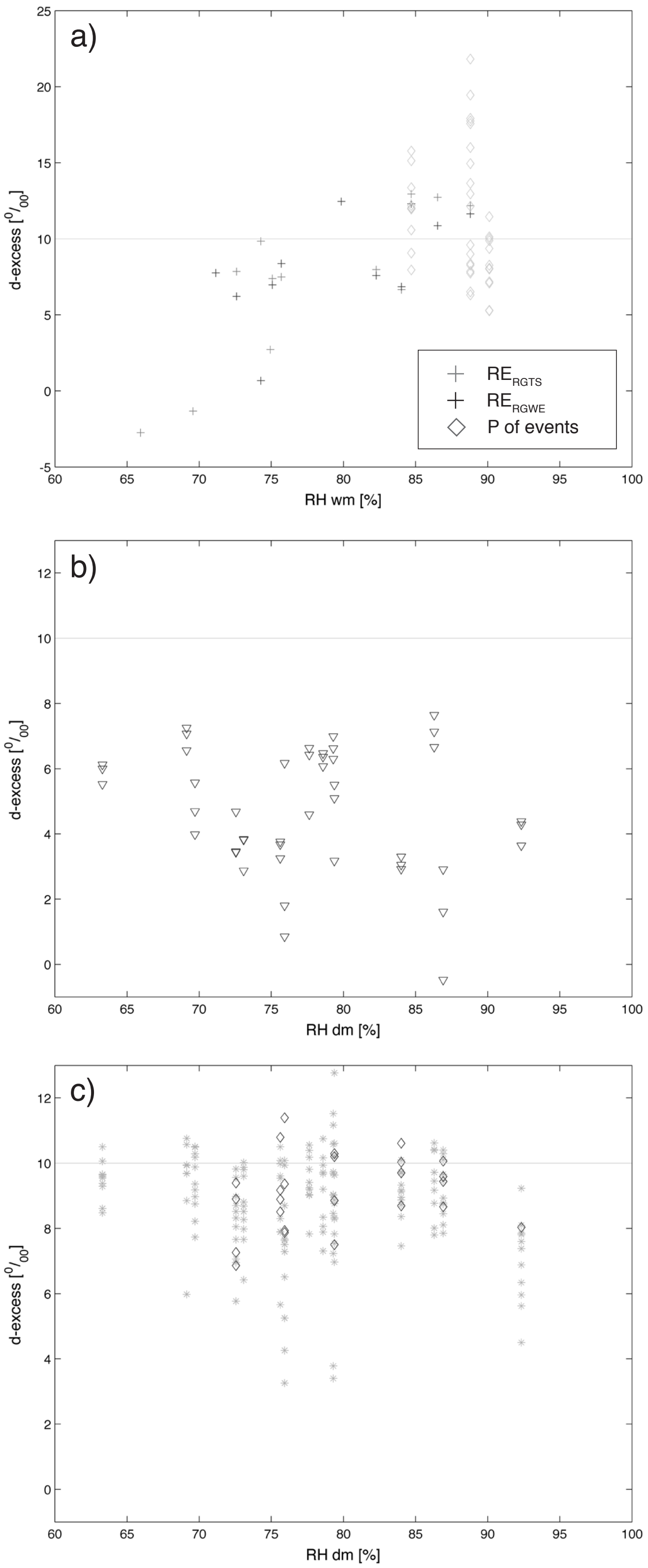

Figure 32 (Continued)

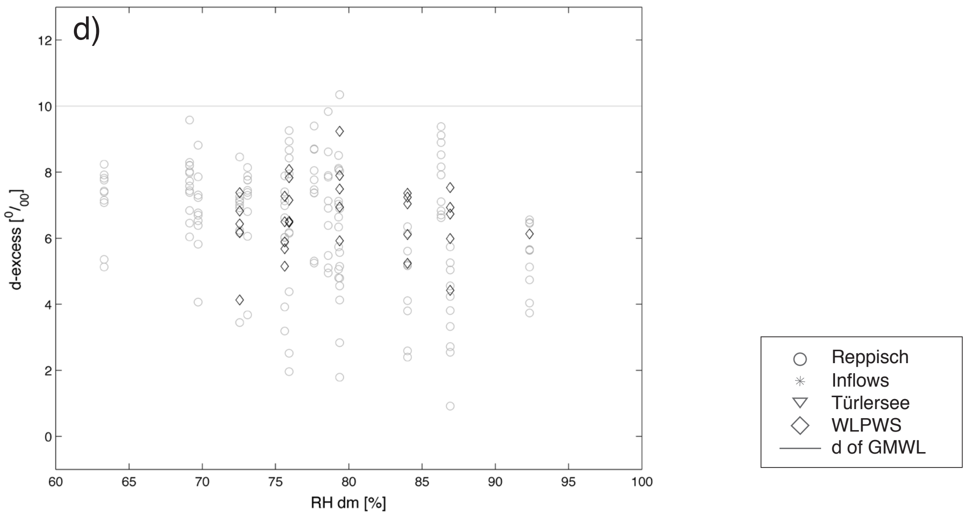

Figure 32 Weekly and daily mean relative humidity [%] (data source: METEOCENTRALE) from June to September 2013 versus d-excess of grab samples of *a)* weekly integrated and event precipitation water, *b)* the Türlersee surface water, *c)* of the inflows and *d)* of the Reppisch.

Most samples were taken during relative humidity conditions between 70 and 85 % *(Figure 33)*. This is also the range where most d-excess values are found in the plots where the examined waters are displayed separately with relative humidity (*Figure 32 a) to d)*). Hence, the thinning out of marks at lower and higher relative humidity values is a consequence of the amounts of samples. The weekly integrated rainwater samples depict an increase in d-excess from lower relative humidity to a higher one. Though at the same relative humidity conditions (weekly means) several d-excess values appear, sometimes with ranges up to 8 ‰ (for instance around relative humidity of 75 %). Rainwater samples collected during events are found in atmospheric conditions of higher relative humidities between 85 and 92 %. As mentioned earlier, their means lay within the ranges of the weekly rainwater samples.

In the range between 60 and 75 % of relative humidity, the d-excess values show a kind of a clear border at the lower edge of their scatter where they do not get any lower. All the other marks seem to be randomly distributed. These patterns appear with all the three surface water types.

In the Reppisch the values gained by *WLPWS* are found within the scatter of the grab samples, whereas the data from the inflows *WLPWS* produced some outliers at relative humidities of 76, 77 and 84 % into higher d-excess areas.

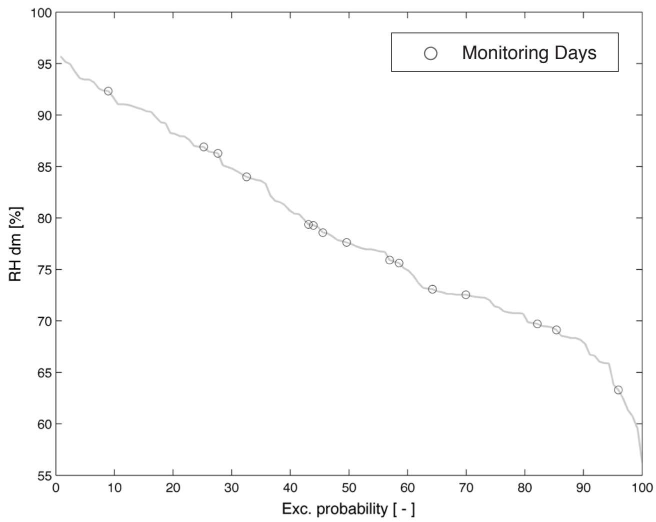

Figure 33 Exceedance probability of daily mean relative humidity [%] (data source: METEOCENTRALE) for the monitoring period of 2013.

3.4 Antecedent Conditions

The setting of the Reppisch catchment and the climatic and meteorological conditions before and during the monitoring period of summer 2013 lead to the topic of *Antecedent Conditions*. The discharge behaviour of the Reppisch, the Türlersee and the inflows also strongly depend on happenings during the time before taking a snapshot of them. The same accounts for the isotopic composition of all the waters sampled.
The first part of this chapter describes the situations concerning the meteorology and runoff of all the three monitoring periods. It elucidates the received data on *Current Precipitation Index (CPI)* with a moving window of seven days (*CPI7*). It further describes the building of *CPI7* classes and where the sampling days of summer 2013 could be allocated to and presents these findings compared to already described d-excess and discharge data.

3.4.1 Precipitation and Discharge: Comparison of the Summer 2013 to 2010 and 2011

Table 8 Total precipitation [mm m^{-1}] (data source: METEOCENTRALE) and daily mean discharges in Birmensdorf [m^3 s^{-1}] (data source: AWEL) per month during all monitoring periods. In 2010 only July and August were sampled.

	2010		2011		2013	
	P_{acc} [mm m^{-1}]	Mean Q_{BD} dm [m^3 s^{-1}]	P_{acc} [mm m^{-1}]	Mean Q_{BD} dm [m^3 s^{-1}]	P_{acc} [mm m^{-1}]	Mean Q_{BD} dm [m^3 s^{-1}]
June	116.4	0.673	72.2	0.093	126.4	0.945
July	158.8	0.330	162.2	0.495	87	0.219
August	150.8	0.570	109.4	0.235	72.4	0.103
September	81.2	0.377	78.2	0.282	78.4	0.248
Total	*507.2*	*0.488*	*422*	*0.276*	*364.2*	*0.379*

Comparing the summers of 2010, 2011 and 2013 with each other in *Table 8* shows a different setting of precipitation sums and mean daily discharges of the Reppisch in Birmensdorf. 2010 and 2011 were summers of up to 140 mm more accumulated precipitation than in 2013. The mean discharge rates of the entire monitoring period 2013 though were higher than in 2011, whilst the area received in total 58 mm less precipitation.
During June and July of 2013 a decrease in total precipitation and in mean discharge rates took place. June and July of 2010 though, exemplify that months of higher precipitation sums following months of lower ones do not necessarily induce mean higher discharge rates.
Similar precipitation sums do also not necessarily mean that runoff rates are similar as well. Monthly precipitation sums between 72.2 and 81.2 mm/m came together with discharge rates between 0.377 and 0.093 m^3/s.
This short overview exemplifies the way that the Reppisch was expected to behave: a certain input during a certain time span does not necessarily always induce the same output during the same time span. The upcoming chapter *Antecedent Conditions in 2013* captures this simplified precipitation-input - Reppisch-output situation for monitoring period 2013 and looks for some linkages to the isotopic signals of the collected water samples.

3.4.2 Current Precipitation Index Settings in 2013

Already the summary and comparison of precipitation amounts and mean discharges in *Table 8* of three monitoring years show how different antecedent conditions were and that they can lead to different discharge regimes of the Reppisch in Birmensdorf. In the estimation of antecedent conditions for summer 2013 shown in *Figure 34*, July 2013 depicts a special case. Many reservoirs seemed to have emptied on 18/07/13. This was confirmed in the field by very low discharge amounts of the inflows. They ranged between 0.05 and 6.2 l/s for that day whereas on other monitoring days mean inflows reached more than 10 l/s. The other monitoring day when *CPI7* was 0.0 mm/d was on 06/09/13. On that day, the value 0.0 mm/d could be confirmed in the field by dry falling inflows RE5.1 and RE9.1. Also other inflows reached their minimal measured discharge. They ranged between 0.01 and 2.4 l/s.

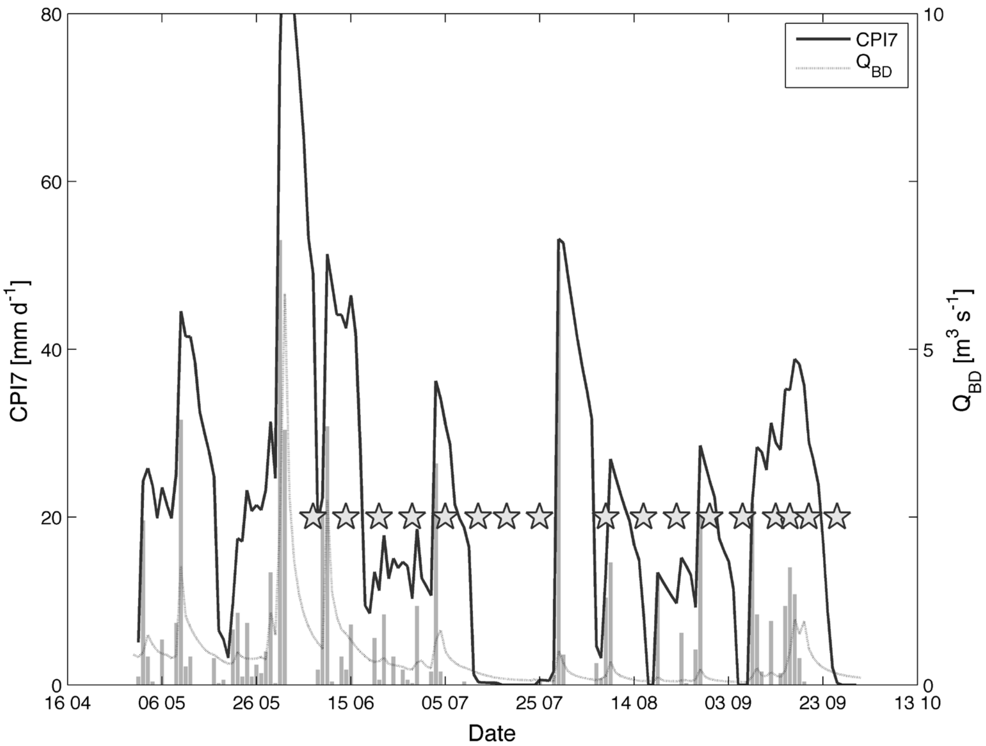

Figure 34 Precipitation, *CPI7* [mm d^{-1}] and daily mean discharges in Birmensdorf [m^3 s^{-1}] (data source: AWEL) are illustrated with on-going time. Bars illustrate daily precipitation [mm d^{-1}] (data source: METEO-CENTRALE). Stars mark the dates of the sampling days in monitoring period of 2013.

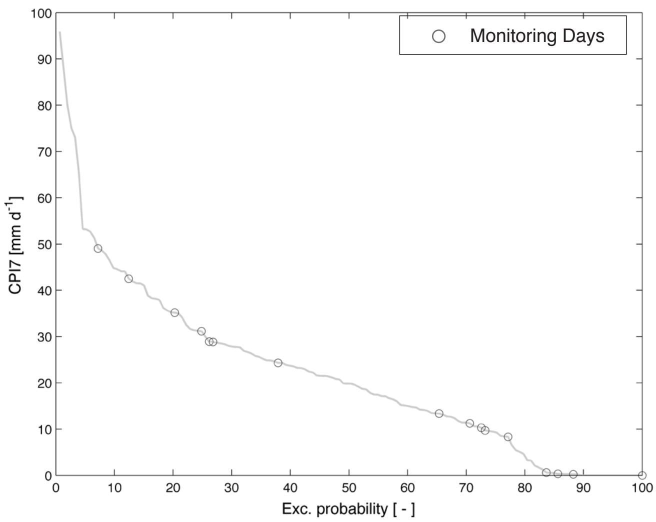

Figure 35 Exceedance probability of *CPI7* [mm d^{-1}] for the months May to September 2013.

According to the distribution of the *CPI7* values and sampling days (*Figure 35*), *CPI7* conditions during summer 2013 were classified into three groups in *Table 9*.

Table 9 Classification of *CPI7* conditions of monitoring period 2013 into three groups.

Class	CPI7 [mm d^{-1}]	Occurrence during May to September 2013 [%]
dry (1)	0 - 3.24	20
humid (2)	4.65 - 27.75	50
wet (3)	27.83 - 95.92	30

Table 10 is a summary of the allocation of all sampling days in 2013 to the modelled *CPI7* conditions, to *CPI7* classes determined in *Table 9* and to discharge measurements of the inflows, where they were available. The above mentioned confirmation of the days with *CPI7* = 0.0 mm/d is also found for other monitoring days. Tendencies of drier and wetter conditions in the Reppisch basin are also confirmed by decreasing and increasing inflow and Reppisch discharges.

In some cases a rising or falling *CPI7* comes with a mean discharge moving into the opposite direction (*Table 10*, grey, italic and assigned by arrows). Although, these confirmations or rejections of the *CPI7* model by parallel rising or falling mean runoff might be distorted by using a mean of all inflows or by the precipitation amounts used for the model. The drifts are also weekly jumps (discharge measurements and *CPI7* results), so more smooth changes are not captured within these time steps. Nevertheless, 9 of 12 tendencies in *CPI7* scenarios for our monitoring days lie in their calculated tendencies back in mean measured inflow discharges and 11 of 14 tendencies in mean discharges in Birmensdorf as well.

Table 10 Allocation of monitoring days of 2013 to *CPI7* conditions, own mean discharge measurements of the inflows and discharge in Birmensdorf (data source: AWEL) and to *CPI7* classes. Opposite tendencies between *CPI7* and measured runoffs are assigned with arrows and in grey italics. On 16/09/13 and 26/09/13 no regular grab samples were taken, therefore they are not taken into account to analyse parallel or opposite trends.

Monitoring Day Date	P [mm d-1]	CPI7 [mm d-1]	$Q_{inflows}$ Mean [l s-1]	Q_{BD} dm [m3 s-1]	CPI7 class
07/06/13	0	49.03	NaN	0.726	wet
14/06/13	1.8	42.51 ↓	NaN	*0.759 ↑*	wet
21/06/13	0.6	11.25	4.900	0.351	humid
28/06/13	0.2	10.29 ↓	*5.300 ↑*	0.230	humid
05/07/13	0	31.15	10.444	0.495	wet
12/07/13	0	0.31	3.178	0.175	dry
18/07/13	0	0.00	1.978	0.089	dry
25/07/13	0.6	0.60 ↑	*1.689 ↓*	*0.063 ↓*	dry
08/08/13	10.4	13.35	4.750	0.137	humid
16/08/13	0	8.33	1.164	0.058	humid
23/08/13	0	9.72 ↑	*0.615 ↓*	*0.053 ↓*	humid
30/08/13	0	24.31	1.461	0.089	humid
06/09/13	0	0.00	0.581	0.043	dry
13/09/13	0	28.83	2.164	0.138	wet
16/09/13 event	14	35.16	NaN	0.501	wet
20/09/13	0	28.91	12.167	0.543	wet
26/09/13 series	0	0.23	NaN	0.167	dry

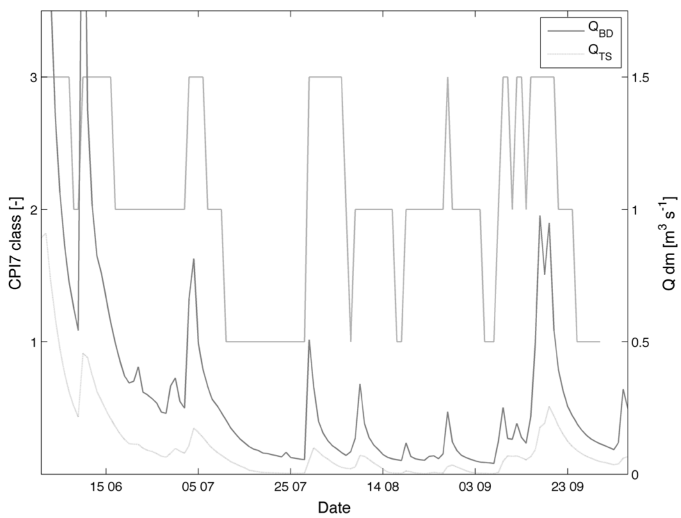

Figure 36 *CPI7* classes for each day and daily mean discharges in Birmensdorf and at the outflow of the Türlersee [m³ s⁻¹] (data source: AWEL) with on-going time during the monitoring period of 2013. The coarse *CPI7* classes still reflect the conditions in the Reppisch basin.

The classification of the antecedent conditions into only three classes still reflects the situations in summer 2013 (*Figure 36*).

In *Figure 37* the three *CPI7* classes in *GMWL* space are clearly distinguishable.
Clear trends of lower or higher d-excess value ranges in plots with *CPI7* classes and geographic characteristics (distance, area etc.) could not be made out.

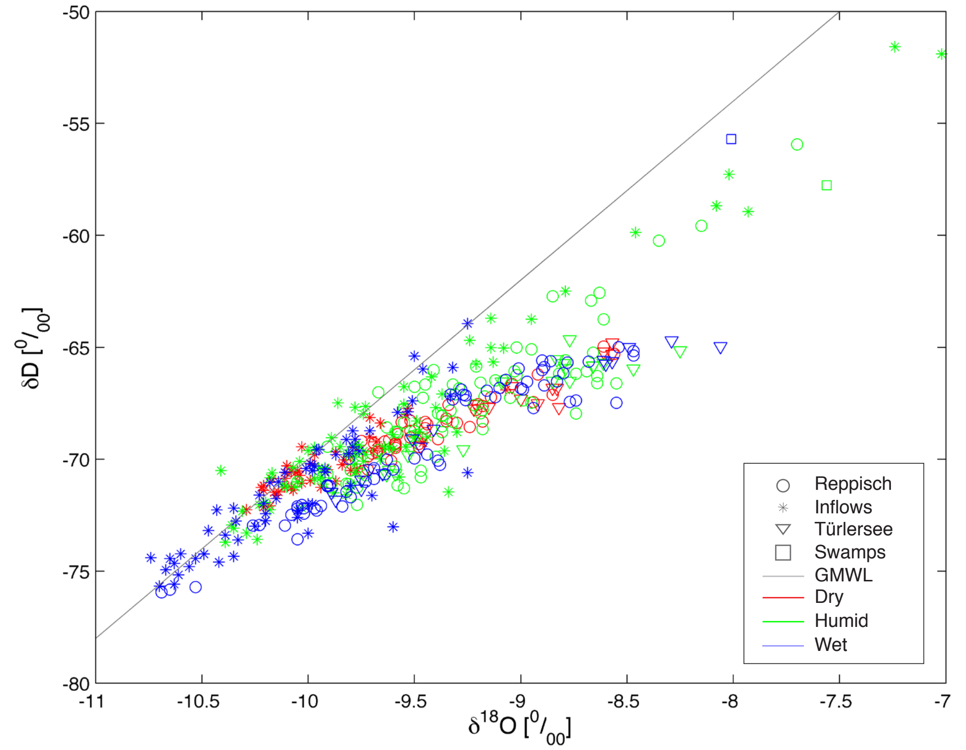

Figure 37 Isotopic compositions [‰] of all water samples (except RE_{RG}) of the summer 2013 in the *GMWL* space with the *Global Meteoric Water Line*. Colours represent *CPI7* classes.

3.4.3 Discharge and d-excess Behaviours according to CPI7 in 2013

In *Figure 38* where antecedent condition classes are looked at over time with d-excess signatures and compared to discharges in Birmensdorf and at the lake's outflow, trends from one class into another with on-going time become clearer. At the beginning of June the valley was "wet" after the heavy rainfalls by the end of May and beginning of June. Then runoffs decreased and the water samples switched into class "humid", their d-excess values began to decrease as well, particularly the ones of the lake and the Reppisch.
A next increase in discharges took place at the beginning of July. Samples of 05/07/13 are marked by "wet" again. Their d-excess values depict the widest range so far. The inflows RE14 and RE22.1 decreased to values in d-excess of 3.78 and 3.4 ‰ respectively. With the newly started recession of discharges, d-excess values were descending as well. The rest of July was marked by dry antecedent conditions.
With four peaks in runoff during July and August, the Reppisch valley was in a humid condition. During these weeks the range of d-excess values of all samples began to increase. The lake's and Reppisch's values reached very low levels whereas the ones of the inflows increased. The spread-

ing stopped by the end of August.
At 06/09/13 when the area was characterised by dry conditions, the d-excess range was smaller. The smaller d-excess range was also the case for 13/09/13, although the basin was classified to wet conditions. On 20/09/13 when the valley was also wet and the Reppisch discharge reached peaks of more than 1 m³/s, the d-excess range was the widest.

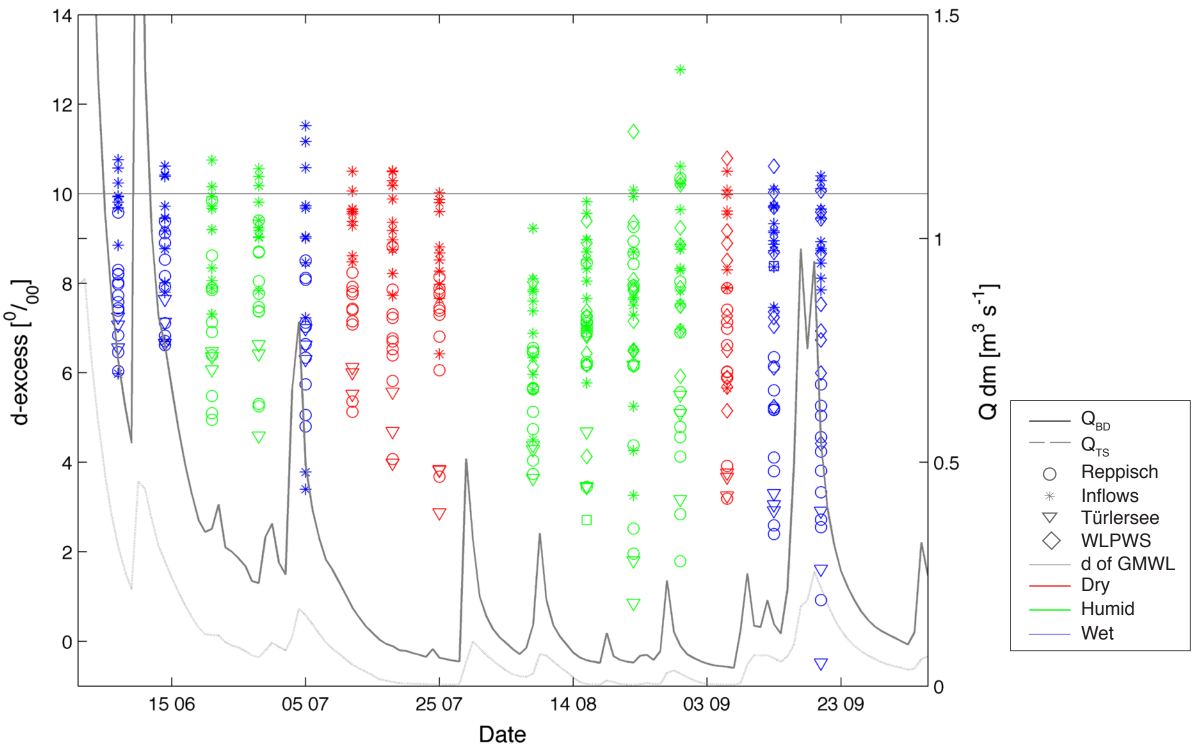

Figure 38 Days of monitoring period 2013 versus d-excess [‰] of all water samples (except RE_{RG}) and mean daily discharges of the Reppisch in Birmensdorf and at the lake's outflow. Colours represent *CPI7* classes.

3.4.4 CPI7 Classes compared to Baseflow and Stormflow situations

A comparison between peakflow analysis of daily mean discharges in Birmensdorf (data source: AWEL) of the time span 2010 to 2013 with one from the monitoring period 2013 led to the determination of a threshold of 0.0894 m³/s. This threshold was further used to differentiate between baseflow and stormflow. Hence, a daily mean of 0.0894 m³/s or more was discharged in Birmensdorf for 80 % of all days from June to September 2013 or for 70.6 % of the according monitoring days (12 of 17). For the three-year period this means that in 68 % of the days this amount or more ran off in Birmensdorf. This difference appears due to the long-lasting low flows in summer 2013.

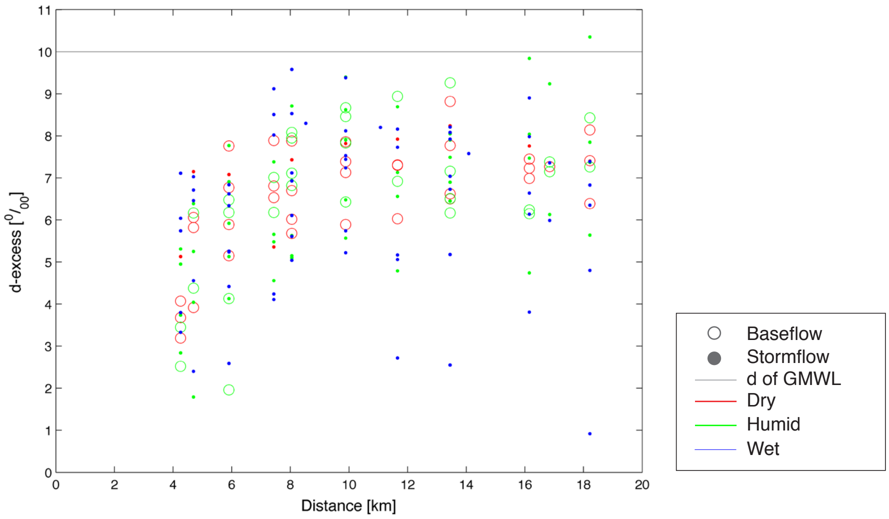

Figure 39 Distance versus d-excess [‰] of all Reppisch water samples (except events). Baseflow – stormflow threshold is 0.0894 m^3/s of daily mean discharge rates in Birmensdorf. Colours represent *CPI7* classes.

The above mentioned connections between low flows and *CPI7* classes are more comprehensible with the illustrations of *Figure 39* where baseflow situations in the Reppisch are marked by circles and stormflow situations which exceed a mean daily discharge of 0.0894 m^3/s in Birmensdorf are marked by dots.

The d-excess values for "dry" situations are mostly placed in the centre of the d-excess scatter. The upper and lower borders are preferentially marked by "humid" and "wet" basin settings.

There was one stormflow situation that was classified to dry conditions. This happened on 12/07/13 when the Reppisch discharged 0.175 m^3/s and was still in recession from the peak of 0.814 m^3/s on 04/07/13. The moving window of seven days of *CPI7* had already left the days of heavy precipitation for more than seven days before 12/07/13. Accordingly the basin was classified to a dry setting in the *CPI7* model.

All the other "dry" conditioned days were marked by baseflow situations. Hence, mean daily Reppisch discharges within the arbitrary threshold of baseflow/stormflow situations confirm so far the *CPI7* classification into dry settings. All the other baseflow situations are confirmed by *CPI7* classifications as well, namely none is marked by "wet" settings.

Stormflow situations are classified into "humid" or "wet" basin settings. They are also the ones representing the lowest d-excess values. Very close to the lake, baseflow conditions come together with the lowest d-excess values of the specific sample point. Downwards the valley d-excess distributions are less clearly allocatable to a certain flow and antecedent condition setting. Strongly different distributions took mostly place in the lower half of the valley and in September.

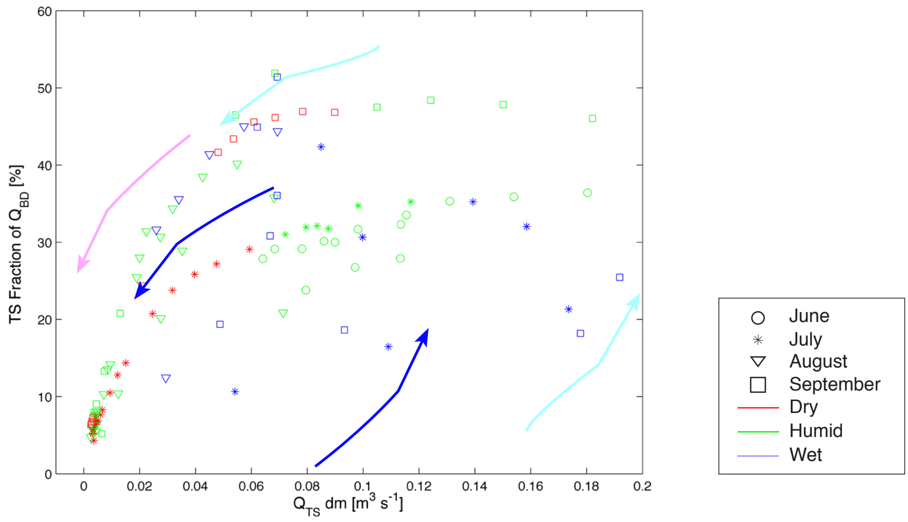

Figure 40 Observed Türlersee fractions with daily mean discharges at the outflow of the Türlersee (data source: AWEL). Colours indicate *CPI7* classes of the monitoring period 2013. Discharge is depicted in a limited window of 0 to 0.2 m^3/s of Q_{TS}. Arrows indicate time lapse of the specific successions and are coloured as their according months (as *Figure 27*).

In *Figure 40* the Türlersee portions in the Reppisch are coloured according to their *CPI7* classes. Like this, additionally rising and recession limbs are observable in the context of the basin's antecedent condition's setting (arrows as in *Figure 27*). The highest discharges at the Türlersee outflow came together with wet conditions in the Reppisch basin during June 2013 (from 0.2 to 1 m^3/s, not depicted in *Figure 40*). During July when the basin was draining, hence runoffs decreasing, also the Türlersee fractions decreased and *CPI7* class changed from humid to dry. August also depicted a draining basin just from wet to humid conditions. September marked the same behaviour like the August curve, *CPI7* classes though changed from dry to humid.

3.5 Events

The following graphs show the six events that were captured in August and September 2013. For some of them only one or two of the five installed *ISCO Samplers* took samples of the streams. Often they did not fill the 24 available bottles or only some samplers were activated. The heavy event of 15/09/13 was caught with all of the five machines. One of them even ran through the whole programme and filled all 24 bottles. On the 16/09/13 two machines caught another strong event by filling all 24 bottles.
Between 08 and 20/09/13 additional rain samples were collected with *Tipping Buckets*. This data, in comparison to the ones of the gauging station of METEOCENTRALE in Stallikon, were added to the plots of *Figures 43* to *50*. Where no own data was available, precipitation intensities of the gauging station in Stallikon were used. For this station, no determination of the isotopic composition of rainwater exists. The discharge amounts of the Reppisch in Birmensdorf (data source: AWEL) are also illustrated in the subsequent plots.
To recall the acronyms: $RE_{ISCO2.1}$ and RE_{ISCO7} were placed at RE2.1 and RE7, two inflows, one into the Türlersee and one into the Reppisch. RE_{ISCO12}, RE_{ISCO20} and $RE_{ISCO23.1}$ were placed at RE12, RE20 and right before RE23 in Birmensdorf in hidden parts of the Reppisch.
The subsequent paragraphs qualitatively describe the sampled events.

3.5.1 Event of 24/08/2013

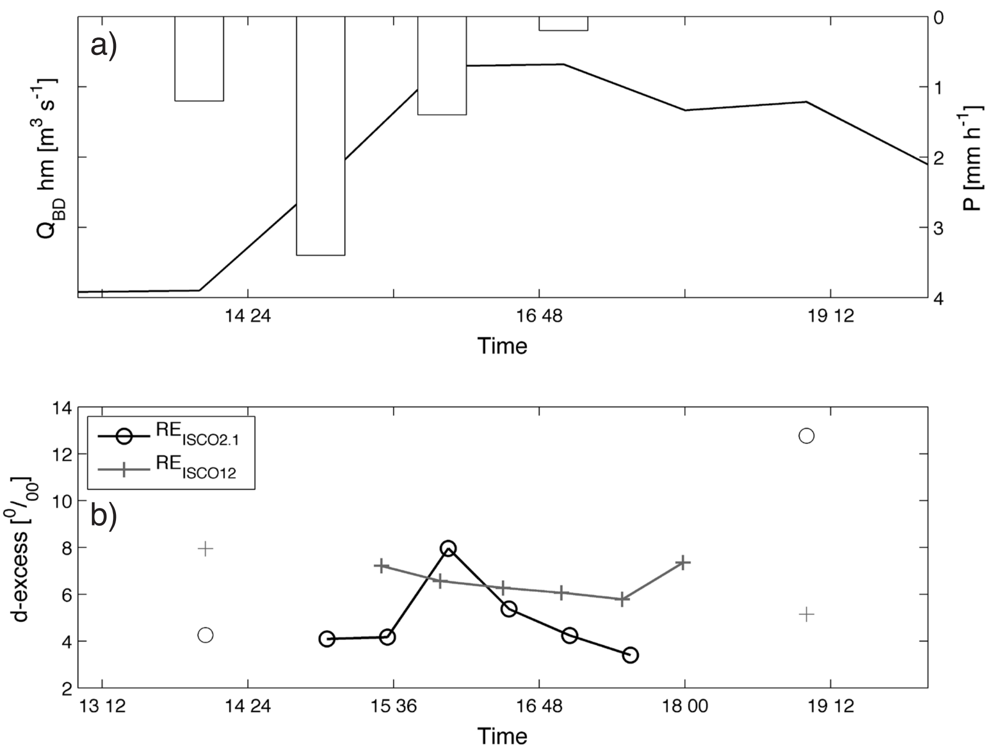

Figure 41 *a)* Time, on 24/08/13, versus discharge of the Reppisch in Birmensdorf [$m^3 s^{-1}$] (data source: AWEL) and hourly sums of precipitation in Stallikon [$mm h^{-1}$] (data source: METEOCENTRALE). *b) ISCO* sampling series of 24/08/2013. One straight line indicates d-excess in [‰] of a water mixture of samples taken half hourly. Marks indicate new bottles. Solely standing marks depict grab samples of the monitoring days before and after the event, hence of 23/08 and 30/08/13.

Both d-excess curves of $RE_{ISCO2.1}$ and RE_{ISCO12} show parallel decreasing values to the recession limb of the Reppisch's discharge. Interestingly $RE_{ISCO2.1}$ sampled water of quite low d-excess values which was unusual for this inflow (see *Figure 41* and *Figure 8*).
Time and amount steps of this event were quite small and show limited data. The Reppisch's discharge changed at a few tens of litres within five hours, whereas time steps of the *ISCO* sampling were half hourly. Additionally, the samples data do not show whether these d-excess values will change again or if they had a different tendency than might be assumed by the sparse event's data.

3.5.2 Event of 28/08/2013

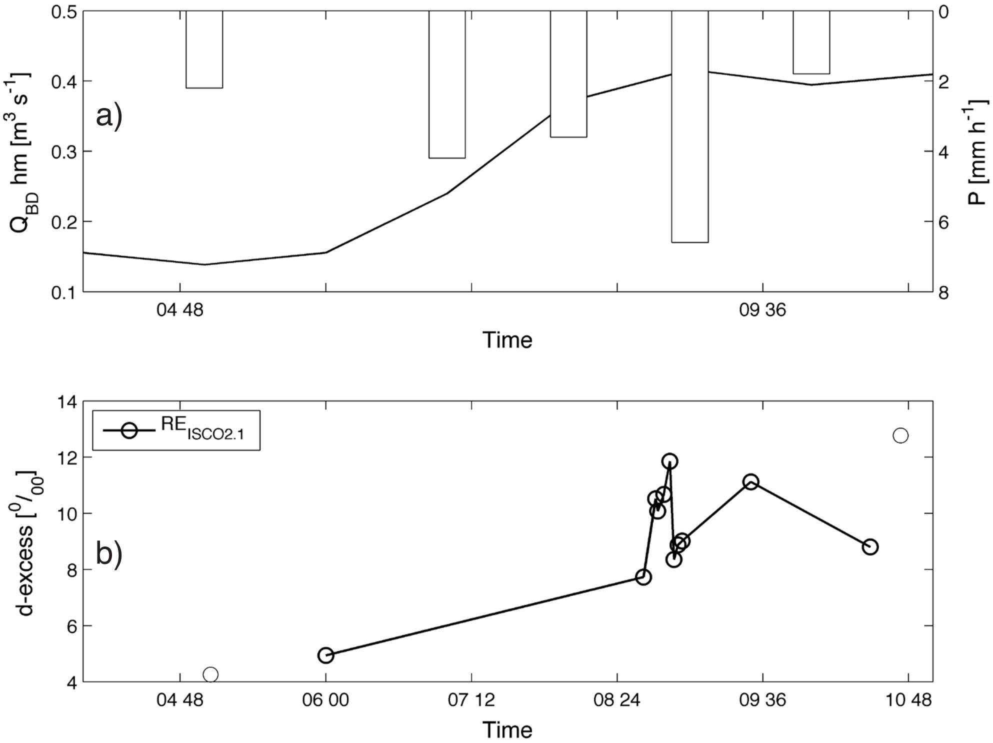

Figure 42 *a)* Time, 28/08/13, versus discharge of the Reppisch in Birmensdorf [$m^3 s^{-1}$] (data source: AWEL) and hourly sums of precipitation in Stallikon [$mm h^{-1}$] (data source: METEOCENTRALE). *b) ISCO* sampling series at $RE_{ISCO2.1}$ of 28/08/2013. One straight line indicates d-excess in [‰] of a water mixture of samples taken in irregular time steps. Marks indicate new bottles. Solely standing marks depict grab samples of the monitoring days before and after the event, hence of 23/08 and 30/08/13.

During the event of 28/08/13 it rained in total 20.4 mm and the Reppisch's discharge in Birmensdorf rose by 0.336 m^3/s within 13 hours.
At $RE_{ISCO2.1}$ eight samples were taken within minutes between 8 and 9 a.m., hence, the marks are depicted as an aggregation. Nonetheless, the d-excess values increase with increasing discharge. A sudden drop took place when the Reppisch runoff stabilised. Anew the runoff and d-excess values increased at 9 a.m. to decrease once more between 9.30 and 10.30 a.m.

3.5.3 All Sampled Events of September 2013

From 09/09/13 onwards when the additional two *Tipping Buckets* began to collect rainwater as well, there was also a meteorological change from hot dry weather to many days of rain. With the new *ISCO* batteries and a rain event the sampling of real events was started.

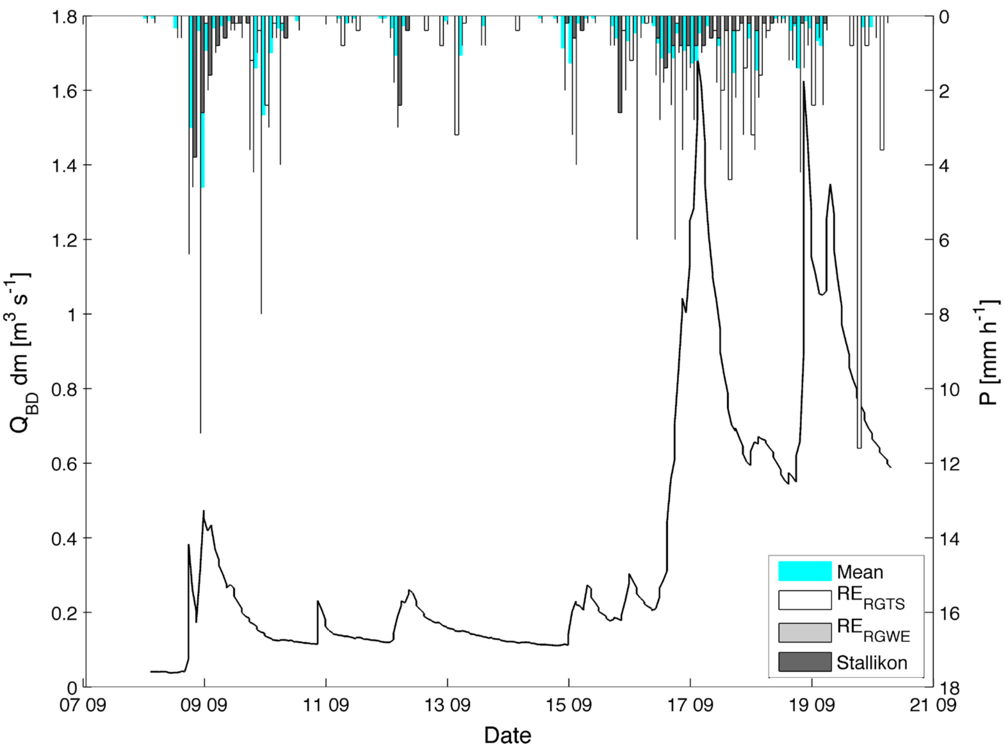

Figure 43 Time, 08 - 19/09/13, versus discharge of the Reppisch in Birmensdorf [m^3 s^{-1}] (data source: AWEL) and hourly sums of precipitation in Stallikon (data source: METEOCENTRALE), at RE_{RGTS} and RE_{RGWE} and a mean of the three rain gauges all in [mm h^{-1}].

Figure 43 gives an overview of the meteorological and hydrological situation during the event sampling period in September 2013. It represents it in the same way as, in the following graphs. Precipitation amounts recorded in Stallikon (data source: METEOCENTRALE) and at the rain gauges (own data) are presented separately. In cyan the mean of all the three amount determinations are illustrated. The black line depicts discharge in Birmensdorf (data source: AWEL).
The precipitation d-excess data in *Figures 45 - 50* is also always represented in the same way; the closer the marks of the precipitation curve are, the more intense the rain was. So the sampling of precipitation was not time-dependent like it was with the programmed *ISCO Samplers*, it was amount-dependent. One horizontal line between two marks shows the isotopic composition of 5 mm precipitation. Hence, marks depict the start and the end of a 5 mm collection. For the RE_{ISCO} depiction, one straight line indicates d-excess in [‰] of a water mixture of first six samples taken half hourly. After three hours the programme was changed to one-hour time steps of sampling. Marks indicate new bottles. All solely standing marks depict grab samples of the monitoring days before and after the illustrated event.
In the following sections, the individual events are presented separately.

3.5.4 Event of 08 - 09/09/2013

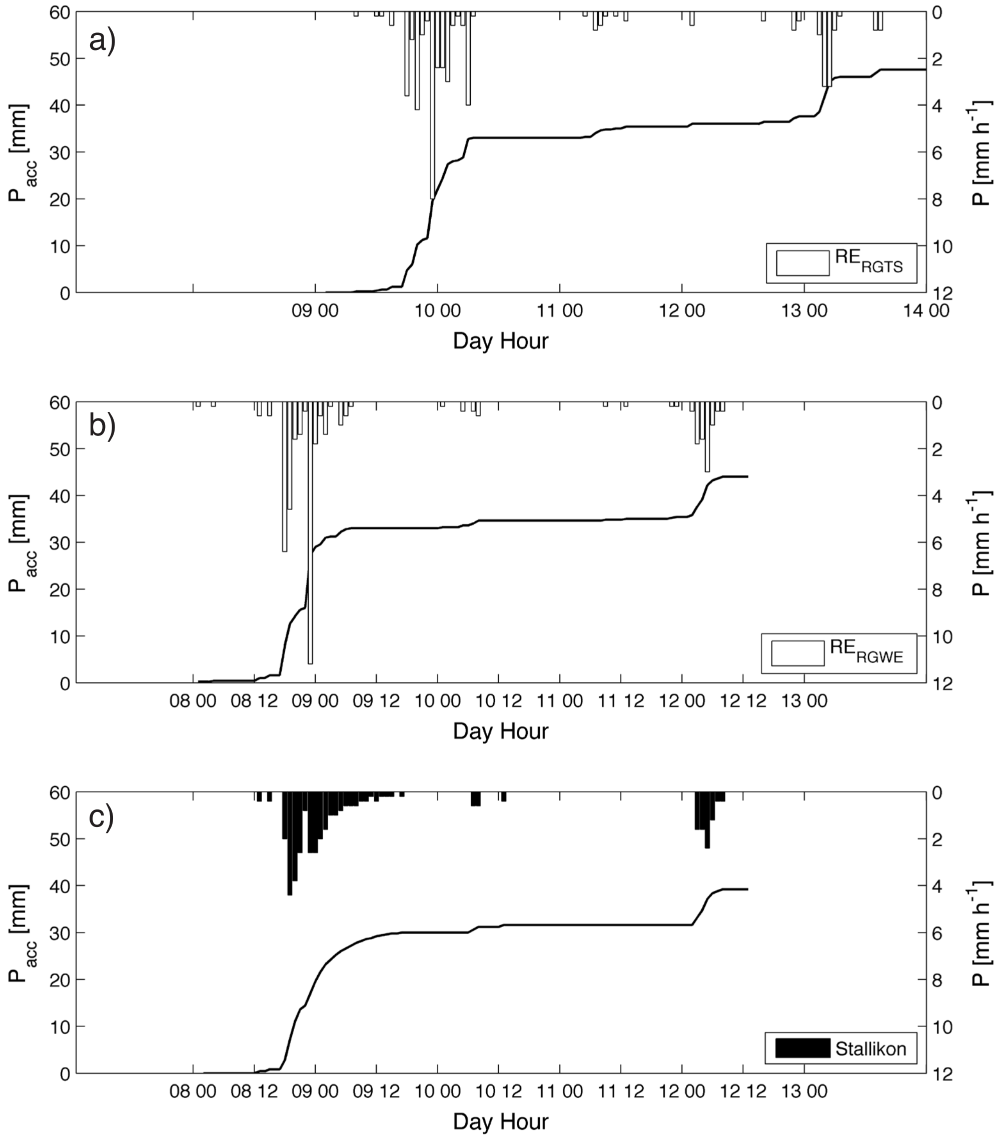

Figure 44 Time, 08 - 14/09/13, versus total accumulated precipitation (P_{acc}) and hourly precipitation rates *a)* at RE_{RGTS}, *b)* at RE_{RGWE} (own data) and *c)* in Stallikon [mm h^{-1}] (data source: METEOCENTRALE).

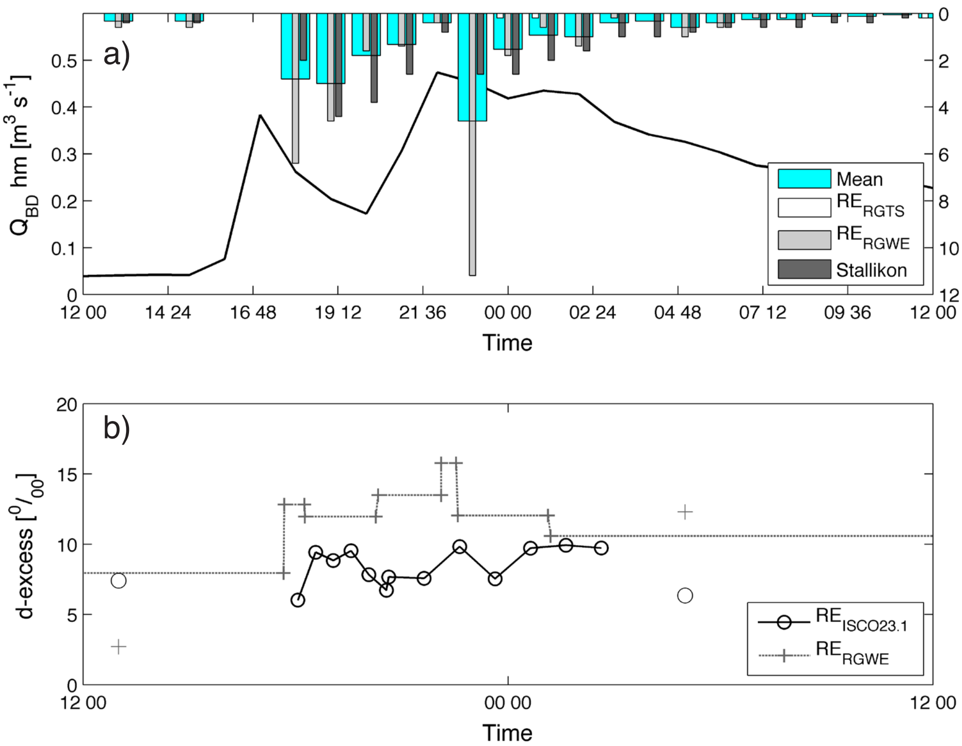

Figure 45 *a)* Time, 08 - 09/09/13, versus discharge of the Reppisch in Birmensdorf $[m^3 s^{-1}]$ (data source: AWEL) and hourly sums of precipitation in Stallikon (data source: METEOCENTRALE), at RE_{RGTS} and RE_{RGWE} and a mean of the three rain gauges all in $[mm\ h^{-1}]$. *b)* D-excess values of *ISCO* and RE_{RGWE} sampling series of 08 - 09/09/13. Solely standing marks depict grab samples of 06/09/13 and 13/09/13.

For the event of 08 - 09/09/13 the precipitation amounts collected by RE_{RGTS} could not clearly be allocated to a certain time step, because counted tips (resolution of 0.2 mm) and the collected water amount in the glasses for further isotopic analysis did not match properly. Therefore the determined isotopic composition of RE_{RGTS} was not included in the graph of *Figure 45 b)*. RE_{RGTS} started sampling anyway only on 09/09/13 (*Figure 44 a)*).

In *Figure 45 b)* the d-excess values of the precipitation are marked by an increase with on-going time until 11 p.m. Between 10 and 11 p.m., when 2.6 mm (Stallikon, or 11.2 mm at RE_{RGWE}) of precipitation was recorded, d-excess values of precipitation reached their peak at 15.77 ‰. With recessive rain, d-excess values of precipitation amounts decreased to 12.04 ‰ at midnight. Henceforward, they oscillated by little precipitation between 12 and 7.95 ‰ until 12/09/13. From then on no more rain fell at RE_{RGWE} and in Stallikon until 14/09/13 (see also *Figure 44* with P_{acc}).

$RE_{ISCO23.1}$ started sampling when the first discharge peak had already been reached. Hence, $RE_{ISCO23.1}$ took the first five samples of water portions of the falling limb. The sixth sample was taken when the discharge changed direction and rose again. The following three samples showed a tendency to increasing d-excess values at the same time like the discharge was rising too. Interestingly, at the drop of the discharge at midnight the d-excess values also reached a low point of 7.54 ‰. Again the last three samples rose and slightly decreased parallel to the discharge amounts.

3.5.5 Event of 15/09/2013

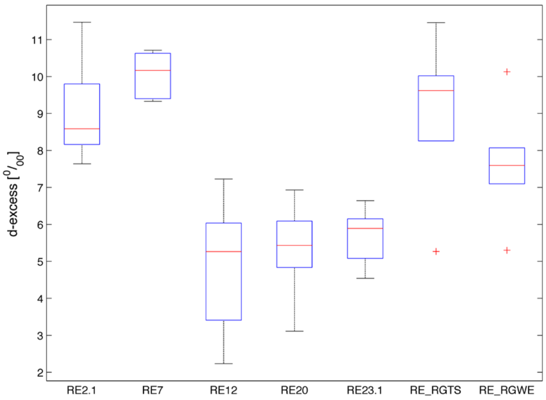

Figure 46 Variations in d-excess [‰] of all sampled components of the event of 15/09/13. The box plot of the inflow RE2.1 consists of 14 values, the inflow RE7 consists of 6 values, the Reppisch RE12 consists of 24 values, the Reppisch RE20 consists of 16 values, the Reppisch RE23.1 consists of 6 values, RE_{RGTS} and RE_{RGWE} consist of 6 values.

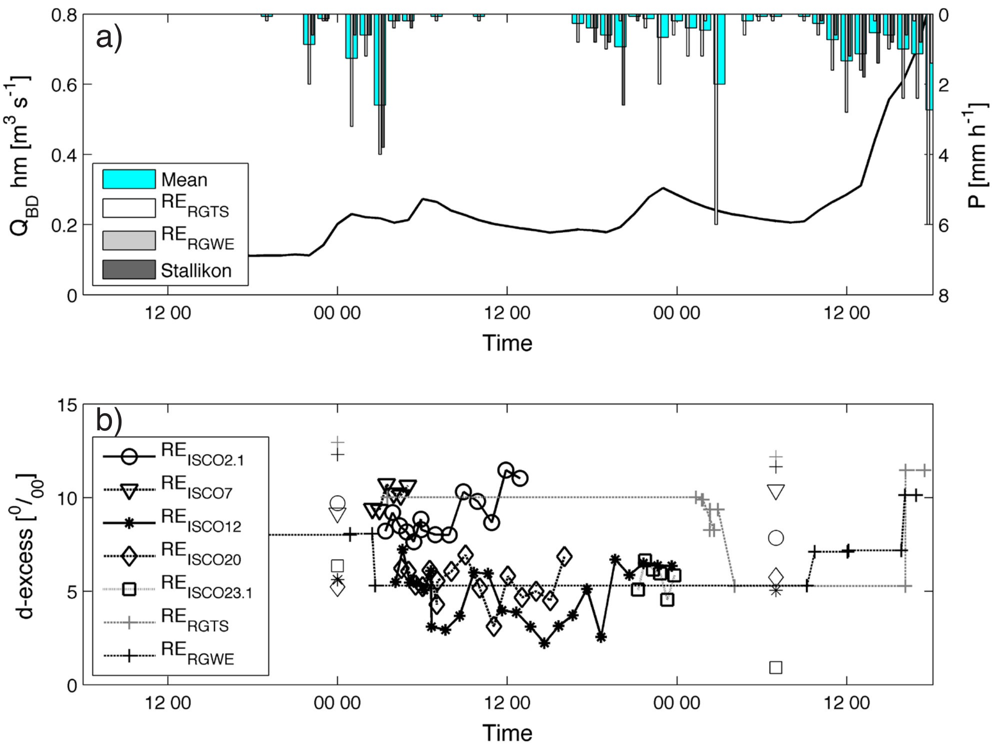

Figure 47 *a)* Time of 15/09/13, versus discharge of the Reppisch in Birmensdorf [$m^3 s^{-1}$] (data source: AWEL) and hourly sums of precipitation in Stallikon (data source: METEOCENTRALE), at RE_{RGTS} and RE_{RGWE} and a mean of the three rain gauges all in [mm h^{-1}]. *b)* D-excess values of *ISCO* and RE_{RG} sampling series of 15/09/13. Solely standing marks depict grab samples of 13/09/13 and 20/09/13.

At RE_{RGWE} and in Stallikon accumulated precipitation of 9 mm, respectively of 5.6 mm were recorded during the first hours of 15/09/13. But 0 mm were recorded at RE_{RGTS}. Anyway, these data of RE_{RGTS} are very uncertain because collected rainwater amounts did not match the number of tips. During the event of 15/09/13 d-excess values of precipitation at RE_{RGWE} did not reach as extreme values and variations as on 09/09/13. They ranged between 5 and 8 ‰. D-excess values of the inflows and Reppisch varied in the beginning with rising and falling discharge. Further at midday when discharge was still on the falling limb, d-excess values rose again. The d-excess values of the inflows and Reppisch stayed in their usual ranges of 8 to 10 ‰ for the inflows and 2 to 8 ‰ for the Reppisch respectively.

3.5.6 Event of 16/09/2013

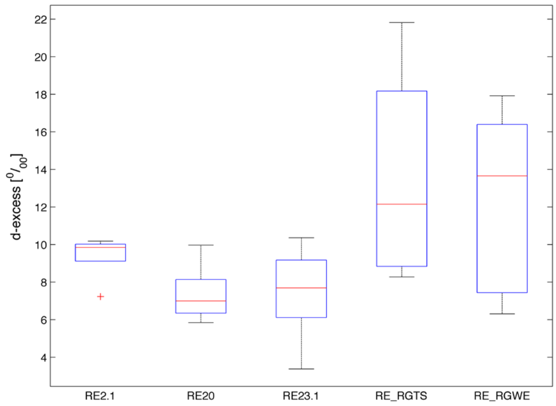

Figure 48 Variations in d-excess [‰] of all sampled components of the event of 16 - 17/09/13. The box plot of the inflow RE2.1 consists of 6 values, the Reppisch RE20 consists of 24 values, the Reppisch RE23.1 consists of 24 values, RE_{RGTS} and also RE_{RGWE} box plot consist of 9 values each. The collected data of RE_{RGTS} and RE_{RGWE} include the days until 20/09/13 and 19/09/13 respectively.

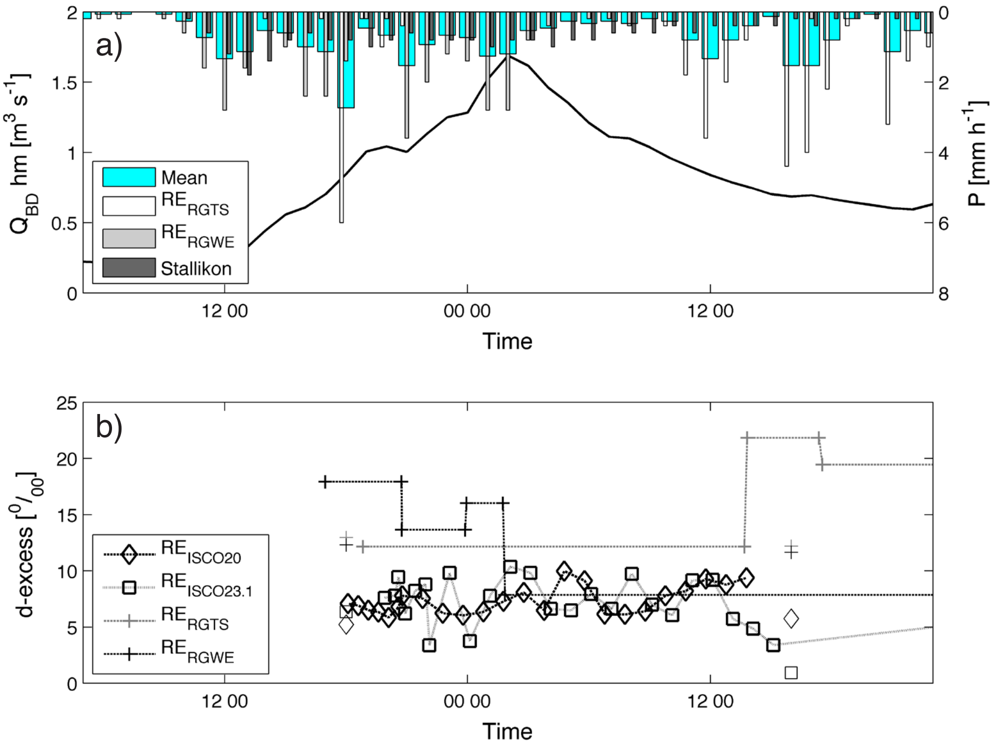

Figure 49 *a)* Time, 16 - 17/09/13, versus discharge of the Reppisch in Birmensdorf [m^3 s^{-1}] (data source: AWEL) and hourly sums of precipitation in Stallikon (data source: Meteocentrale), at RE_{RGTS} and RE_{RGWE} and a mean of the three rain gauges all in [mm h^{-1}]. *b)* D-excess values of *ISCO* and RE_{RG} sampling series of 16 - 17/09/13. Solely standing marks depict grab samples of 13/09/13 and 20/09/13.

Fot the event of 16 - 17/09/13, the d-excess curves of the two Reppisch monitoring points were undulating in the same manner like discharge in Birmensdorf (*Figure 49*). When runoff in Birmensdorf was at a changing point, either to a more increased discharge or from increasing to stable or to decreasing discharge, the d-excess trends changed as well.

Both curves of RE_{RGTS} and RE_{RGWE} were found in remarkably higher d-excess areas than for all the sampled events before. They ranged between 7.85 and 21.82 ‰ for this event and both rain collectors had a minimum of 6.31 ‰ for the event of 18/09/13. However, collected water amounts and tips at RE_{RGTS} did not come out even.

3.5.7 Event of 18/09/2013

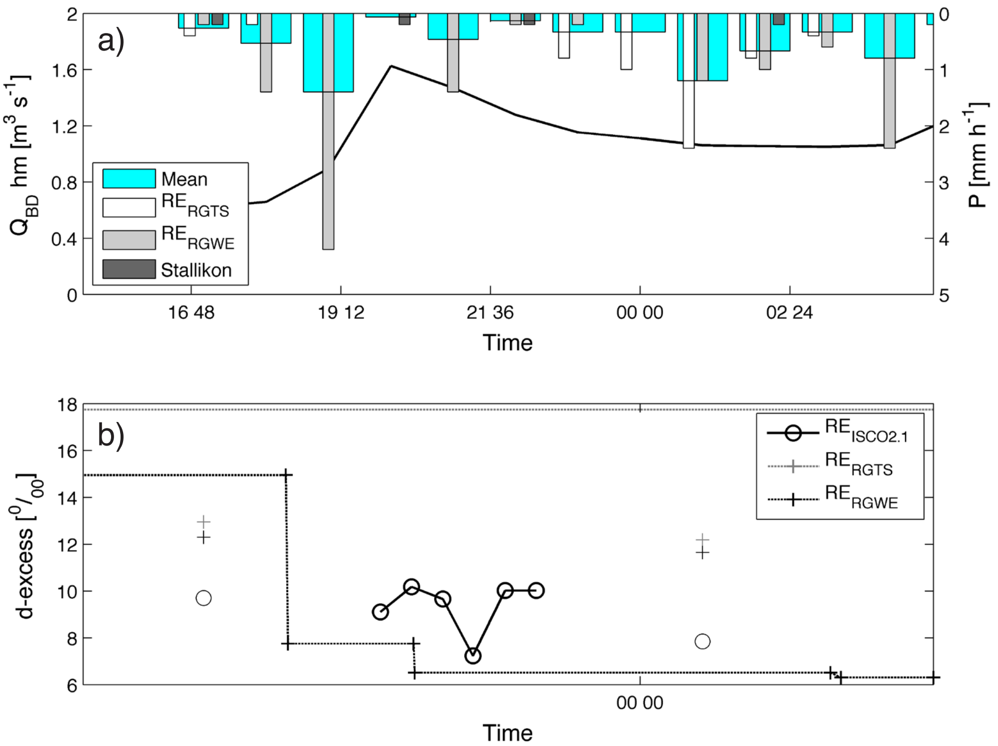

Figure 50 *a)* Time of 18/09/13 versus discharge of the Reppisch in Birmensdorf [$m^3\ s^{-1}$] (data source: AWEL) and hourly sums of precipitation in Stallikon (data source: Meteocentrale), at RE_{RGTS} and RE_{RGWE} and a mean of the three rain gauges all in [$mm\ h^{-1}$]. *b)* D-excess values of *ISCO* and RE_{RG} sampling series of 16 - 17/09/13. Solely standing marks depict grab samples of 13/09/13 and 20/09/13.

For this event of 18/09/13, data gained by RE_{RGTS} should be looked at with care again due to deviations between tips and water amounts.
At $RE_{ISCO2.1}$ six samples were taken during this event. A remarkable drop in d-excess was found at 9.19 p.m. This mark might be an outlier, although standard deviations were within the accepted range (0.01 for $\delta^{18}O$ and 0.46 for δD) . One sample before 9.19 p.m. was also on a downwards trend. Hence, the values are accepted and discussed (see *4.5 Events*).

3.6 Potential Distortions in Precipitation d-excess Data in 2013

Precipitation's d-excess data for summer 2013 showed some values which were not expected to be the signal of precipitation of the Reppisch area. The extremest calculated d-excess value of -2.75 ‰ was even lower than the lowest one of the Türlersee (-0.48 ‰).
This chapter elucidates possible reasons of how the very low d-excess values of the collected precipitation might have emerged. It compares means of d-excess values of event data with the weekly integrated signals (*Figure 51*) to evaluate if they were in similar ranges. Finally, each sample's d-excess values were compared to their according collected water amounts which were measured in the *Totalisators* (*Figure 52*). Potential correlations might be an argument for evaporation effects within the closed system of the *Totalisators* bottles.

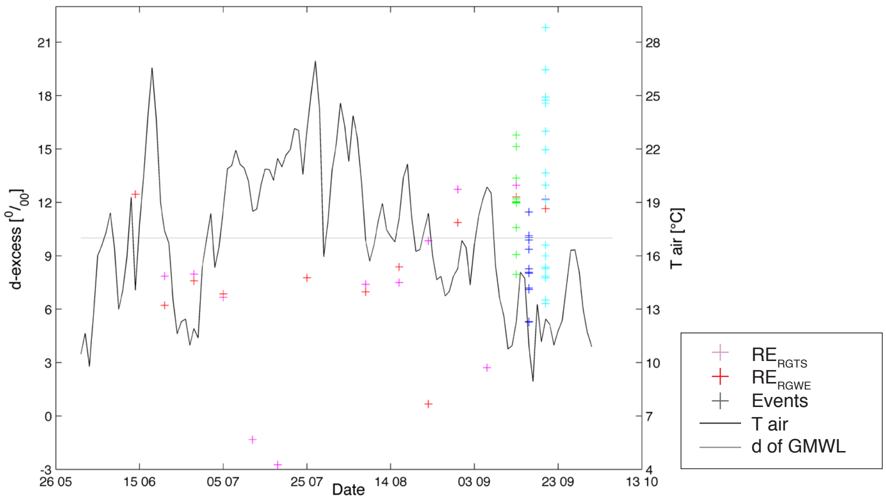

Figure 51 Time versus d-excess of collected precipitation at RE_{RGTS} and RE_{RGWE} and temperature (data source: METEOCENTRALE) in summer 2013. For September the event d-excess data of *Tipping Buckets* is added.

The d-excess values of the precipitation for the monitoring period of the summer 2013 ranged between -2.75 and 12.95 ‰ for the weekly integrated grab samples and between 5.27 and 21.82 ‰ for the sequential samples. For the grab samples, the two extreme marks of -1.33 and -2.75 ‰ in d-excess in July were taken into account, always bearing in mind that they might be outliers distorted by evaporation effects. Both samples were taken after weeks when little rain fell and temperatures rose, so that evaporation with the according fractionation could have taken place even in the collecting bottle of the *Totalisator*.
The other gained d-excess values of the integrated samples were treated as being more realistic (of course always in the discussion of how far reality can be measured) since they did not vary more than 1.3 ‰ from the means of the precipitation samples collected sequentially during events (*Figure 52*).

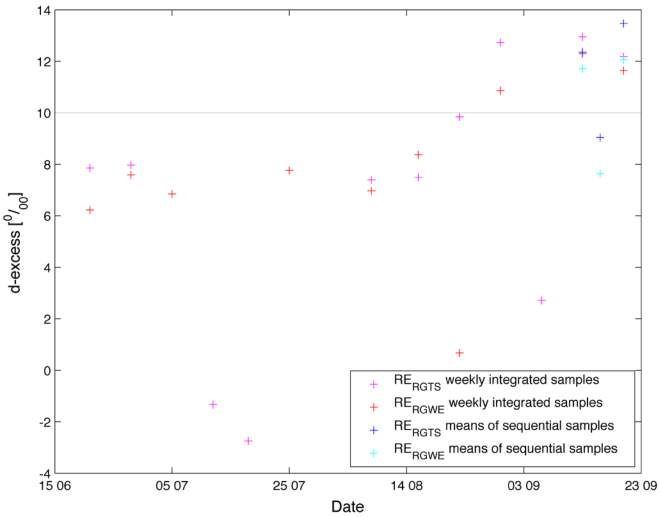

Figure 52 Time versus d-excess of collected precipitation in RE_{RGTS} and RE_{RGWE} and means of d-excess data of precipitation sequential samplers for September. The grey line depicts d-excess of 10 ‰ of the *GMWL*.

In *Figure 52* means of the sequential samplers (precipitation collection only in September) are added to weekly collected integrated RE_{RG} data. The medians of the same sequential samples are not illustrated since they do not vary more than 0.6 ‰, except for the date of 20/09/13, where the means and medians differ by a maximum of 1.6 ‰.
These values should be handled cautiously since precipitation was collected sequentially for only three events. However, for further analysis of events and the behaviour of the Reppisch basin, it was mainly important to know that the d-excess data of events was in a similar range. Hence, the d-excess values were looked at as being representative for the Reppisch area during the weeks of sampling.

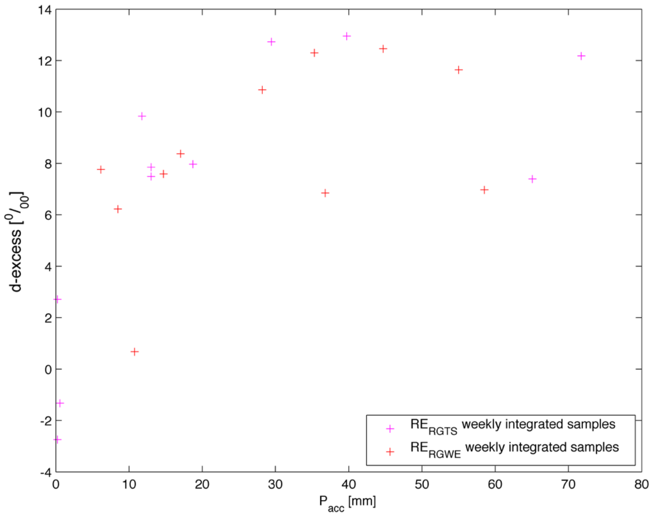

Figure 53 Collected precipitation amounts [mm] (own data) versus d-excess of collected precipitation in RE_{RGTS} and RE_{RGWE} in summer 2013.

Figure 53 illustrates the outliers of the RE_{RG} weekly data as well as the according correlation between very little input and low d-excess values. The two extreme marks of -1.33 and -2.75 ‰ in d-excess in July were both from samples of RE_{RGTS} close to the lake in an open space. The four lowest marks indicate d-excess values between -2.75 and +2.71 ‰ with the according collected water amounts of precipitation values between nearly zero and 12 mm.

4. DISCUSSION

4.1 Signal Description

4.1.1 D-excess Signals of the Observed Water Components in the Reppisch Basin

Fingerprint

The d-excess signals of all the collected water samples, throughout all monitoring periods were allocatable to Türlersee, inflows, precipitation and Reppisch and they assigned characteristic positions in the *GMWL* space (*Figure 6*). The water's journeys within the Reppisch system led to clearly distinguishable d-excess signals as well (*Figure 7*), because they varied from precipitation d-excess signals. Due to their distinctiveness, these signals could be used as fingerprints.

A nice example for the obvious signal happened, when comparing historical (2010, 2011) with actual (2013) data and taking a deeper look at RE4, a lake sample point. Not all of the signals of RE4 showed the isotopic composition which the lake was expected to have, namely somewhere around 0 to 6 ‰ in d-excess. Some d-excess signals were more like the ones of the inflows around 7 to 11 ‰. Checking up again on protocols of 2010 and 2011 brought forward two different coordinates for RE4. Some samples were not taken in the lake, they were taken in an inflow only a few meters away from RE4. In the field the coordinates that were shown by the *GPS* were probably not that exact and for new student apprentices it was not clear whether the sample point was in the lake or in the inflow. So two different coordinates emerged. However, this example shows that it was even possible to attribute mixed-up samples of the Türlersee of the summer 2011 to their real source.

Precipitation

The evolution of d-excess values of rainwater samples in the area over monitoring period 2013 was from around 6 to 8 ‰ during most of the time to quite high ones of around 12 ‰ in September (*Figures 9* and *28 b)*). Some very low d-excess values were not beyond doubt concerning the hermetic closing *Totalisators'* collecting bottles (Palmex, 2013) (see discussion chapter 4.6). Still, precipitation d-excess signals, especially the ones of the events, were distributed extensively. Like this they exemplified the characteristics of isotopic precipitation compositions, namely extreme differences which also have been observed in other studies (Smith et al., 1979, Siegenthaler & Oeschger, 1980 in Ingraham, 2006). The samples not just confirmed big variations between storms, but also intra storm variations as shown in September (Ingraham, 2006) (*Figures 45, 47, 49, 50*). Convective systems are also known to produce great variations in isotopic signals of their precipitation within small geographic scales (Miyake et al., 1968 in Ingraham, 2006). Some of the collected precipitation water in the Reppisch basin came along with midsummery cloudbursts. This might explain great variations in d-excess values and maybe even some outliers (evaporation on raindrops).

However, precipitation samples of summer 2013 should not be taken separately for further examination, because solely standing they do not reflect the isotopic compositions of average precipitation of the area and least of all a yearly scale (Ingraham, 2006). Nevertheless, for comparisons in the Reppisch basin in summer 2013, the precipitation samples nicely depict their distribution around *GMWL* (*Figure 6*) and so they contribute to the isotopic signals of the following other components.

Inflows

Shallow groundwater is said to reflect long-term average isotopic composition of precipitation in the area of interest. It should always be considered that selective recharge may distort the long-term signal (Ingraham, 2006). The distribution of d-excess values of the inflows in the Reppisch basin was actually also found within the range of the ones of the precipitation samples (*Figure 7*). Hence, many of the inflows reflected a d-excess signal which was at least close to the one of groundwater. The mean d-excess value of all inflow grab samples was 8.8 ‰ for the monitoring period 2013. This was slightly higher than the mean d-excess of 8.06 ±0.13 ‰ of precipitation collected between 2002 and 2009 at the "Isotopen Messnetz in der Schweiz" (*ISOT*) stations all over Switzerland (Schotterer, 2010).

Türlersee and Reppisch

The clear d-excess positioning of the Türlersee is also disposed in findings of other studies in Europe, for example of lake *Garda* in northern Italy (Longinelli et al., 2008). At the lake *Garda's* surface, no strong fractionation effects could be detected due to mixing with large amounts of groundwater (Longinelli et al., 2008). In contrast, the Türlersee did show clear evaporation effects. The d-excess values were even decreasing constantly during monitoring period 2013. Hence, large groundwater contributions are neglected for the Türlersee or at least if they existed so, they did not mix with its surface water.

Moreover, the Türlersee achieved slope values, the so-called *Evaporation Line*, of its isotopic composition close to lakes of other studies in remote and extreme areas. The Türlersee's isotopic composition reached a slope of 5.7 in summer 2011 and one of 4.4 in summer 2013. Even in the tropics Payne (1970) found Lake Chala of 4.2 km^2 in area in Kenya being placed in the *GMWL* space in characteristic positions of open water bodies which have undergone evaporation. Such open water bodies show slopes of 4 to 7 instead of 8 of the *GMWL* (Dansgaard, 1964). The characteristic lower slopes of 4 to 7 indicate a higher enrichment (bigger values) in D and ^{18}O, and thus evaporation effects (Ingraham, 2006).

Whereas the Reppisch's slope in summer 2013 was 5.2, the inflow's slope was 6.1 and the one of precipitation 7.9 (all collected precipitation including events). The Reppisch consequently is a mixture of all the other observed surface waters and precipitation, and of not sampled subsurface water. In *GMWL* space, Payne (1970) could distinguish clearly between the lake, spring and precipitation waters in the study site Lake Chala as well. Whereas Payne (1970) proved a disconnection between Lake Chala and certain springs, the d-excess signals of the Reppisch were nicely found to be in the centre of the other observed components (*Figures 6* and *9*). Hence, the Reppisch samples depict a mixture of the fingerprints of the other components.

It was assumed for this project that the lake's surface water was the bulk of water that provides the Türlersee signal in the Reppisch. Further researches could check these hypothesis by sampling profiles of the lake water. This should be done so in summer and winter because winter lake water circulations are artificially intensified by ventilation. During summers no anthropogenic interventions affect lake water stratification (AWEL, 2013 a)). It would be interesting to find out more on lake interactions with adjacent swamps or soil- and groundwater.

To gather all this information of course an all year-round sampling would be helpful. Additionally, the meteorological special years of 2011 and 2013 showed, that for a better comparison of seasonal and meteorological effects on d-excess signals it would be advisable to sample for several years.

Monitoring Strategy

Altogether, the sampling strategy of this project was too extensive (*Figure 6*). Weekly grab samples could already capture the d-excess signals and their changes over time. Actually, *WLPWS* samples were not necessary. For this project, their samples could confirm weekly grab signals (see *APPENDIX C)*). Hence, for further investigations in the Reppisch valley they would not be necessary anymore, because now it is known that the Reppisch system's isotopic signals do not change abruptly. An exception is found with the events. To reveal more information on the Reppisch system during events, an *IHS* should be undertaken. This would include groundwater sampling, which would also lead to a deeper understanding of the overall Reppisch basin.

4.1.2 D-excess Behaviours according to different Parameters

Time
During monitoring period 2013 d-excess values of all samples together varied gradually in their ranges with a tendency to a wider spread (*Figure 9*). The biggest range on 20/09/13 might have been either an abnormal situation or the starting point of an increased spread for the following period. This day fell into a period of dry weather after a week of heavy rainfalls (*Figure 43*). These heavy rainfalls showed d-excess values between 5 and 22 ‰. Their medians were between 9.5 and 14 ‰, depending on the sampled event. Of course, these events do not explain the lowest d-excess values at all (for instance in *Figure 16*).

Discharge Amounts
It was expected that with rising discharge amounts d-excess values rose as well and vice versa. Though such a clear trend was not detectable all over the basin and throughout the monitoring period (*Figures 10 - 13*). Sometimes an increase in runoff came with an increase in d-excess values, sometimes it came with a decrease in d-excess values. Even for certain sample points, the phenomenon lead not into the same direction throughout.
Correlations between absolute runoff rates and d-excess values could not clearly be found with the Reppisch monitoring points (*Figure 14*), nor with the inflows. The mostly random scatter confirms the sometimes parallel and sometimes reverse behaviour of discharge rates and d-excess values. Discharge-proportional water sampling could have brought more information on possible runoff rate – d-excess value relationships as recommended by Schleppi et al. (2006). Though, beneficial findings are not for sure, because the *WLPWSs* have already sampled water level proportionally. Their weekly integrated d-excess signals did not vary significantly from the weekly grab samples (see *WLPWS* in *APPENDIX C)*).

In the subsequent paragraphs connections between runoffs and d-excess values are discussed:
The parallel behaviour can be explained by rising discharges which also stand for precipitation entering the basin. Precipitation brought new water that tended to higher d-excess values than water already stored in the catchment (especially the Türlersee and Reppisch). These newly mixed waters showed higher d-excess values than waters sampled during recession curves. During recession curves water ran off that had undergone evaporation and mixing processes within the catchment for a longer time span. Most samples actually showed decreasing d-excess values when they were taken during discharge recessions.
Clear connections between discharge amounts and d-excess values could be found with data of RE5, of the Türlersee sample points in all the monitoring years and of RE2 in 2011. After downpours the lake's surface water was mixed with direct precipitation or with inflowing water (sub- and surface). Therefore, the d-excess values were higher than after days when evaporation was the predominant process. RE5 showed the same characteristic due to its position at the outflow of the Türlersee. After downpours the Reppisch discharge rates were higher as well, hence discharges and

d-excess values were both increasing.
Whereas for RE5 and the Türlersee these connections were logic, it was firstly confusing for RE2. RE2 is an inflow to the Türlersee and to which the sample point is located very close-by. The performance of RE2 in 2011 was not equally pronounced in 2010 and 2013. According to observations in the field in summer 2013 the assumption suggests itself that during low flow situations in the Reppisch the inflows did not have high runoff either. During some Reppisch low flow situations, the Türlersee water was moving into the inflow to sample point RE2. Therefore, samples were actually taken of the Türlersee surface water instead of the inflow water. This explains low d-excess values coming with low discharge rates in the Reppisch. Whilst during high flow situations samples taken at RE2 were truly samples of RE2 waters' signature.
Visually there is no slope between RE2 and the lake, and their waters seemed to exchange between each other and the swamps around as well. Due to this observed situation an additional sample point RE2.1 was added further uphill in the same inflow already at the initial monitoring period 2013.
However, one more reason for this correlation between RE2 d-excess values and Reppisch discharge rates could be that during low discharges, there was hardly any precipitation. Hence, evaporation effects could have taken place in the stream RE2 as well as in the lake. Long parts between RE2 and RE2.1 are of low slopes as well, so the water was sometimes standing. Therefore, with high discharges RE2 was fed with newly incoming precipitation, stream- and groundwater. The increased discharge rates flushed out the older standing water in the lowland part. Then the samplers' bottles were fed with fresh water with higher d-excess values than the one of the standing waters during hot and dry summer days.
In summer 2013 such a trend at RE2 was not as obvious as in 2011. Sometimes rising discharges came with rising d-excess values, sometimes with falling d-excess values and vice versa. On 05/07/13 though an interesting setting took place in the stream of RE2 and RE2.1. On that day, the Reppisch runoff rose, d-excess values of RE2.1 rose too to 11.52 ‰ while d-excess values of RE2 further downstream in the same stream sank to 9.01 ‰. This was contradictory to observations in 2011. Beside variance of measurement precision it can be explained by mentioned evaporation effects between RE2 and RE2.1. D-excess values at RE2 would probably have been even lower than 9.01 ‰, but it was mixed with the incoming new waters of higher d-excess values and did not decline further. Additionally, for the monitoring period in 2013 RE2 had a mean d-excess of 8.58 ‰ and RE2.1 had a mean d-excess of 9.52 ‰ and a double range compared to RE2. These observations are a reference to more pronounced evaporation effects at RE2 compared to upstream RE2.1.

Mentioned reverse effects are displayed as a selection of monitoring points in *Figures 10 - 12*. With reinforced discharges, the d-excess values of some inflows decreased by magnitudes of 6 ‰. Samples sometimes showed d-excess values as if they had undergone strong evaporation even though it was pouring. Due to a continuous signal of such a manner for all the samples for example on 08/08/13, bad prevention from evaporation while sampling and working in the laboratories can be rejected. In contrast, during some recession curves d-excess values of only some inflows showed a reverse effect (05/07/13).
With the information collected up to this point of the project, these reverse and parallel behaviours can only be partially explained. Therefore geographic quantity differences between the sample points are discussed in the following paragraphs.

Distances and Areas
Throughout the three monitoring years the observed summer signals were quite similar (2010 monitoring period was only July and August). *Figures 17* to *21* of distances, stream lengths and areas

versus d-excess values of the Türlersee, Reppisch and the inflows exemplify once more that the Reppisch must be a mixture of the inflows and the Türlersee and of groundwater as well.
Supplementary the three years showed a trend in gradually rising d-excess values of the Reppisch samples with growing distance from the lake downstream the Reppisch. This increase seemed to stabilise around RE15.
Between the inflows RE11 and RE14, there was a slight saltation to lower d-excess values (*Figure 8*). This explains partially why d-excess values of the Reppisch stabilised around RE15. From this point on, the d-excess difference between the inflows and the Reppisch were not big enough anymore to keep on tearing the Reppisch's d-excess signal curve into higher magnitudes.

The spread of the d-excess values with growing catchment areas and distances did not become obviously wider or narrower. Taking out the outliers in *Figures 20* or *21* would narrow the spread of course. Though it would affect both spreads of the inflows and Reppisch signals and not lead to new conclusions. In contrast, Didszun & Uhlenbrook (2008) found that silica concentrations changed with scale. Therefore, for the Reppisch basin, area thresholds were looked for as well. But, as mentioned earlier, changing specific discharges or d-excess signal scatters with changing sizes were not clearly deduced. Local effects of the vegetation, soils and geology have more pronounced influences in the magnitude orders of the Reppisch valley. Such local influences might be blurred and relatively decreased when talking about catchment sizes of several dozens and hundreds of square kilometres like in other projects (Didszun & Uhlenbrook, 2008). Findings in the Reppisch basin though, question these effects anyway. Growing influences of urbanisation with growing catchment sizes (Didszun & Uhlenbrook, 2008) do already have an (important) influence in the small subcatchments of the inflows in the Reppisch basin (see discussion on RE11 and RE14, next subchapter).
Instead of geometry-linked tendencies, comparisons of specific discharges brought up once more the often observed bend in d-excess data between RE11 and RE15 (*Figure 25*). With specific discharges it became visible which parts of the Reppisch basin were more active relative to other parts within the basin.
For example, RE14 at 10 km distance had very low discharge rates per area, namely 1.5 l/s/km^2, whereas RE7 and RE11 drained 5 l/s/km^2 (these are all medians of Q_{spec}, own data). A comparison illustrated as box plots in *Figure 8* showed that interestingly RE7, RE11 and RE14 also varied quite strongly in their d-excess values. RE14 provided less scattered d-excess values than RE7, and a 0.79 ‰ lower median than RE11 (median 9.13 ‰).

Characteristics of RE11 at RE14

RE11 must have played an important role as trigger in changing the Reppisch d-excess signals remarkably. The inflows RE11 and RE14 acted similarly during monitoring period 2013. Their d-excess signals mainly varied parallel with each other. RE11 mostly showed d-excess values lifted up by about 2 ‰ compared to RE14.
RE11 has a subcatchment area of 1.27 km^2, RE14 has one of 0.8 km^2. They are comparable in their geological setting. Clay, silt and sand build up the grounds on the plateau of their sources (Peyer et al., 1988). Nonetheless, their specific runoff definitely differed.
One reason for this disparity in runoff behaviours could be found in the soils that are categorised to be of medium thickness in RE11 subcatchment compared to shallow soils in RE14 subcatchment (Swisstopo, 2013).
Probably the biggest influence was induced by anthropogenic sealing of the grounds. In RE11 subcatchment many streets and houses are found, whereas in RE14 there are no houses and only one street. In other studies lowest pre-event contributions to stormflow have been observed among

others in urbanised and agricultural areas (*Horton Flow*) (Buttle, 2006). Hence, the constructions in RE11 subcatchment might as well be the reason for higher d-excess values. Event water runs off quicker than in RE14 catchment, so d-excess values of RE11 were closer to precipitation d-excess signals. Also Scherrer (2006) found more areas in RE11 catchment to be "slightly delayed contributory" ("leicht verzögert beitragend") than in RE14, where relatively more areas are categorised as being "delayed contributory" ("verzögert beitragend").
For instance, on RE11 and RE14 the sampling day of 05/07/13 showed samples of the already mentioned reverse behaviour compared to the other monitoring days. When strong rainfall took place, RE11 and RE14 delivered water of lowered d-excess values. Whilst at RE11 d-excess values decreased from 9.41 ‰ at 28/06/13 to 8.46 ‰ at 05/07/13, they decreased at RE14 from 9.02 ‰ to 3.78 ‰.
RE11 contains some swamps in its source area and one arm of RE14 origins in a pond. Heavy rainfalls could have flushed out these reservoirs where before evaporation had taken place. Hence, increased runoffs sent an evaporation signal (lower d-excess values) instead of an event signal (higher d-excess values). This interesting situation confirms that during events saturated areas are often declared as a source of rapid streamflow generation in a catchment (McGuire & McDonnell, 2007).
At RE11 also precipitation came to quicker runoff than at RE14. A mixing of rain and swamp water may explain the smaller decrease in d-excess than at RE14. Additionally, at RE14 the possibly washed out pond, could have undergone stronger evaporation processes than the swamps in RE11 subcatchment. Such reverse situations were also observed in d-excess signals for the monitoring period of 2011.

Characteristics of Türlersee Portions
Mixing ratios calculated according to subcatchment areas, showed as well that from RE15 onwards tributary waters should constitute more than 50 % of total Reppisch water (*Table 5*). From there on, the Türlersee signal should make less than half of the total signal and therefore be predominated.
This bend was again detectable in *Figures 22* and *23* where distance versus all discharge measurements of 2013 for the Reppisch and the inflows are illustrated separately. At RE15 there was truly an expansion of the Reppisch discharge rates. Although it was not at RE11 (distance 8 km) where the highest inflow rates were found, it could still be triggered by the inflow RE11. Because, between RE11/12 (8 km) and RE14/15 (10 km), no measurements were undertaken.

In Figure 27 the rising limbs of the Reppisch runoffs, are depicted by anticlockwise distributed marks of the Türlersee portions. They illustrate an anomalous behaviour of the Reppisch basin when storages were filling or emptying. Such hysteresis was as well observed between riparian zone runoff and catchment runoff (McGlynn & McDonnell, 2003). With the rising limb of the catchment runoff, the riparian zone runoff was found to increase disproportionately, whereas on the falling limbs riparian zone runoff decreased to relative smaller portions of total runoff. The authors argued that hillslope zone runoff was firstly buffered by riparian zones. However, these findings were in a clockwise manner. The clockwise situation in the Reppisch basin is illustrated by the relationship of Reppisch runoff rates with all the other tributary portions instead of the *Türlersee* portion (*Figure 54*). During rising limbs their contribution to total Reppisch runoff was greater than at equal discharge rates on the falling limb (*Figure 54*, grey arrows). The opposite situation took place for the Türlersee.
Tributary flows in the Reppisch basin constitute of surface and subsurface contribution to the Reppisch, hence also riparian zones. Altogether, they confirm the hysteresis findings of McGlynn & McDonnell (2003). Additionally, the findings in the Reppisch basin induce that on rising limbs

different mechanisms of runoff contributions must be activated than during recession limbs.

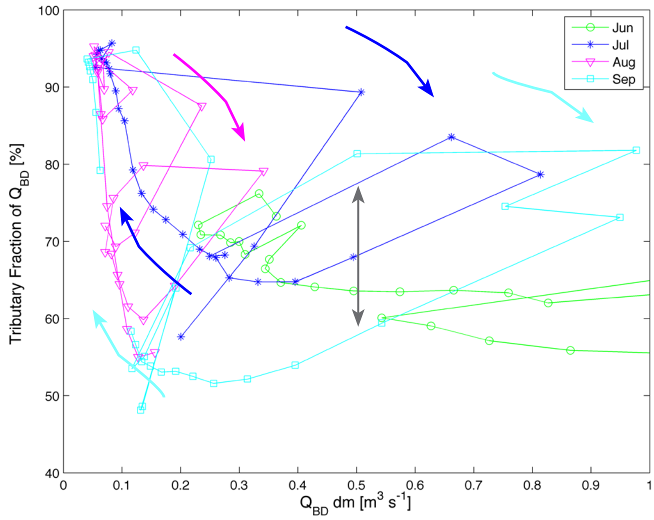

Figure 54 Daily mean discharge in Birmensdorf in [$m^3\ s^{-1}$] (data source: AWEL) versus contribution fractions (tributary flows = Q_{BD} - Q_{TS}) of total daily mean discharge in Birmensdorf in 2013. The coloured arrows indicate the clockwise hysteresis. The grey arrows depict different portions at the same runoff rates.

The sudden change in discharge portions (*Figure 27* and *54*) was induced by fast rising stages in the Reppisch which were triggered by events. Discharge portions were firstly not entirely clear. Because as mentioned earlier, according to the *AWEL* data, the runoff peak at the lake's outflow was reached in delay compared to the peak in Birmensdorf. Therefore, the comparison and calculation with daily mean discharge amounts led to delayed peaks of approximately one day. In order to account for these discrepancies, discharge portions on rising limbs should better be calculated with hourly means. Then a conclusion on the behaviour of the system during rising stages would be easier to draw. However, after some days, discharge recessions found back to their clearest proportion curves (*Figure 54*).

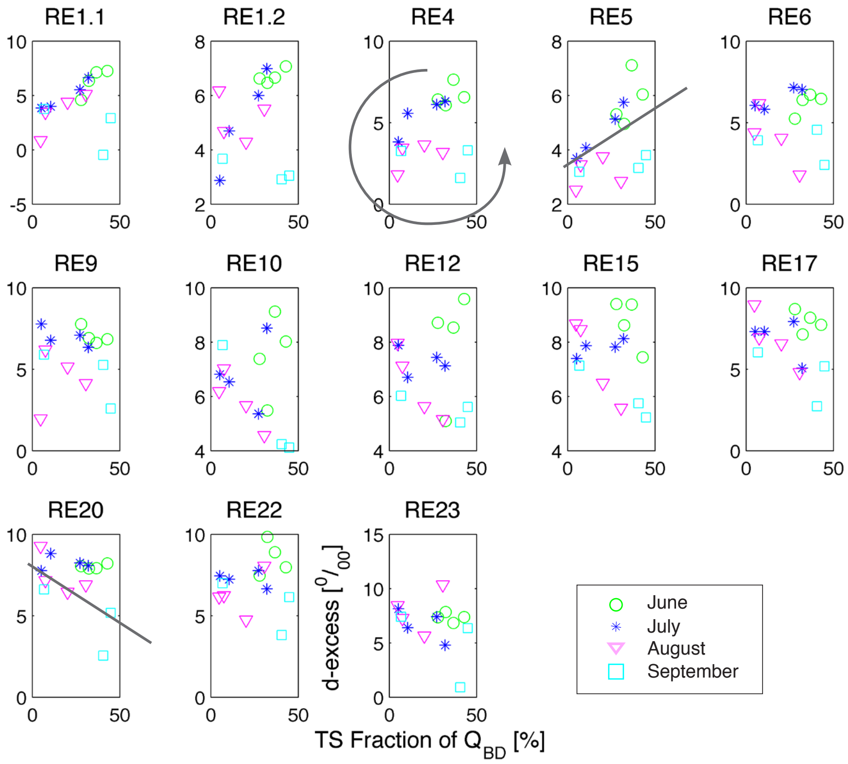

Figure 55 Türlersee fraction of daily mean discharge in Birmensdorf [$m^3 s^{-1}$] (data source: AWEL) versus d-excess of all the Türlersee (RE1.1, 1.2, 4) and Reppisch sample points in 2013. The grey circle points out the distribution of the months from June to September. The grey lines depict TS fraction – d-excess values tendencies.

Comparing the isotopic signals of the Reppisch sample points separately with coloured months, let appear in *Figure 55* that the individual months showed different behaviours. The runoff fraction signals varied among the months and so did the d-excess signals. The range in the Türlersee fractions rose from June until September (*Table 7*).

RE5 was most strongly influenced by the lake. Low d-excess values came with low Türlersee fractions and higher d-excess values with higher fractions (*Figure 55,* grey line at RE5). The Türlersee d-excess signals were clearly connected to its portions in the Reppisch. This is logical when higher discharge fractions are assumed to come with precipitation or increased inflow rates of higher d-excess values.

Valley downwards at RE20 a new pattern appeared: With highest Türlersee portions, lower d-excess values were measured (*Figure 55,* grey line at RE20). This is most pronounced at the lower border of the scatters. This pattern shows that a mixing of relatively higher rates of Türlersee water of low d-excess values with relatively lower rates of tributary waters of higher d-excess values led to the opposite relationship between Türlersee d-excess signal and discharge proportions.

As classified by Scherrer (2006), the Türlersee belonged to the discharge type of "quick and strong contribution" ("rasch und stark beitragend"). Effectively, this was confirmed by the disproportionally rising Türlersee fractions with increased runoff rates (*Figure 27*). For example, the Türlersee fraction rose from 19/09/13 to 20/09/13 from 27 to 41 % and stayed on a high level above 40 % during the following 12 days. Its signal reached Birmensdorf with an intensity that was not seen throughout the entire monitoring period 2013. At the same time the Türlersee reached the lowest d-excess values between -0.48 and 2.91 ‰ on 20/09/13. The ones of all the Reppisch samples varied between 0.92 ‰ at RE23 and 5.74 ‰ at RE15 on the same day. The low and even sinking d-excess values of the Reppisch can not be explained by some exceptionally low inflow d-excesses as on 05/07/13. On 20/09/13 they were in their normal ranges. Measurement errors can not explain this special setting either. The standard deviations of the measurements were in the accepted ranges of being lower than 0.05 for $\delta^{18}O$ and lower than 0.6 for δD. Possible explanations for this newly sinking d-excess values in the Reppisch could be evaporation effects happening in the Reppisch or other small inflows of unknown d-excess signatures which fed the Reppisch as well.

The series sampling in September confirmed above discussed hypothesis of decreasing d-excess values in the Reppisch coming together with increasing Türlersee portions: At $RE_{ISCO23.1}$ the d-excess values decreased from 7.25 ‰ on 20/09/13 (samples were taken few hours later than the grab sample of 20/09/13) to 3.27 ‰ on 23/09/13. Runoff was decreasing as well and no precipitation fell during those days. In return, inflow portions in the Reppisch were decreasing and observed Türlersee fractions were increasing from 43 to 48 % during the three days. During the following hours, d-excess values of the other *ISCO* series samples ($RE_{ISCO23.1}$ ran out of power) rose again (*Figure 61* in *APPENDIX B)*). This implies that the Türlersee portion started to sink again. Effectively, observed discharges (data source: AWEL) confirmed decreasing Türlersee portions.

When discussing the characterisation of the months in the Türlersee's portions in the Reppisch, the varying specific discharges, varying d-excesses over time and space, and the days of very special signals and settings, the very important topics of meteorology and antecedent conditions were still excluded. Although, all influences together form the measured isotopic composition of a certain water sample. They can never be looked at in isolation. Only by involving all the formers of an isotopic composition, a specific behaviour maybe comprehensible.

4.2 Hydrology meets Meteorology

Some of the many responsive factors for enhanced or reduced evaporation and the according fractionation of water molecules are the temperature and the ambient humidity (Ahrens, 2009; Kendall & Caldwell, 1998). For the Reppisch basin, precipitation, temperature and relative humidity data of the observation station in Stallikon of the monitoring period 2013 were kindly provided by Meteocentrale. This data is discussed in its causes and effects on the collected isotopic data in the following paragraphs.

4.2.1 Precipitation, Air and Lake Temperatures

The Türlersee did react quite clearly with precipitation and temperature changes (*Figures 28 a), b)*). By the end of July it rained and evaporation effects decelerated and so did the d-excess values of *Türlersee* surface waters in its downward trend (*Figure 28 b)*, third segment of red line). Mixing of newly incoming water with lake water of lower d-excess values even led to shortly rising d-excess values of the lake samples between 25/07/13 and 08/08/13. An additional reason for this rise in d-excess values of the lake's surface water could be the slightly lower air and lake temperatures compared to 12/07/13 and 25/07/13. Cooler water is less prone to evaporation than warmer water (Kendall & Caldwell, 1998). Hence, less additional kinetic fractionation modified the lake's d-excess signal.
However, this trend decelerated in September. The d-excess values of the Türlersee and accordingly of the Reppisch were decreasing again. The air and lake temperatures were descending as well. Finally, there was no obvious direct connection between temperatures and d-excess signals of the lake and the Reppisch anymore. In contrast, d-excess values of precipitation and of the inflows rose in September. They confirmed possible temperature-dependant decelerated evaporation signals.

The overall downward trend of the Türlersee d-excess values was surprising: *a)* The d-excess values did not rise with lowering temperatures from 14/08/13 on (*Figure 28 b)*). *b)* They were slightly higher at lower temperatures *(Figure 29 b),* temperature-d-excess relationships). *c)* They did not rise with admixture of newly incoming water of higher d-excess values.
The Reppisch d-excess values behaved similarly, which was mainly due to the influence of the lake's d-excess signature.
a) and *c)* may be answered by their strength: *a)* Although day and night temperatures differed in September more than in midsummers, their decreases were not big enough to slow down the strong evaporation of the Türlersee. Hence, despite decreasing daily mean temperatures, daytime evaporation was still strong. The temperature peaks of midsummer character of up to 26 °C contributed as well to strong evaporation in September. *b)* Only five of 15 monitoring days took place at daily mean air temperatures between 12 and 16 °C. The other ten days were at temperatures between 16 and 23 °C. Hence, the samples distribution among temperature situations of nine to 27 °C daily means was not balanced. *c)* Newly incoming water (precipitation and inflows) of higher d-excess values do mix with the lake surface water, but these incoming components are not strong enough. They might not have been of big enough water amounts to rise d-excess values of the lake. And additionally, the lake's d-excess values are the signature of surface waters. Newly incoming water could have been colder than lake water and hence did sink below surface water. The sampled surface water kept its isotopic signature.
Another explanation for no elevation of the d-excess values of the Türlersee in September 2013 suggests itself that even though the Reppisch catchment is a small area of 24 km^2, precipitation

was not distributed evenly. During monitoring period 2013 strong discrepancies between measured precipitation in Wettswil (RE_{RGWE}), Stallikon (by METEOCENTRALE) and at the Türlersee (RE_{RGTS}), became especially obvious with events (for instance *Figure 44*).
Also for example in summer 2011, precipitation sums recorded in *Stallikon* (by METEOCENTRALE) and Birmensdorf (by AWEL) differed in June by 20 mm/m and in July by 30 mm/m, whereas in August and September they differed by three and seven millimetres per month (data source: METEOCENTRALE; AWEL, 2014b).
The local topography like the length of the catchment and its south-north distribution between two ridges, might strongly influence local meteorology. Therefore, local variabilities in precipitation intensities and intra storm variations are assumed to be probable. Meteorological variations, especially with thunderstorms, should be captured adequately at least with three *Tipping Buckets*. The third one should be positioned in the lower part of the valley to account for isotopic variations in precipitation also there.

Summarised, changes in d-excess with temperature can only be detected when considering them over time. Isotopic signals always comprise several processes and not just a snapshot of temperature when sampling a certain moisture.
This fact comes out more clearly with *Figure 29 a)*, where weekly (and not daily as before) mean air temperatures are compared to the weekly integrated bulk samples of precipitation. They show a tendency from higher d-excess signatures of 8 to 12 ‰ around 13 °C to lower ones of -2.75 to 8 ‰ around 20 °C. These findings of course are snapshots too, though snapshots which already include waters and temperatures that represent a mixture of one week of precipitation and temperature happenings. However, beside ambient temperatures as a trigger of variations in d-excess of precipitation, precipitation's d-excess values are also a complex reflection of the water vapour's source, of temporal variations in climate and rainfall seasonality and of the local geography (MCGUIRE & MCDONNELL, 2007). Differences in d-excess between the specific rain samples are not just explained by temperatures, but also by many other factors having influenced the incoming moisture.

4.2.2 Relative Humidity

According to literature it was expected that the higher the ambient humidity is, the less fractionation would take place, because more humid air can take less additional humidity and less D and ^{18}O would exchange (KENDALL & CALDWELL, 1998). Surface water data of the summer 2013 (*Figure 31*) did not clearly confirm this humidity-dependant lowered fractionation signals. Neither when they were looked at separately as a relationship of absolute values between relative humidity and d-excess (*Figure 32*). This might be again due to the uneven distribution of monitoring days along the relative humidity situations (*Figure 33*). Another reason could be that the humidity-evaporation relationship as well depends on actual temperatures, though both were looked at separately (KENDALL & CALDWELL, 1998).
The d-excess values of the lake and the Reppisch behaved sometimes contradictorily to the rising and sinking of daily mean relative humidities. In contrast for the inflows and precipitation, their evolution over time in d-excess values seemed to rise and sink unidirectional with the mean daily relative humidity. Bearing in mind that this illustrated sensitive reaction to changes in ambient humidity is always also a signal in relation to the setting before a certain monitoring day.
Finally, the weekly integrated rainwater samples (*Figure 32 a)*) exemplified the expectations according to KENDALL & CALDWELL (1998): Their d-excess values rose with growing weekly mean relative humidity. This implies, that rainwater samples collected in periods of higher relative hu-

midity of 80 to 92 % have undergone less fractionation while their condensation in the atmosphere or while evaporation from their moisture's source than the ones at lower relative humidity around 65 to 77 %. Despite these confirmations, we bear in mind that again the bulk of water samples were collected at relative humidities of 70 to 80 %. Additionally, the here discussed relative humidity might have less influenced the precipitation's fingerprints than the actual relative humidities during precipitation formations.

Weekly means of relative humidity brought up that the Türlersee's and the Reppisch's d-excess signals were even more contradictory to above expected relationship. On the other hand, they confirm findings of Merlivat & Jouzel (1979) saying that the effects of kinetic processes are inversely related to relative humidity, hence the Türlersee's d-excess values became smaller with increasing relative humidity (*Figure 31 a)*).
Relative humidity affects differently the various evaporation processes and leads into differently modified isotopic signals (d-excess, slope). Therefore, these findings will not be discussed more profoundly, because the time and intensity magnitudes of ambient humidity needed to evidently influence a certain surface water body within the setting of the Reppisch watershed are topics beyond this thesis.

The relationships between relative humidity and d-excess values should not be looked at with too narrow perspectives. Because in *Figure 6* the Reppisch and the Türlersee actually do show deviations from *GMWL*, especially with on-going times during summers. By the end of the summers they had deviant signals of drier regions like the rivers *Rio Grande* and *Darling* in the *U.S.* and *Australia*, whereas at the beginning of the monitoring periods they lay on the *GMWL* like the *Amazon* river in a very humid area (Sahra, 2005).

4.3 Antecedent Conditions

In the discussed reactions of d-excess signals to geographical, meteorological or hydrometric variations, the finding came up that looking solely at a certain parameter did not explain the entire isotopic signals. The isotopic composition of a certain water sample is a complex reflection of its pathways. Meteorology is not terminated: the chapter *Antecedent Conditions* takes the setting that was shaped previously to a sampling day of the Reppisch basin into account.
Antecedent conditions were determined by the behaviour of the catchment to precipitation and dry periods and by the current precipitation. Actual temperatures, humidities or winds were not considered with the here used *Current Precipitation Index* (*CPI*). Still, *CPI* serves as a perception of what conditions were set within the Reppisch valley while sampling its components.

4.3.1 CPI7, Discharge, Baseflow and Stormflow Situations

The distribution of all *CPI7*-classified samples in the *GMWL* space (*Figure 37*) and with baseflow/stormflow classification (*Figure 39*), showed scatters where the "dry" class was set in the centre and the borders were marked by "humid" and "wet" conditions.
Different processes must have led to the isotopic signatures of the scatters' borders. Higher d-excess values were expected to come together with newly incoming precipitation. This explains the upper border of the scatter in *Figure 39* and the lower border of the scatter in the *GMWL* space (*Figure 37*). In the *GMWL* space these marks were the ones of "wet" conditions and of precipitation with higher d-excess values, coming from farther sources or cooler conditions (areas, periods) (Ingraham, 2006). The lower border of the Reppisch scatter showed the signal of the Türlersee (see chapter 4.1.2 *Characteristics of Türlersee Portions*), because during those events, grounds were wet and could not take any water anymore. Hence, precipitation mobilised the surface water of the lake, which had undergone evaporation prior to the event. A confirmation of this hypothesis is also that on sampling days when conditions were "wet" also highest Türlersee fractions took place (between 32 and 45 %, *Figure 56* blue ellipse).

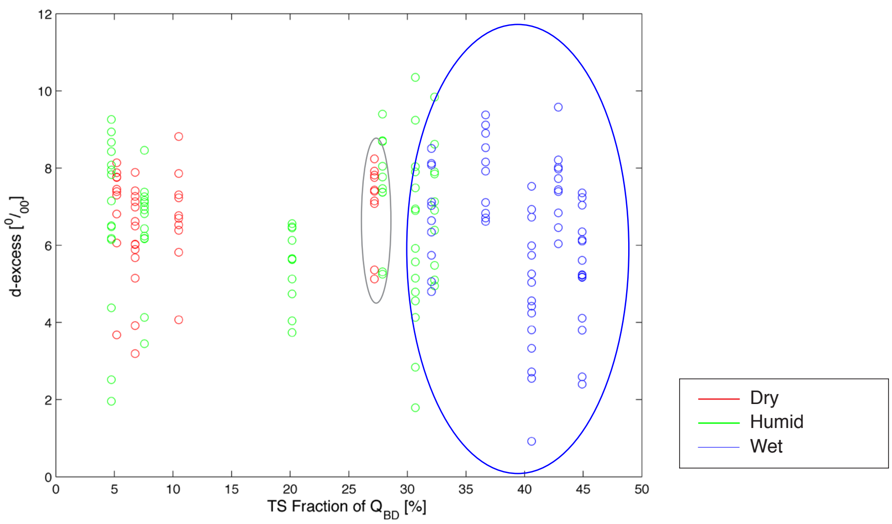

Figure 56 Türlersee fraction of total daily mean discharge in Birmensdorf [$m^3 s^{-1}$] (data source: AWEL) versus d-excess of all Reppisch samples in 2013 (except events). Colours indicate *CPI7* classes. One vertical line of marks represents one sampling day. The grey ellipse indicates the monitoring day of 30/08/13.

When further comparing d-excess emergence over time the sudden change in July from “wet” on 05/07/13 to “dry” on 12/07/13 (*Figure 38, Table 10*) can be explained by the limitations of the *CPI7* moving window of seven days. Hence, strong precipitation of eight days before the actual day was not taken into account anymore by the moving window of seven days. Thus the actual day fell abruptly into a dry setting *(*see also *APPENDIX C))*.
For the sudden class change on 30/08/13 (*Figure 56*, grey ellipse) it was assumed that precipitation at a time shortly lead to a rise in *CPI7* and discharges, even though actually, the area was on its way to dry. The d-excess values confirmed this trend by shifting their range. The lowest values were not as low as during the week before and the highest were higher. Both can be explained by the newly incoming precipitation of higher d-excess values.

Türlersee Portions
June and July, in which the Reppisch basin setting that was hit by heavy rainfalls was emptying, were positioned in lower Türlersee fractions than August and September (*Figure 40*). These months were additionally marked by very low Reppisch discharge rates. August and September were also hit by strong rainfalls and dry periods, but the basin setting was not changing from very extreme precipitation amounts to very extreme dry conditions. It was rather oscillating between dry and wet days.
These different settings of August and September must have led to usually higher Türlersee fractions. Whereas for example when 0.15 m^3/s ran off the Türlersee, in June this was 31 % and in September 48 % of total discharge in Birmensdorf. So during June and July between the Türlersee and Birmensdorf there was relatively more water added by inflows and groundwater than during August and September. This is contradictory to the dry conditions in July. Except, if groundwater of the valley bottom does replace missing surface inflow water.
In the first week of July which was classified as being dry (12/07/13) the stage in the Türlersee (own observations) was still “high” (126 cm) compared to the following eight weeks (118 - 120 cm). According to the stages which ranged from 123 to 140 cm between 07/06/13 and 12/07/13, the following hypothesis emerges:
For the summer 2013 high stages in the lake came together with low Türlersee fractions in the Reppisch and vice versa. If lake stages were used as an indicator for conditions in the whole basin, then this would mean that when stages are low, there is not much water stored in other parts in the basin either and the lake’s contribution to Reppisch discharges is relatively higher.
According to different yearbooks of the stages of the Türlersee and its runoff amounts (AWEL, 2014a), they really can vary. Same stages must not produce same discharge rates.

Isotopic data though does whether reject nor confirm above discussed influences of groundwater. The Reppisch samples of the dry periods of the last week in July and of September lay almost in the same d-excess ranges (*Figure 57*, grey ellipse). Also their lake stages were almost equal (119 and 118 cm), although not their mean daily discharges. Probably, with more *CPI7* classes, they would not have been put into the same category. Because obviously, the different discharge rates are results of different antecedent conditions, and thus different basin settings.

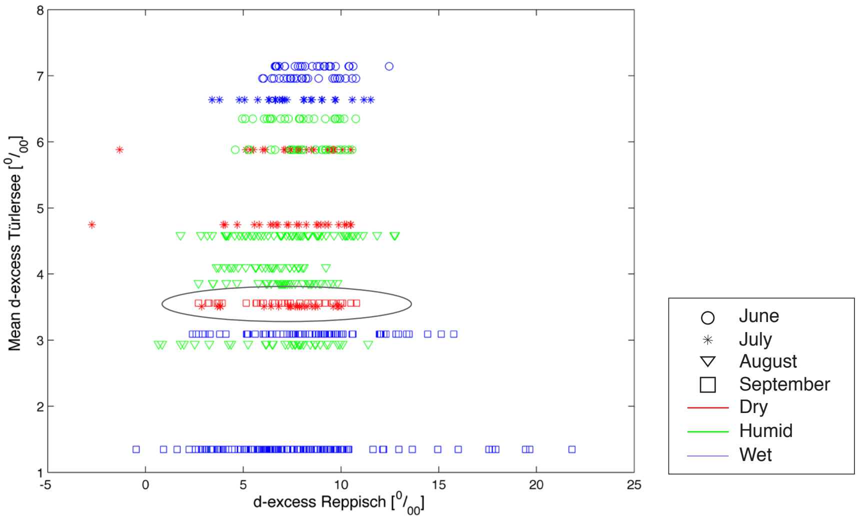

Figure 57 The d-excess of the Reppisch sample points versus mean d-excess of the Türlersee. The coloured marks indicate *CPI7* classes of the monitoring period 2013.

4.5 Events

In the subsequent paragraphs the events sampled in August and September 2013 are discussed qualitatively and elucidated in the context of the Reppisch basin.

4.5.1.1 Event of 24/08/13

The first sampled event of 24/08/13 showed d-excess values at RE_{ISCO12} (Reppisch) that confirmed above discussed influences of the Türlersee portion in the Reppisch. Namely, the Reppisch's d-excess values decreased from 7.21 to 5.78 ‰ parallel to sinking discharge in Birmensdorf between 3 and 6 p.m.. This confirms that when discharge recession takes place at already low discharge rates in the Reppisch, Türlersee portions do not recess at equal rate, so it relatively delivers a stronger signal. Therefore d-excess values of the Reppisch descended during those hours. They also rose again (only one value though) while the discharge stabilised for one hour at 6 p.m..
The low baseflow d-excess values between 3 and 4.5 ‰ in the inflow at $RE_{ISCO2.1}$ (*Figure 41*) were rarely found within ranges of other samples at RE2.1 (*Figure 8*). Several reasons – from suggesting itself to adventurous – may explain this special setting during 24/08/13 event: *a)* Evaporation and fractionation effects within *ISCO* bottles: Bottles were not emptied immediately after the event. *b)* Sampling of pre-event water: Before the event of 24/08/13 the weather was dry and marked by high temperatures, so evaporation and fractionation induced strong effects on d-excess values (23/08/13 d-excess was 4.26 ‰). *c)* Event-water flush: The outlier at d-excess of 8 ‰ in bottle number 3 and the following decrease of d-excess values show a flush of water mobilised by the event (rainwater or subsurface water).
Despite this unusual setting of low baseflow d-excess values, the highest d-excess, δ-values and discharge peak in the Reppisch in Birmensdorf nearly overlapped in time (d = 7.96 ‰ at 16.03 and at 15.33 $\delta^{18}O$ = -4.71 ‰, δD = -33.51 ‰, Q_{BD} peak at 17.00). This confirms other findings of coinciding peaks of isotopic composition (highest δ-values) with hydrograph peaks (Sklash & Farvolden, 1979; Buttle, 1994 among many others). Hence, the d-excess curve showed usually found characteristics, it was just shifted to unusual low values of stream RE2.1 due to antecedent weather influences. Even though discharge measurements and $RE_{ISCO2.1}$ were geographically positioned 24 km from each other, this can coincidingly be confirmed by the outflow of the Türlersee in 4 km distance to $RE_{ISCO2.1}$. There it effectively fell into the hour of highest d-excess values at $RE_{ISCO2.1}$.

4.5.1.2 Event of 28/08/13

During the second sampled event of 28/08/13 at $RE_{ISCO2.1}$ the bottles two to eight were filled within minutes (*Figure 42*). Nevertheless, their isotopic signals can be interpreted: Between 7 and 8 a.m. d-excess values were rising from 4.94 ‰ to a peak of 11.85 ‰ (baseflow signal of 23/08/13 was 4.26 ‰). The bouncing in d-excess values might have emerged due to different mechanisms of stormflow generation which resulted in distinct tributary flows to RE2.1, activated at different times (summary in Buttle, 2006). It might also have happened due to the often observed (summary in Ingraham, 2006) fluctuations in isotopic composition of the rainwater during events. Some very signals very close to each other, might only differ due to natural abundance or due to measurement errors.

For the upcoming discussed events also isotopic compositions of rainwater samples were available.

4.5.1.3 Event of 08 - 09/09/13

The event of 08 - 09/09/13 could be caught properly by $RE_{ISCO23.1}$ and RE_{RGWE} (*Figure 45*). This is a good combination for further interpretation, because RE_{RGWE} was the closest possible *Tipping Bucket* to $RE_{ISCO23.1}$.
During the first three sampling hours at $RE_{ISCO23.1}$ its d-excess was mostly around 6 to 8 ‰ compared to the one of the actual precipitation of 8 to 12 ‰. During these hours the Reppisch also reached a first peak. Whereas in the following precipitation's d-excess rose even higher, the one at $RE_{ISCO23.1}$ firstly seemed to follow the rain's signal and then the behaviour of the discharge. Altogether, $RE_{ISCO23.1}$'s d-excess curve seems to be a conglomeration of precipitation d-excess signal and of discharge behaviour.

4.5.1.4 Event of 15/09/13

The event of 15/09/13 delivered numerous isotopic data to interpret, although the behaviour over time was less clear as with data of the events sampled before (*Figure 47*). 15/09/13 includes two events at midnight, one from 14 to 15/09/13 and one from 15 to 16/09/13. The d-excess values of precipitation this time did not fluctuate as strongly as during other events, they ranged mostly between 7 and 10 ‰ (*Figure 46*). The d-excess curves of the stream waters fluctuated parallel to fluctuations in discharge. Some seemed to be delayed. Nevertheless, when the recession curve of the Reppisch was changing its rate, changes in d-excess also stabilised or changed direction to an increase. This means that with every slight rate change in the Reppisch discharge, the basin setting must have changed as well. Either tributary flows, such as overland and subsurface flows, to the Reppisch recessed or increased or, or and, the Türlersee contribution changed as well. Precipitation was hardly falling during daytime of 15/09/13. Therefore every bend in the discharge curve was a basin conditions related reaction. With this changed behaviours, isotopic compositions in the streams were differently mixed and so their signals and d-excess values changed as well.

4.5.1.5 Event of 16 - 17/09/13

The same observations between d-excess of the streams and discharge behaviour could be made for the event of 16 - 17/09/13 (*Figure 49*). It rained and consequently discharge in Birmensdorf rose to a peak – including mentioned bends – of more than 1.5 m^3/s at night from 16 to 17/09/13. Then it recessed slowly because it was still raining. The d-excess values of precipitation of the same hours were scattered in a much higher range from around 7 up to more than 20 ‰.

4.5.1.6 Event of 18/09/13

On 18/09/13 only at RE2.1 six samples were taken (*Figure 50*). This time the d-excess signals looked reverse. Where a peak was expected, a recess of 7.23 ‰ appeared. This was quite low for an inflow during those weeks. It can be explained though by the low d-excess values of precipitation of RE_{RGWE} of that day. It might have been a flush of event water, since the d-excess values calculated from RE_{RGWE} data ranged between 6 and 8 ‰ during the same hours.

During the last two discussed events, δD values of precipitation waters consecutively became more negative. $\delta^{18}O$ values became more negative until 19/09/13 at RE_{RGTS} and at RE_{RGWE} only until 18/09/13 and afterwards abruptly less negative (heavier). Though, the calculated d-excess values became lower (lighter) at RE_{RGTS} and RE_{RGWE} for the 16 - 19/09/13. This finding is to some degree in agreement with what can be expected from literature concerning the isotopic compositions of

long-lasting events: The longer an event's duration is, the more depleted the rain will be in heavy isotopes (the lighter, more negative values) (Ingraham, 2006). This was the case until 18/09/13, then a shift between hydrogen and oxygen took place, so d-excess started to change dramatically.
However, here as well, precipitation data need to be enjoyed with care, sometimes they changed for example by 30 ‰ in δD within 6 hours and differed significantly between RE_{RGTS} and RE_{RGWE}.

Mainly elevated d-excess signals in streams during storm runoff were found for the discussed events. Also their signals did mostly not top the ones of the according precipitation samples. This is in agreement with findings of other studies, saying that storm runoff is mostly found to be composed also by a large pre-event component (Bishop, 1991 in Buttle, 2006). They say that pre-event water fractions are more than 50 % (Genereux & Hooper, 1998). Hence, in the case of this project, a mixing of pre-event waters with event waters led to d-excess signals in the sampled streams positioned somewhere between the signal of the same stream prior to the event and of the collected rainwater.

4.6 Rain Gauge Sampling Method

In the context of this project it is not important to know the reasons for realistic or unrealistic precipitation values, for instance to know the journey of the measured rainwater samples. As previously said, isotopic compositions of precipitation can vary greatly between storms and even within the same storm (Ingraham, 2006). Nevertheless, *Figures 51* and *52* pay some attention to the outliers in d-excess of the integrated weekly precipitation samples, they might also have emerged due to other reasons than intra storm variabilities.
The lowest d-excess values were not even measured at the *Türlersee*, they were measured at rain water samples. The correlation between very little input and low d-excess values in *Figure 53* is contradictory to the *Amount Effect* saying that short events are by trend more enriched in heavier isotopes (Dansgaard, 1964). These calculated low d-excess values have emerged by the relationship between δD and $\delta^{18}O$ (Dansgaard, 1964), but also both heavy isotopes did show extremely high values (e.g. $\delta^{18}O$ -3.32 ‰ and δD -29.31 ‰ for 18/07/13), for instance these samples are really depleted in heavier isotopes. The assumption seems likely that the approximately 10 millilitres of 12/07/13 (P = 0.6 mm w^{-1}) and „almost no water“ of 18/07/13 (remark in the protocols) in the 3 litre-bottles could have undergone evaporation and related fractionation within the system of the bottle. Even shaking the bottles would not have helped to gather all the condensed water of the bottle's walls and of the (probably almost saturated) air within the bottles.
Figure 53 shows a remarkable increase in d-excess with the amount of collected water of 500 to 800 millilitres in the bottles (P = 28 to 45 mm w^{-1}). So not only evaporation effects within the bottle could be a reason for changing d-excess signals in precipitation waters. Also fractionation effect on falling raindrops, within the air parcel or even the source of humidity could affect amount and d-excess correlations (Ingraham, 2006). Also according to observed *Amount Effects* by trend rain out water becomes more depleted in heavier isotopes during long events (Dansgaard, 1964). This could be the reason for not further increasing or even decreasing d-excess values from 45 mm precipitation amount onwards in *Figure 53*.
One more influence onto d-excess values of the collected precipitation is the positioning of the rain gauges. RE_{RGTS} was installed close to the lake in an open field. No trees nor houses stood close to the *Totalisator*. Though there is a frequently used walking path right next to it and a camping site very close-by. That nobody disturbed the rain collector can not be excluded. Though the collected water never smelt like any other liquid far away from local precipitation water. The recorded tips did also not show too many counts, as if someone would have shaken the *Totalisator*. RE_{RGWE} was installed in a less optimal position in a garden between two houses. Bushes higher and right to RE_{RGWE} as well as houses in 3 m distance surely distorted collected precipitation amounts and received isotopic data. The shade though may have prevented RE_{RGWE} from as much incident solar radiation and heat as at RE_{RGTS}.
However, d-excess data of RE_{RG} seem to correlate strongly with collected water amounts, they are also found under conditions of very low relative humidity and high temperatures (chapter 3.3). So they correlate with the ambient conditions enhancing evaporation. It is now not exactly clear, to what amount in d-excess values RE_{RG} samples correlate with which condition and to what degree these correlations take place within the bottles and outside the bottles when condensing and falling down as precipitation. RE_{RG} sample's d-excess values are a mix of all these discussed effects.

4.7 The Reppisch Basin – a Characterisation

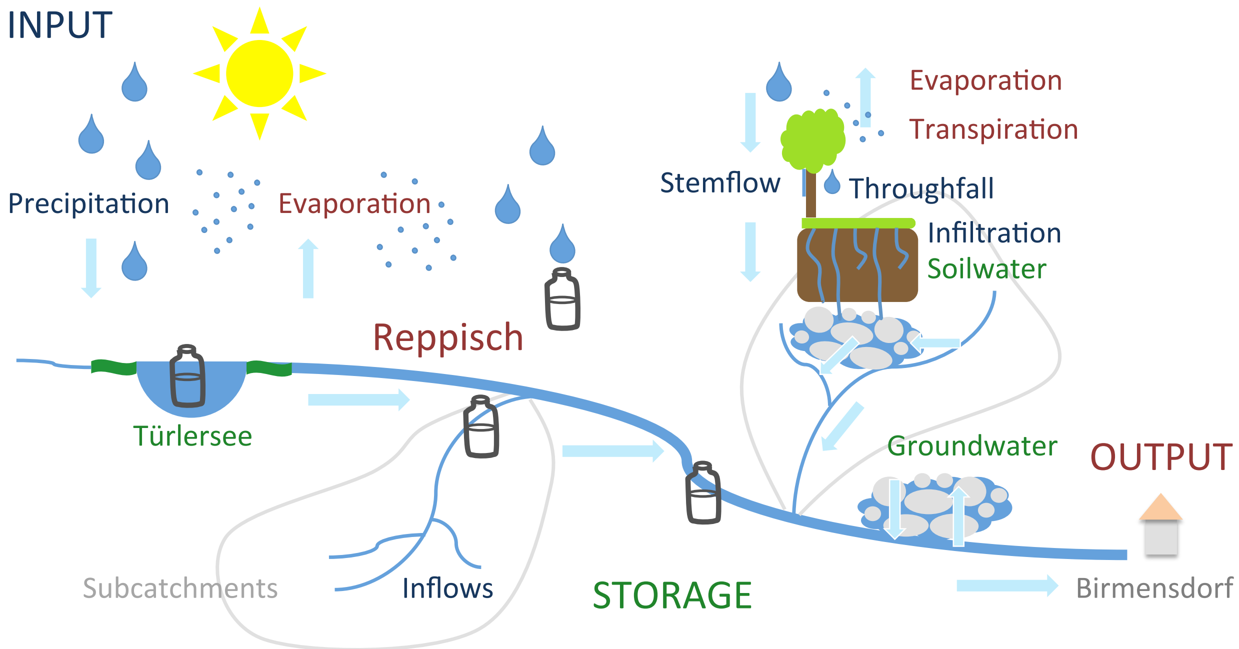

Figure 58 Simplified perceptual model of the hydrological components of the Reppisch basin. Inputs are depicted in blue, storages in green and losses in red. Arrows assign flow directions, for example seepage from and to groundwater. Bottles illustrate components which were sampled (own sketch).

Different effects formed the isotopic signals of the moisture entering the Reppisch basin. Further phase change and mixing effects modified them within the basin. The ways of the sampled waters within the basin could be traced by following the simplified idea of different catchment components depicted in the perceptual model presented in *Figure 58*. The perceptual model illustrates the expected major water balance components of the Reppisch catchment which have an important influence to the shaping of d-excess signals. Bottles show the sampled and discussed basin components. Precipitation, deposition from fog and clouds, snow and ice are the inputs. The output of the small catchment is the Reppisch as channel runoff, seepage of Reppisch water to groundwater, evaporation from the different stores and transpiration from the vegetation canopy. The latter two are explicitely not taken as *Evapotranspiration*, like hydrologists often do, because isotopically they are two different processes (Ingraham, 2006). The soilwater may percolate to groundwater storage or leave to the channels as subsurface flow through the soil matrix and macropores.
Steep flanks and small groundwater stores as well as the small catchment area of 24 km^2, classify the Reppisch catchment into a typical small catchment (Buttle, 2006). Therefore, the temporal and spatial scales of the phenomena in the Reppisch basin were expected to be as studied by Henderson-Sellers & Robinson (1986 in Buttle, 2006). They found rainfall, evaporation and soilwater content to take place in the scale of hours and within 10^1 to 10^4 m in horizontal distance. They allocated groundwater recharge to the temporal scale of months and to the spatial scale 10^2 to 10^3 m. During the months of June, July and August in monitoring period 2013, it was observed that groundwater throughout the entire basin was sustainably recharged. For these months a precipitation deficit of 66 %, a plus of solar radiation of 124 % (of the standard value 1981 – 2010) and a plus of 0.8 degrees of temperature deviation were recorded (Meteoschweiz, 2013a). The Reppisch and the inflows constantly discharged less during these months, but they did not fall dry.

The fingerprints of precipitation, inflows, Türlersee and Reppisch were clearly distinguishable. These fingerprints fit into the concept of *Equifinality*. *Equifinality* was also encountered by many other authors as a difficulty when searching for source combinations, flow paths and dynamics within a hydrologic system, a black box, at whose outlet a single signal was measured (Kendall et al., 2001; Beven, 2012; McGlynn & McDonnell, 2003). Different combinations could lead to the same isotopic fingerprint of a water sample, also in the *Reppisch* basin.
Therefore, there is no solely standing predominant creator of the isotopic signal of the sampled waters in the Reppisch basin. Trends over time combined with other parameters clearly showed distinguishable fingerprints of the observed components. Solely observed signals with geographic or meteorological settings were more diffuse but still detectable. This arises because changes over time showed that isotopic signals were a product of all influences having shaped the fingerprint during the time before sampling. This is also one reason, why d-excess signals, antecedent conditions or discharge amounts do not behave simultaneously, they were formed in different time horizons and so can not be entirely captured by a snapshot.
Clear fingerprints appeared with uncertainties of not exactly knowing the ways to a certain isotopic composition, but the fact that such uncertainties appeared, answers the question to where the Reppisch water came from. Namely from all the possible sources mentioned in the perceptual model of *Figure 58*. The Reppisch water contains mainly Türlersee water right after the lake and the further downstream, the more it is admixed with water of tributaries (sub- and surface), direct precipitation and direct throughfall (where the Reppisch is covered by vegetation) and the more it is influenced by seepage and phase changes.

The Türlersee works as a reservoir in the uppermost part of the Reppisch basin. It receives water from the inflows (surface and subsurface) and from direct precipitation. Water is lost by evaporation and by runoff into the Reppisch and swamps and by seepage to groundwater. The evaporation process and runoff into the Reppisch could be observed with isotopic signals: *a)* The d-excess values of the lake's surface water constantly decreased during summer. Therefore, in this project evaporation could be observed even on a monthly scale. *b)* The isotopic compositions of all collected lake surface water created a slope in the *GMWL* space which is typical for surface water bodies which have undergone evaporation. *c)* The Reppisch shows a d-excess signal like the lake right at the outflow. Further downstream this signal tended to become weaker.
The Türlersee discharge was whether at a constant rate, nor a constant fraction of the total Reppisch discharge in Birmensdorf. Hence, the Reppisch d-excess signals integrated different runoff situations at the lake's outflow and of the inflows (surface and subsurface) between the lake and Birmensdorf.
Moreover, the Türlersee portions in the Reppisch revealed a hysteresis: This means that at equal runoff Türlersee portions were not the same on the falling and on the rising limb. Türlersee portions also depended on the overall actual conditions in the basin. A classification of the monitoring days into different antecedent conditions revealed that when the basin was classified to be in a humid condition, Türlersee portions were the highest. Consequently the d-excess values of the Reppisch samples were the lowest with highest Türlersee portions.
Notwithstanding the Türlersee portions, after 5.7 km downstream the Reppisch (or 10 km distance from the uppermost part in the catchment) the Türlersee's area ratio becomes less than 50 % (*Table 5*). At the same location, observed d-excess values stabilised from their prior increase. Hence the Türlersee's signal was still there, although weak.
From 5.7 km onwards, the inflows became relatively more important and thus stronger in importing their signals. The inflows' d-excess values ranged around 9 ‰ during all the three monitoring periods. Among each other they varied in their specific discharge rates and thus in their isotopic signals.

These differences could not be attributed to the sources of the inflows. Some origin in plateaus others in steep flanks, all arise in similar settings concerning geology, soils and vegetation. The differences were found to appear due to different levels of urbanisation in their catchment areas.

5 CONCLUSION

5.1 Answers to Hypotheses

1) The further away from the Türlersee downstream the Reppisch, the more the d-excess values of the Reppisch approach the *GMWL*.

Historical data led to hypothesis number *1)*. Data of the monitoring period 2013 revealed a similar image like in 2010 and 2011. The further downstream the Reppisch, away from the Türlersee, the weaker was the lake's characteristic d-excess signal (mean 4.7 ‰ in 2013). Hence, the d-excess values of the Reppisch actually gradually showed higher values the further away from the Türlersee they were sampled.
Within the monitored distance though, d-excess means or medians of the Reppisch sample points did not reach the d-excess of the *GMWL* of 10 ‰. This was because the d-excess values of precipitation of the area and of the sampled inflows were not this high either.

The reason for elevating d-excess values was the mixing of lower d-excess values of Türlersee water with waters of inflows of d-excess values around 9 ‰, precipitation of around 8 ‰ and not sampled subsurface contribution. Downwards the Reppisch tributaries became relatively more important.
From monitoring point RE15 onwards, a clear stagnation of the increase of Reppisch d-excess values appeared. A striking change in the contributory regimes to the Reppisch happened due to the strong influence of the inflow at RE11. It contributed with great amounts of water relative to the other inflows. At the same time, RE11 and the following inflows downwards the Reppisch valley were marked by lower d-excess values than the inflows more valley upwards. With the last monitored inflow RE22.1 an overlapping d-excess signal of the Reppisch and the inflows appeared. No subsurface contributions to the Reppisch was sampled. Nevertheless, groundwater in the Reppisch basin may have a close isotopic composition to the monitored inflows, since some of the inflows were sampled in a few meters distance from their source. The Türlersee's isotopic signal was clearly traceable as far as RE11. Therefore, for the first 5.7 km downwards the Reppisch basin any inflow contributions, especially of groundwater, are assumed to be of minor importance, since they do elevate but not diminish the Türlersee's signal. From then on, as also calculated mixing ratios according to subcatchment areas show, the Türlersee influence was most of the time evanescently small.

2) Due to the obvious Türlersee's d-excess signal in the Reppisch, the Reppisch's baseflow d-excess values are lower than its stormflow d-excess values.

This hypothesis could be refused, when considering d-excess values distribution of the Reppisch divided by a discharge threshold value into two classes of base- and stormflow. Stormflow situations in the Reppisch revealed the highest and the lowest d-excess values. Hence, they took place during different settings of the Reppisch basin.
The only sample point clearly confirming hypothesis *2)* was RE5 at the outflow of the lake. Samples taken during baseflow situations showed the lowest d-excess values and most (three exceptions) stormflow samples showed the highest d-excess values.

A further classification into antecedent condition settings with *CPI7* could clarify that dry antecedent conditions came together with baseflow situations (except of one day). Baseflow situations were a mix of lake water of low d-excess values and of sub- and surface contributions of higher d-excess values, consequently they did not take positions of extreme values.
The Türlersee portions of the Reppisch played a crucial role in the strengths of the Türlersee d-excess signals. Türlersee fractions stayed quite high (which means less other tributaries to the Reppisch) during the dry conditions in September 2013, because groundwater stores could not be as full as in early summer after wet spring conditions. Therefore in July, although dry conditions were even more dominant, Türlersee fractions were lower and hence, sub- and surface tributaries could contribute relatively more to the total discharge. This was additionally confirmed by discharge measurements in the inflows: In July when much less precipitation was recorded, none of the sampled inflows fell dry. In September when dryness according to *CPI7* was only during a few days, two inflows fell dry. Anyway, with the on-going summer, all measured inflows delivered less water. Different settings of the components and as a consequence varying interactions lead to a more complicated formation of d-excess signals. Variations in isotopic signals of precipitation, its mix with pre-event water and different precipitation intensities lead to varieties of modifications of d-excess signals. Further processes like interactions between groundwater, riparian zones and streams, influences of throughfall and soilwater, effects of land cover like urbanisation, agriculture, artificial channels, forests or grasslands, or components as swamps, ponds and the Türlersee as reservoirs played even stronger and more incalculable into the simple 2-class baseflow-stormflow determination. More classes characterising discharge situations in the Reppisch would have probably led to more specified d-excess distribution of the simplified determination of stormflow situations.

Hypothesis number *2)* could be more clearly confirmed, when considering the sampled events of the end of August and beginning of September 2013. During those weeks, d-excess values of the Türlersee and accordingly of the Reppisch were lower and precipitation's d-excess was higher than in June. As a consequence, d-excess values differences between Reppisch and precipitation water were anyway bigger in the event sampling period than during the rest of monitoring period 2013. Therefore, while baseflow situations the d-excess values of the Reppisch were clearly lower anyway, and thus stronger influenced by the Türlersee than during events. The event data additionally confirm findings with weekly collected grab samples: with increasing discharge rates d-excess values increase too and vice versa.

3) During event situations, precipitation inputs cause quick and large tributaries to the Reppisch, whereas the lake contribution rises only slowly.

Field experiences brought up hypothesis number *3)*. During a cloudburst stages of the inflows immediately rose and showed quick runoff. The Türlersee on the opposite was thought to be an inert system, contributing to stream runoff with retention.
The qualitative interpretations of gained data by events in 2013, revealed a reaction of the basin's components within minutes due to the sensitively varying d-excess values with varying discharge rates. With rising stages the d-excess values increased as well, hence the Türlersee's reaction was not clearly determinable. In contrast, with decreasing runoff rates, d-excess values immediately decreased as well. These lower values were clearly allocatable to the Türlersee.

According to observed discharge proportions in the Reppisch, hypothesis number *3)* can not be answered simply and terminatory. The Türlersee acted as a buffer of newly incoming waters in the upper part of the Reppisch basin. This was also shown by discharge peaks at the lake's outflow, they were more smoothed out curves compared to the runoff rates in Birmensdorf.

On the time scale of single days, hypothesis number *3)* must be rejected according to the anomalous behaviour of the observed Reppisch proportions. They revealed that on rising limbs Türlersee portions rose disproportionately, compared to other tributary portions (surface and subsurface).
Hypothesis number *3)* must also be rejected according to its classification by Scherrer (2006), after which the Türlersee belonged to the discharge type of "quick and strong contribution".

Additional information on runoff proportions revealed that at least two different basin settings causing differently proportioned runoff in the Reppisch took place during monitoring period 2013. The recession curve of June and July discharged lower Türlersee fractions, thus higher tributary fractions than the recession curves of August and September, although all curves were formed similarly. This induces that the structure of the valley was the same, but the storages were filled differently and thus drained with distinct intensities.
Therefore, it can be concluded that it is not only one event that induces rising discharge portions of the Türlersee, it is the overall setting of the basin, filled or drained storages which determine whether Türlersee portions are higher or lower and whether the Türlersee's reaction is quicker or more inert.

4) By combining isotopic with discharge data, a quantification of runoff proportions of the Reppisch until Birmensdorf will reveal that during baseflow situations the main runoff component is the Türlersee portion.

Hypothesis number *4)* could not be answered with the *Isotopic Source Separation* (*ISS*) model used in this project because it did definitely not lead to beneficial findings. However, some more general findings on the combination of isotopic with hydrometric data are listed below.

The *ISS* model was too uncertain to push it further to estimate the unknown part of the Reppisch basin, for instance the groundwater portions and to determine conclusions on any proportions. Hence, the entire *ISS* part is presented in the *APPENDIX*.
Nevertheless, some conclusions could be made or confirmed once more: *a)* “The closer to the lake, the bigger is the influence of lake waters”, was confirmed by trend in simulated discharge amounts. *b) ISS* with data of series sampling confirmed as well that the higher Türlersee portions were, the lower the d-excess values were in the Reppisch.

A qualitative, combined interpretation of hydrometric and isotopic data has so far led to an enhanced understanding of certain connections and reciprocal influences. Amount specific connections could be determined for some situations, although the data was too sparse to establish rules. Still, some conclusions on relative behaviours can be drawn: *a)* Isotopic and discharge data located a change in the runoff regime after 5.7 km downstream the Reppisch. *b)* Increasing or decreasing discharge rates in the Reppisch did not always reveal parallel increasing or decreasing d-excess values. *c)* The d-excess signals of the monitored inflows did not depend on their discharge rates. *d)* The d-excess signals in the Reppisch reached lowest values when Türlersee portions were higher. *e)* Higher or lower specific discharge rates did not reveal higher or lower d-excess values. *f)* The d-excess values of the Türlersee were lower with lower Türlersee stages. *g)* Türlersee portions did not depend on Türlersee stages. *h)* Observed highest Türlersee portions in the Reppisch correlated with the *CPI7* classification into a wet antecedent conditions setting. *i)* Observed discharge proportions in the Reppisch were characterised by a hysteresis. Equal runoff rates on rising limbs were not constituted by equal runoff proportions on recession limbs.

6 OUTLOOK

This project provided a first overview of the hydrological situation in the Reppisch basin. Insights to the basin's characteristic and important relations between precipitation, Türlersee, surface inflows and the Reppisch were elucidated with the d-excess signals as tools. This was the first survey of such a kind in the Reppisch basin. It offered first insights into several topics and so it let to new questions and asked for a more detailed understanding of flowpaths, connections and specific behaviours during certain conditions.
At some points, the monitoring strategy of this project was not adequate. Too many samples of the monitored components were collected, whereas no isotopic information on groundwater was available. Adjustments could have been an extended grab sampling to more inflows and a leaving out of the time consuming *WLPWS* construction, installation and sampling. Like this a more detailed overview of all inflows could have been developed. The additional grab samples should not just have been taken right before the inflow drains into the Reppisch, but also more upwards on the flanks aside. This is especially recommended for the ones that source in or cross ponds and swamps. Processes leading to outliers of very low d-excess values showing evaporation effects could then be better understood.
Some inflows could additionally have been monitored in their water levels. Regular discharge measurements and continuous water level records could be used to estimate continuous runoff curves with stage-discharge relationships.
Sampling of groundwater in the valley bottom as well as on the plateaus aside, should not have afforded too intensive investigations, because groundwater bodies should not be too extensive within the monitoring area. Maybe as assumed in this project, isotopic compositions of groundwater are actually close to the ones of the already sampled inflows. It would have been helpful to know if this was really the fact. A more precise knowledge on the longterm isotopic compositions of groundwater would have allowed to undertake proper *IHS* calculations. Although, if it is really worthwhile to undertake *IHS* calculations in the Reppisch should firstly be checked carefully because *IHS* is not recommended for streams strongly influenced by lakes during storm runoff (Sklash & Farvolden, 1979).
At least one more precipitation collector should have been positioned in the lowest part of the Reppisch basin, since amounts and isotopic signals of precipitation collected in summer 2013 were not the same throughout the entire period. Especially in August and September when precipitation's d-excess became higher, the signal of the Türlersee was still on a downwards trend. It would have been beneficial to estimate whether the different subareas were really not hit by equal rain intensities.
During the three monitoring periods of this project, the Türlersee showed fascinating strong evaporation effects. It would also have been worthwhile to additionally investigate one sampling mission of the Türlersee isotopic profile to state if there was any isotopic stratification. Like this the Türlersee's water source in the Reppisch could possibly be determined whether it was surface water or water of lower parts and thus its signal more exact trace- or even quantifiable.

Just for curiosity, according to our findings in this study, it would additionally be interesting to know if the biosphere is a different one between the lake and RE12/RE15 and hence, between RE15 and the outlet in Birmensdorf. Because flora and fauna depend strongly on water temperature and on dynamics in discharge behaviours, what differed evidently between RE12 and RE15.

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APPENDIX

A) Isotopic Source Separation

Theory

Each water sample has its own "fingerprint" generated by possible distinctions of the isotopic compositions mentioned in chapter *Stable Water Isotope Tracers*. This "fingerprint" of a certain water sample in combination with hydrometric data like discharge measurements helps in quantifying the Türlersee's contribution to the Reppisch's discharge at specific monitoring points.

The following mass balance and two-component mixing equations (modified after Kendall & Caldwell, 1998; Sklash et al., 1976) make this quantification possible:

$$Q_{Reppisch} = Q_{Türlersee} + Q_{Inflows} \qquad [m^3\ s^{-1}] \qquad (5)$$
$$C_{Reppisch}Q_{Reppisch} = C_{Türlersee}Q_{Türlersee} + C_{Inflows}Q_{Inflows} \qquad [‰ * m^3\ s^{-1}] \qquad (6)$$

Equation (6) can be solved by substitution for $Q_{Inflows} = Q_{Reppisch} - Q_{Türlersee}$ and rearrangement. The result is equation (7):

$$Q_{Türlersee} = Q_{Reppisch}\ (C_{Reppisch} - C_{Inflows}) / (C_{Türlersee} - C_{Inflows}) \qquad [m^3\ s^{-1}] \qquad (7)$$

Where $Q_{Reppisch}$ = discharge Reppisch (total after inflow) in [$m^3\ s^{-1}$], $Q_{Türlersee}$ = discharge Türlersee (or Reppisch before inflow) in [$m^3\ s^{-1}$], Q_{Inflow} = discharge of the inflow in [$m^3\ s^{-1}$], $C_{Reppisch}$, $C_{Türlersee}$ and C_{Inflow} are δ-values in [‰] of Reppisch, Türlersee and tributaries waters.
These mixing equations are originally performed as the so-called *Isotopic Hydrograph Separation (IHS)* for storm hydrographs to determine the contributions of event- and pre-event waters (Sklash et al., 1976).

Results

For estimations of the Reppisch discharge portions the above mass balance equation was followed. The following describes the results received with the *Isotopic Source Separation* (*ISS*) for total Reppisch discharge at a certain sample point. The next chapter applies the same method to estimate Türlersee portions of the Reppisch discharge as well at certain sample points. In both chapters only some specific sample points will be elucidated.

ISS Calculations of Total Reppisch Discharges of Monitoring Period 2013

For an *ISS* estimation of the total Reppisch runoff at a certain point in the stream, the introduced mass balance equation is rearranged as follows:

$$Q_{Reppisch} = Q_{Türlersee} / ((C_{Reppisch} - C_{Inflows}) / (C_{Türlersee} - C_{Inflows})) \qquad [m^3\ s^{-1}] \qquad (8)$$

Where $Q_{Reppisch}$ is the total Reppisch runoff at the sample point of interest in [$m^3\ s^{-1}$], $Q_{Türlersee}$ is the runoff at the lake outflow (data source: AWEL) in [$m^3\ s^{-1}$] and C are each $\delta^{18}O$ or d-excess values of the specific component. $C_{Inflows}$ is a mean of all inflow sample points, because for some Reppisch locations no inflow water samples were taken within a reasonable proximity. $C_{Türlersee}$ is a mean of all the sample points of the lake as well, this is to account for a mean lake signal.

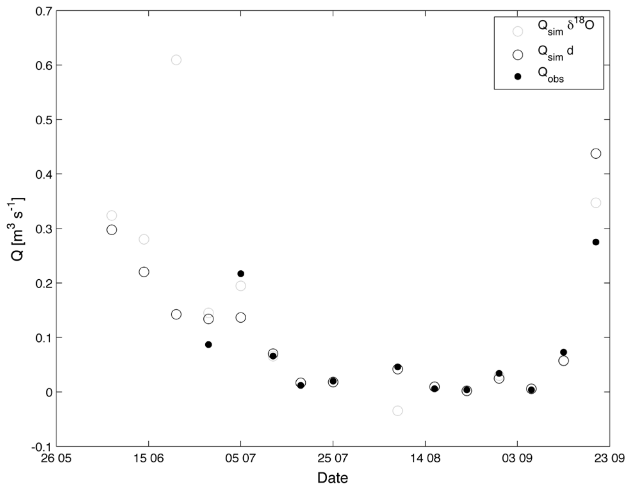

Figure 59 *ISS* calculation of total Reppisch discharge at RE9 (Q_{sim}) with Q_{TS} (data source: AWEL), $\delta^{18}O$ and d-excess information, for the monitoring period 2013. Q_{obs} indicates own discharge measurements at RE9.

Table 11 *ISS* calculation of the total Reppisch discharge at RE9 (Q_{sim}) with Q_{TS} (data source: AWEL), $\delta^{18}O$ and d-excess information. Deviation Q_{sim} to Q_{obs} compares calculations with own discharge measurements (Q_{obs}) at RE9.

Date	Türlersee		Inflows		RE9				
	Mean $\delta^{18}O$	Mean d	Mean $\delta^{18}O$	Mean d	Q_{sim} $\delta^{18}O$	Q_{sim} d	Q_{obs}	Deviation Q_{sim} to Q_{obs}	
								Q_{sim} $\delta^{18}O$	Q_{sim} d
	[‰]	[‰]	[‰]	[‰]	[m^3 s^{-1}]	[m^3 s^{-1}]	[m^3 s^{-1}]	[%]	[%]
07/06/13	-9.70	6.96	-10.39	9.55	0.324	0.298	NaN	NaN	NaN
14/06/13	-9.84	7.14	-10.34	9.14	0.280	0.220	NaN	NaN	NaN
21/06/13	-8.32	6.35	-10.10	9.10	0.609	0.142	NaN	NaN	NaN
28/06/13	-9.44	5.88	-9.85	9.51	0.145	0.134	0.087	67.02	53.99
05/07/13	-9.46	6.64	-10.20	8.51	0.195	0.137	0.217	-10.24	-36.95
12/07/13	-9.19	5.88	-10.09	9.57	0.066	0.070	0.066	-0.47	6.75
18/07/13	-8.96	4.75	-10.01	9.41	0.018	0.017	0.012	46.01	37.89
25/07/13	-8.86	3.51	-9.86	8.69	0.018	0.018	0.02	-12.46	-9.04
08/08/13	-8.80	4.10	-8.70	7.11	-0.034	0.042	0.046	-174.97	-8.97
16/08/13	-8.71	3.86	-9.78	8.12	0.008	0.010	0.006	40.10	60.24
23/08/13	-8.60	2.94	-9.40	7.74	0.003	0.002	0.004	-24.85	-48.31
30/08/13	-8.74	4.59	-9.86	9.11	0.030	0.025	0.034	-11.98	-26.68

Table 11 (Continued)

06/09/13	-8.58	3.56	-9.80	8.24	0.006	0.006	0.004	49.23	44.84
13/09/13	-8.59	3.09	-9.74	9.24	0.056	0.057	0.073	-23.22	-21.38
20/09/13	-8.28	1.35	-9.87	9.24	0.347	0.438	0.275	26.28	59.11
Mean								*40.57*	*34.51*
Median								*25.57*	*37.42*

Figure 59 depicts the calculated and measured total discharge of the Reppisch at the sample point RE9. For the *ISS* calculation the isotopic means of all inflow sample points and the one of the Türlersee have been included as $C_{Inflows}$ and $C_{Türlersee}$. For $C_{Reppisch}$ the isotopic composition of the corresponding sample point, here C_{RE9}, was taken.
RE9 was picked out as example for illustrating the *ISS* calculations, because its modelled discharges are compared to others in a moderate position. They do not show the biggest outliers nor the most reasonable ones, which are the closest to the observed discharges.
Figure 59 shows that visually during low flow situations the calculated and measured discharges fit quite well and in higher flow situations they vary strongly. The percentage deviations in *Table 11* although show that assumed higher variations at higher discharges disappear. The deviations are not dependent on the discharge amount. A deviation of 10 % at a discharge of 0.020 m^3/s results in a deviation of 0.002 m^3/s. For a discharge of 0.500 m^3/s the same deviation of 10 % leads to a deviation of 0.050 m^3/s. This looks much more scattering when illustrated.
Altogether, the deviations are distributed between a deviation of 0.47 and 174.97 % for *ISS* calculations with $\delta^{18}O$. For calculations with d-excess they vary between 6.75 and 60.24 %. In this case of RE9, the scatter for *ISS* calculations with d-excess is much smaller than the one with $\delta^{18}O$.

Table 12 *ISS* calculation of total Reppisch discharge at RE23 (Q_{sim}) with Q_{TS} (data source: AWEL), $\delta^{18}O$ and d-excess information. Dev. Q_{sim} to Q_{obs} compares calculations to discharge measurements (Q_{obs}, here Q_{BD}) of the cantonal gauging station at RE23 (data source: AWEL). Like in *Table 10* each row belongs to the according monitoring day and the last two rows show means and medians.

RE23				
Q_{sim} $\delta^{18}O$	Q_{sim} d	Q_{BD}	Deviation Q_{sim} to Q_{BD}	
			Q_{sim} $\delta^{18}O$	Q_{sim} d
[m^3 s^{-1}]	[m^3 s^{-1}]	[m^3 s^{-1}]	[%]	[%]
0.496	0.373	0.726	-31.72	-48.58
0.485	0.241	0.759	-36.11	-68.32
0.387	0.249	0.351	10.26	-29.03
0.634	0.109	0.230	175.37	-52.68
0.142	0.080	0.495	-71.23	-83.83
0.086	0.081	0.175	-51.08	-53.77
0.019	0.014	0.089	-79.28	-83.81
0.011	0.031	0.063	-82.53	-51.40
0.006	0.056	0.137	-95.53	-58.71

Table 12 (Continued)

0.017	0.022	0.058	-70.86	-62.54
-0.033	-0.017	0.053	-162.10	-133.03
0.160	-0.100	0.089	78.78	-212.06
0.019	0.016	0.043	-55.24	-61.67
0.122	0.132	0.138	-11.47	-4.39
0.266	0.209	0.543	-51.09	-61.49
			70.84	*71.02*
			70.86	*61.49*

In the case of RE23 (*Table 12*), where calculated discharges could be compared to observed ones of the cantonal gauging station in Birmensdorf, the performance with $\delta^{18}O$ or d-excess was almost equal. Means and medians of the deviations are found around 70 %, except the median of deviations with Q_{sim} calculated with d-excess is slightly lower at 61.5 %. Compared to *ISS* at RE9, the overall performance at RE23 reaches higher deviations. Possible reasons for variations in performance are discussed in the following chapter *Discussion*.

Table 13 Minimal and maximal deviations of Q_{sim} to Q_{obs} in [%] compares *ISS* calculations (Q_{sim}) to own discharge measurements (Q_{obs}) at certain sample points (data source: AWEL).

Sample Point	Deviation Q_{sim} to Q_{obs} $\delta^{18}O$		Deviation Q_{sim} to Q_{obs} d	
	Min. [%]	Max. [%]	Min. [%]	Max. [%]
RE9	0.47	174.97	6.75	60.24
RE12	2.73	311.6	16.79	457.06
RE15	0.84	196.45	5.44	1504.17
RE20	12.94	757.18	14.89	128.1
RE22	26.27	284.14	6.69	225.26
RE23	10.26	162.1	4.39	212.06

As *Table 13* summarises for RE9, the scatter for *ISS* calculations with d-excess is much smaller than the one with $\delta^{18}O$. This is not the case for all sample points in the Reppisch.
Some *ISS* calculations stand out showing unrealistic discharge values of the Reppisch. An example would be for RE12 on 07/06/13, where the rounded -24 m^3/s does not come close to real observations. Obviously such values distort means of deviations heavily. Thus medians were included to the overall *ISS* data application as well. Nonetheless, for the two types of *ISS* calculations, either with $\delta^{18}O$ or d-excess, no tendency of better performance for either one could be found. Great distortions are found with both types as well as for values quite close to the observed Reppisch discharges. The medians lay between 20.52 and 70.86 %. The median of the median deviations is at 41 % and the median of the mean deviations is at approximately 70 %. Around 80 to 90 % of the simulations underestimate Reppisch discharges, regardless if performed with $\delta^{18}O$ or d-excess. In general *ISS* calculated Reppisch discharges vary easily by 50 % or more from the observed discharges. One tendency that can be found in the median deviations is that the further away from the Türlersee the higher the median deviations are.

ISS Calculations of Total Türlersee Fractions of Monitoring Period 2013

For an *ISS* estimation of the Türlersee fraction at a certain point in the stream, the introduced mass balance equation is used as follows:

$$Q_{Türlersee} = Q_{Reppisch} * ((C_{Reppisch} - C_{Inflow}) / (C_{Türlersee} - C_{Inflow})) \quad [m^3\ s^{-1}] \qquad (9)$$

Where $Q_{Türlersee}$ is the runoff at the lake outflow in [$m^3\ s^{-1}$], $Q_{Reppisch}$ is the total Reppisch runoff at the sample point of interest in [$m^3\ s^{-1}$] (own measurements) and C are each $\delta^{18}O$ or d-excess values of the specific component. $C_{Türlersee}$ is a mean of the three sample points located in the Türlersee. This time the isotopic compositions of the specific sample points for C_{Inflow} are involved.

The *ISS* calculations of Türlersee portions were implemented for all Reppisch sample points, where Reppisch discharge was measured ($Q_{Reppisch}$, own data). In the following graph and tables the picked out calculations with data of the inflows RE5.1, -9.2 and -11 illustrate the performance of the *ISS* estimations. Additionally, the calculations at RE23 with means of all inflows are picked out as well.

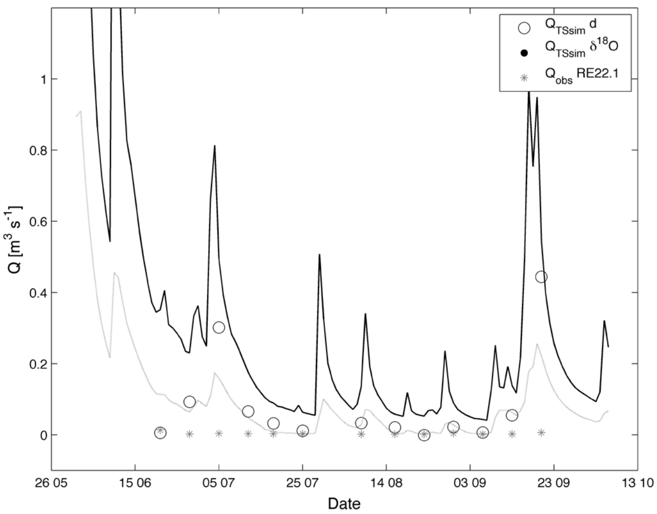

Figure 60 *ISS* calculation of the Türlersee fraction (Q_{TSsim}) of total Reppisch discharge at RE23 with Q_{BD} (data source: AWEL), $\delta^{18}O$ and d-excess information, for the monitoring period 2013. The lower curve indicates Q_{TS} and the upper one Q_{BD} (data source: AWEL). Stars indicate measured runoffs at RE22.1 (own data).

In *Figure 60* the closer circles and dots are to the Türlersee discharge amounts, the better the approach of the model is for the observed discharges. At low flow situations the model seems to perform better in the case of RE22.1 and RE23. This is again due to the amount effect, which was already mentioned in the results of estimating total Reppisch discharge with *ISS*. Therefore the following tables elucidate *ISS* results with more clarity. As references, *Table 16* additionally lists measured discharges at the outflow of the Türlersee, which at the same time is the measured Türlersee fraction and measured discharges in Birmensdorf (data source: AWEL). This data was also the basis for the calculation of "real" Türlersee fractions in Birmensdorf. Each row in the tables stands for one monitoring day, therefore calculations can directly be compared to each other and finally with measurements in *Table 16*. *Table 17* summarises the deviations between simulated and observed discharge amounts.

Table 14 *ISS* calculation of the total Türlersee discharge at RE5.1 resp. RE9 (Q_{sim}) with $Q_{Reppisch}$ at RE9 (own measurements), $\delta^{18}O$ and d-excess information. Q_{sim} indicates the Türlersee portion in the Reppisch at RE9 in [m^3 s^{-1}] and in [%].

	Türlersee		Reppisch at RE9		RE5.1		TS Fraction at RE5.1/RE9			
Date	Mean $\delta^{18}O$	Mean d	Mean $\delta^{18}O$	Mean d	Mean $\delta^{18}O$	Mean d	Q_{sim} $\delta^{18}O$		Q_{sim} d	
	[‰]	[‰]	[‰]	[‰]	[‰]	[‰]	[m^3 s^{-1}]	[%]	[m^3 s^{-1}]	[%]
07/06/13	-9.70	6.96	-9.73	6.84	NaN	NaN	NaN	NaN	NaN	NaN
14/06/13	-9.84	7.14	-9.84	6.62	NaN	NaN	NaN	NaN	NaN	NaN
21/06/13	-8.32	6.35	-9.77	6.91	-10.36	9.94	NaN	NaN	NaN	NaN
28/06/13	-9.44	5.88	-9.67	7.77	-9.78	10.56	0.028	32.35	0.052	59.62
05/07/13	-9.46	6.64	-9.6	6.34	-10.39	9.73	0.185	85.25	0.238	109.59
12/07/13	-9.19	5.88	-9.44	7.08	-10.21	9.55	0.050	75.74	0.044	67.30
18/.07/13	-8.96	4.75	-9.45	6.77	-10.1	10.18	0.007	57.18	0.008	62.76
25/07/13	-8.86	3.51	-9.67	7.76	-10.05	9.87	0.006	31.84	0.007	33.18
08/08/13	-8.80	4.10	-8.61	5.13	-8.46	7.81	0.020	43.69	0.033	72.24
16/08/13	-8.71	3.86	-9.22	6.18	-9.92	8.98	0.003	57.69	0.003	54.69
23/08/13	-8.60	2.94	-8.74	1.96	-9.64	7.67	0.003	86.82	0.005	120.72
30/08/13	-8.74	4.59	-8.83	4.13	-9.88	7.54	0.031	91.84	0.039	115.46
06/09/13	-8.58	3.56	-9.21	5.89			no discharge			
13/09/13	-8.59	3.09	-8.47	2.59	-9.96	10.1	0.080	109.02	0.078	107.13
20/09/13	-8.28	1.35	-8.86	5.26	-10.14	10.11	0.189	68.82	0.152	55.34
Mean								*67.30*		*78.00*
Median								*68.82*		*67.30*

Table 15 *ISS* calculation of the total the Türlersee discharge at RE9.2 and RE11 (Q_{sim}) with $Q_{Reppisch}$ (own measurements), $\delta^{18}O$ and d-excess information. Q_{sim} indicates the Türlersee portion in the Reppisch at RE10 and RE15 in [$m^3 s^{-1}$] and in [%]. Like in *Table 14* each row belongs to the according monitoring day and the last two rows show means and medians.

RE9.2				RE11			
Q_{sim} $\delta^{18}O$		Q_{sim} d		Q_{sim} $\delta^{18}O$		Q_{sim} d	
[$m^3 s^{-1}$]	[%]	[$m^3 s^{-1}$]	[%]	[$m^3 s^{-1}$]	[%]	[$m^3 s^{-1}$]	[%]
NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN
NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN
NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN
0.103	44.64	0.154	66.74	0.049	35.79	0.000	0.28
0.317	64.14	0.290	58.68	0.193	49.62	0.073	18.65
0.162	92.78	0.210	120.00	0.065	61.09	0.057	53.59
0.033	36.73	0.050	55.45	0.017	39.45	0.014	32.51
0.003	5.04	0.013	20.48	0.020	32.23	0.024	38.31
-0.056	-40.85	0.060	43.88	0.389	153.06	0.070	27.44
0.016	27.02	0.010	17.11	-0.0017	-6.95	-0.035	-140.84
0.002	3.77	0.015	29.10	0.003	18.16	0.000	0.52
0.069	76.62	0.090	100.64	0.033	62.01	0.039	73.73
0.007	16.86	0.012	27.59	0.007	32.94	0.009	40.99
0.111	80.22	0.114	82.35	0.070	68.26	0.067	64.74
0.380	69.94	0.354	65.20	0.251	54.10	0.236	50.88
	39.74		*57.27*		*49.98*		*21.73*
	40.69		*57.07*		*44.54*		*35.41*

Table 16 *ISS* calculation of the Türlersee discharge at RE23 (Q_{sim}) with $Q_{Reppisch}$ (data source: AWEL), $\delta^{18}O$ and d-excess information. Q_{sim} indicates the Türlersee portion in the Reppisch at RE23 in [$m^3 s^{-1}$] and in [%]. Simulation data is compared to data of *AWEL* at Türlersee and in Birmensdorf. Like in *Table 14* each row belongs to the according monitoring day and the last two rows show means and medians.

Mean Inflows at RE23				RE6		RE23	
Q_{sim} $\delta^{18}O$		Q_{sim} d		Q_{TS} AWEL		Q_{BD} AWEL	
[$m^3 s^{-1}$]	[%]	[$m^3 s^{-1}$]	[%]	[$m^3 s^{-1}$]	[%] in BD	[$m^3 s^{-1}$]	[%]
0.456	62.78	0.606	83.37	0.311	42.87	0.726	100
0.436	57.38	0.878	115.72	0.278	36.66	0.759	100
0.103	29.31	0.160	45.53	0.113	32.32	0.351	100
0.023	10.12	0.135	58.90	0.064	27.87	0.230	100
0.551	111.35	0.980	198.09	0.159	32.04	0.495	100
0.097	55.58	0.103	58.82	0.048	27.19	0.175	100
0.045	50.64	0.058	64.79	0.009	10.49	0.089	100
0.019	29.71	0.007	10.68	0.003	5.19	0.063	100
0.615	450.39	0.067	48.81	0.028	20.15	0.137	100
0.015	25.95	0.012	20.19	0.004	7.56	0.058	100
-0.004	-7.64	-0.008	-14.36	0.002	4.74	0.053	100
0.015	17.16	-0.024	-27.38	0.027	30.68	0.089	100
0.006	15.12	0.008	17.65	0.003	6.77	0.043	100
0.070	50.72	0.065	46.97	0.062	44.91	0.138	100
0.451	83.00	0.573	105.41	0.220	40.60	0.543	100
	69.44		*55.55*		*24.67*		*100*
	50.64		*48.81*		*27.87*		*100*

Table 17 Deviations in [%] of specific *ISS* calculation of the Türlersee discharge Q_{sim} to Q_{obs} (data source: AWEL) with $\delta^{18}O$ and d-excess information. Q_{sim} and Q_{obs} indicate Türlersee portion in the Reppisch in [m^3 s^{-1}]. Like in *Table 14* each row belongs to the according monitoring day and the last two rows show means and medians.

RE5.1		RE9.2		RE11		RE23 (Mean Inflows)	
$\delta^{18}O$	d	$\delta^{18}O$	d	$\delta^{18}O$	d	$\delta^{18}O$	d
Dev. Q_{sim} to Q_{obs} [%]	Dev. Q_{sim} to Q_{obs} [%]	Dev. Q_{sim} to Q_{obs} [%]	Dev. Q_{sim} to Q_{obs} [%]	Dev. Q_{sim} to Q_{obs} [%]	Dev. Q_{sim} to Q_{obs} [%]	Dev. Q_{sim} to Q_{obs} [%]	Dev. Q_{sim} to Q_{obs} [%]
NaN	NaN	NaN	NaN	NaN	NaN	46.45	94.48
NaN	NaN	NaN	NaN	NaN	NaN	56.51	215.62
NaN	NaN	NaN	NaN	NaN	NaN	-9.31	40.90
-56.10	-19.12	60.17	139.46	-22.98	-99.39	-63.69	111.31
16.71	50.04	100.18	83.14	21.79	-54.24	247.55	518.27
5.13	-6.58	241.25	341.35	36.20	19.47	104.43	116.33
-26.80	-19.66	250.18	428.62	78.86	47.41	382.70	517.66
94.37	102.50	-2.87	294.58	520.82	638.13	472.35	105.76
-27.02	20.67	-302.71	117.77	1311.83	153.10	2134.95	142.20
-20.94	-25.06	257.30	126.20	-139.68	-904.19	243.16	166.97
39.47	93.94	-20.58	513.77	23.96	-96.44	-261.03	-402.78
13.76	43.03	149.74	228.04	19.74	42.38	-44.07	-189.23
no discharge		149.25	307.81	137.99	196.20	123.42	160.91
28.25	26.02	78.64	83.38	13.29	7.44	12.95	4.59
-14.17	-30.97	72.29	60.60	13.85	7.06	104.47	159.66
4.79	*21.35*	*86.07*	*227.06*	*167.97*	*-3.59*	*236.72*	*117.51*
5.13	*20.67*	*89.41*	*183.75*	*22.87*	*13.46*	*104.43*	*116.33*

Table 18 Minimal and maximal deviations of Q_{sim} to Q_{obs} in [%] compares *ISS* calculations of the Türlersee portion (Q_{sim}) to discharge measurements (Q_{obs}) of the Türlersee (data source: AWEL).

Sample Point	Deviation Q_{sim} to Q_{obs} $\delta^{18}O$		Deviation Q_{sim} to Q_{obs} d	
	Min. [%]	Max. [%]	Min. [%]	Max. [%]
RE5.1	5.13	94.37	6.58	102.50
RE7	5.13	1595.97	2.75	552.65
RE9.1	68.23	2022.48	17.2	949.07
RE9.2	2.87	250.18	60.60	513.77
RE11	13.29	1311.83	7.06	904.19
RE14	4.86	379.59	39.85	2655.57
RE19	7.6	759.66	35.75	848.27
RE22.1	12.04	371.78	15.07	1234.24
mean of inflows at RE23	9.31	2134.95	4.59	518.27

The mean and median of the deviations between simulated and observed discharges show that the performance of *ISS* with $\delta^{18}O$ and d-excess was not better for either one. Deviations could rise to more than 2000 % or be around 3 %.

Discussion

ISS Estimations of total Reppisch Discharge and Türlersee Portion

With estimations of Türlersee portions at certain monitoring points, groundwater portions might be determinable as well. The simple mass balance model seemed to be promising in determination of all discharge proportions. However, too many *ISS* estimations did not perform satisfactorily. In some few cases simulated discharges approached quite close to observed ones. Even though, they are not enough to recommend to use such a type of discharge portions estimators in the way it was done for this project.

However, one finding or overall trend to detect was that the medians of the deviations of simulated discharges to observed ones increase with increasing distance from the lake. This happens due to convergence of the isotopic compositions of the inflows ($C_{Inflows}$) and the Reppisch ($C_{Reppisch}$) with increasing distance from the lake. Such a case of very similar d-excess values happened also in the now discussed case of RE12.

Very unrealistic values like the one of -24 m^3/s at RE12 on 07/06/13 might have come up due to the very high discharge rates at the Türlersee outflow during these days in June or due to the very low differences between mean d-excess of inflows of 9.546 ‰ and at RE12 of 9.58 ‰.

The bigger effect probably is initiated by the d-excess differences. The calculation for the specific case with d-excess values namely preforms as follows:

$Q_{Reppisch}$ = 0.311 / ((9.58 - 9.546) / (6.96 - 9.546)) = 0.311 / (0.034 / -2.586) = -23.68 m^3/s.

On 07/06/13 the Reppisch basin was still strongly influenced by the heavy precipitation of the weeks before and discharges of inflows and Reppisch were still quite high. On 12/07/13, as well shortly after a strong event, the *ISS* calculations of Türlersee portions performed quite well. For

example RE5.1 and RE7 brought both a portion of 0.050 m^3/s calculated with $\delta^{18}O$ and 0.044 and 0.049 m^3/s with d-excess. Observed Türlersee discharge was 0.48 m^3/s. Many of the other *ISS* calculations of 12/07/13 performed also best on that day, mean deviations were 107 % (compared to overall mean deviation of 184 %). Thus some settings in the Reppisch basin or in the isotopic signals must lead to better and some to worse performances of the *ISS* model.
An example of the *ISS* sensitivity to isotopic signals happened with $C_{Türlersee}$ on 23/08/13: First calculations were undertaken before a complete availability of all data, so $C_{Türlersee}$ d-excess was 0.85 ‰. With additionally involved samples $C_{Türlersee}$ was lifted up to 2.49 ‰. *ISS* calculations became worse. Whereas on 30/08/13 the opposite happened: newly gained d-excess values of $C_{Türlersee}$ were lower than the ones in the first calculation. Consequently *ISS* calculations became enhanced, namely from 151 to 115 % Türlersee portion in the Reppisch. Apparently proportions were still unrealistic, though the *ISS* model seemed to be sensitive to changes in $C_{Türlersee}$.

The case of RE12 and sensitivity to $C_{Türlersee}$ introduced to the weakness of the *ISS* model. As the above equation illustrates, the *ISS* performance depends strongly on the difference between the isotopic compositions of the different components of the equation. This is also the case for *IHS,* where the isotopic composition of event water should differ significantly from pre-event water (Sklash & Farvolden, 1979). With *ISS* this would be $C_{Türlersee}$ and $C_{Inflows}$ and they do vary greatly in all the cases of *ISS* calculations. The problem for instance at RE12 is the very small difference between $C_{Reppisch}$ and $C_{Inflows}$. A comparison of isotopic composition differences showed that *ISS* performs best, when isotopic compositions of the three components differ the most.

Another reason for the random results could be the monitoring strategy: Own discharge measurements of the Reppisch and sample taking of $C_{Reppisch,}$ which were used for the calculation of Türlersee portions, were undertaken up to several hundred meters downstream of the sampling point delivering $C_{Inflows}$ data. Thus in between other components were admixed to the Reppisch. Actually this monitoring strategy must have been one reason for a weak performance, hence *ISS* calculations of total Reppisch discharges performed with a mean deviation of 83 % much better than the ones for Türlersee portions with a mean deviation of 184 % (mean deviation is built by both, $\delta^{18}O$ and d-excess calculations).
Additionally, best performances what means smallest deviations between measured and calculated discharges (of the Reppisch or Türlersee portion), were expected so at RE23, because exactly at this position the total discharge and the Türlersee portion are known (data source: AWEL). Though interestingly, biggest mean deviations are reached at RE23 for Türlersee portion calculations with 287 % with $\delta^{18}O$ values and 196 % with d-excess values. Total Reppisch discharge simulations at RE23 reached a mean deviation of 71 % for both ways. As previously said, isotopic composition differences between $C_{Reppisch}$ and $C_{Inflows}$ decreased the further away from the Türlersee. This leads again into the possible reason of too small differences between $C_{Reppisch}$ and $C_{Inflows}$ for the calculation of Türlersee portions.
Another point to criticise the *ISS* calculations is the use of only one calculation for each sample point and sampling day respectively. Data limitation due to weekly grab samples led to such a way of *ISS* implementation. Using means of high-resolution time series would maybe have led to better results and reduced the analytical uncertainty of the isotope measurements. Since, according to Genereux & Hooper (1998) the uncertainty in Q_{sim}, here the lake fraction, is most sensitive to the uncertainty in $C_{Reppisch}$. Hence, in this context it is important to know if the sampled near shore surface water of the Türlersee actually does represent the mean lake signal which is found in the Reppisch. It would also be interesting to know if the lake does always drain water from the same area within the lake. However, a better understanding of the lake system would clarify the isotopic

lake signal and be subject to further research.
However, deviations between simulated and observed data seem to be random, they rose up to more than 2000 % or were around 3 %. This form of calculations of discharge portion is an unpredictable and very poor model so far.
For better performances a weighting technique like differently weighted means, which are used for precipitation waters for *IHS* (McDonnell et al., 1990), probably would alleviate the by the majority underestimated total Reppisch runoffs. Though it would be difficult to find the best weighting technique because there is no clear trend in distortions detectable. Türlersee portions modelling should firstly be tried by an enhanced monitoring strategy of measuring and sampling water components closer to each other.

B) ISCO Sampling Series of 20 - 24/09/2013

In September 2013 a five days lasting sampling series at the Reppisch sample points RE12, -15 and -23.1 and at the inflow to the Türlersee RE2.1 was undertaken. During these days no precipitation was recorded and the Reppisch discharge was constantly decreasing (*Figure 61*). Hence, the Reppisch water samples could deliver information about the Türlersee's signal, if it was varying or constantly decreasing or increasing.

Results

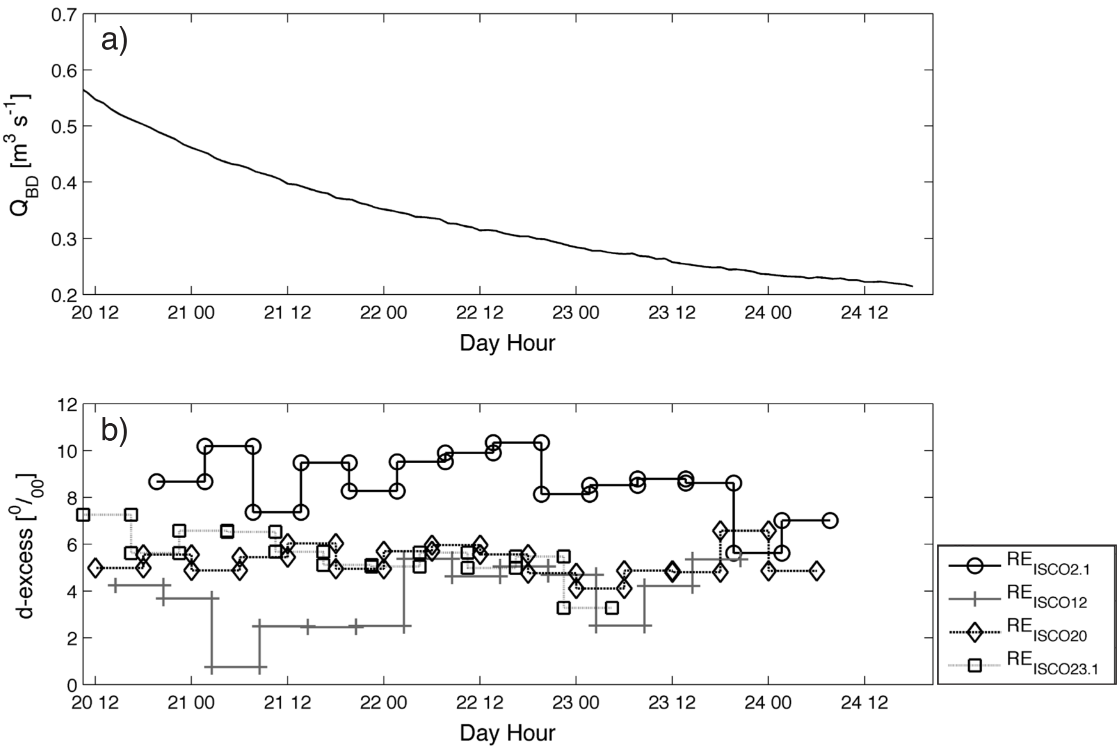

Figure 61 *a)* Time, 20 - 24/09/13, versus discharge of the Reppisch in Birmensdorf [m^3 s^{-1}] (data source: AWEL). No rain fell during these days. *b) ISCO* sampling series of 20 - 24/09/13. One straight line indicates the d-excess in [‰] of a water mixture of samples taken hourly. After six hours the bottle was changed which is indicated by marks in the graph.

The horizontal straight lines between the marks of the series from 20 - 24/09/13 represent the isotopic composition of six hourly taken samples à 100 millilitres into the same bottle. The marks stand for the changing of the bottles every six hours.
Within these four days no rain fell and the Reppisch's discharge in Birmensdorf decreased from 0.547 to 0.214 m^3/s (data source: AWEL). The d-excess signal of the inflow to the Türlersee at $RE_{ISCO2.1}$ is displayed in the typical range of all of the inflows in the Reppisch basin during the monitoring period. It ranges between 10.34 ‰ in the and 5.61 ‰. It is interesting that the signal at $RE_{ISCO2.1}$ moves into the opposite direction than the signals of the Reppisch at RE_{ISCO12}, RE_{ISCO20} and $RE_{ISCO23.1}$. RE_{ISCO12}, the *ISCO* monitoring closest to the lake, shows the lowest d-excess values of the three Reppisch sampling series. This situation is in agreement with all the collected data in the monitoring period: The closer a sample point is located to the Türlersee the closer its isotopic composition is to the one of the Türlersee. From the 23/09/13 on, when the Reppisch discharge dropped lower than 0.300 m^3/s, the d-excess values of the Reppisch dropped as well and rose back

to values around 5 ‰.

ISS of ISCO Sampling Series of 20 - 24/09/2013

An *ISS* calculation for the three *ISCO* sampling series in the Reppisch were also undertaken and the gained data is presented in *Table 19* for $RE_{ISCO23.1}$. At $RE_{ISCO23.1}$ it is possible to compare simulated discharges with the measured ones in Birmensdorf. One focus is on the inflows (surface and subsurface) to the Reppisch between the Türlersee and Birmensdorf. The appearing simulated values are randomly close or far away from the observed ones. The trend of decreasing inflows appears with the simulated data and is confirmed by observed ones. In return the Türlersee portion increased.

Table 19 *ISS* simulations of total Reppisch discharge (Q_{sim}) at $RE_{ISCO23.1}$ (between RE22 and RE23) with data of the Türlersee discharge Q_{TS} (data source: AWEL) and with $\delta^{18}O$ and d-excess information. Inflows are calculated with Q_{sim} and Q_{BD} and Q_{TS} in [m^3 s^{-1}].

		$RE_{ISCO23.1}$					Inflows between		
					Q_{sim}		Q_{sim} - Q_{TS}		Q_{BD} - Q_{TS}
					Mean				
		$\delta^{18}O$	δD	d	$\delta^{18}O$	d	$\delta^{18}O$	d	Q_{obs}
Date	Time	[‰]	[‰]	[‰]	[m^3 s^{-1}]	[m^3 s^{-1}]	[m^3 s^{-1}]	[m^3 s^{-1}]	[m^3 s^{-1}]
20/09/13	16:28	-9.34	-67.47	7.25	0.639	0.845	0.426	0.632	0.287
20/09/13	22:28	-9.2	-67.99	5.61	0.471	0.431	0.273	0.233	0.262
21/09/13	04:28	-9.26	-67.51	6.57	0.512	0.580	0.316	0.384	0.234
21/09/13	10:28	-9.24	-67.4	6.52	0.457	0.526	0.276	0.345	0.224
21/09/13	16:28	-9.16	-67.61	5.67	0.390	0.385	0.216	0.211	0.196
21/09/13	22:28	-9.04	-67.21	5.11	0.320	0.319	0.153	0.152	0.183
22/09/13	04:28	-9.05	-67.36	5.04	0.310	0.300	0.150	0.141	0.178
22/09/13	10:28	-9.11	-67.25	5.63	0.308	0.322	0.161	0.175	0.167
22/09/13	16:28	-9.1	-67.82	4.98	0.302	0.271	0.156	0.125	0.156
22/09/13	22:28	-9.19	-68.05	5.47	0.325	0.291	0.186	0.152	0.143
23/09/13	04:28	-8.91	-68.01	3.27	0.220	0.175	0.087	0.043	0.141

Discussion

ISS with ISCO Series Sampling

For the *ISCO* sampling series the *ISS* model did not perform any better than with the grab samples. Nevertheless, the series sampling brought up some other interesting findings and confirmations of already discussed phenomena:

Table 19 of *ISS* at $RE_{ISCO23.1}$ brought up a trend of decreasing d-excess from 7.25 ‰ on 20/09/13 to 3.27 ‰ on 23/09/13. This decreasing d-excess together with decreasing discharges and no precipitation falling during those days, led to the following hypothesis: With sinking d-excess close to Birmensdorf the Türlersee portion of the Reppisch must have been increasing. Hence in return inflow portion in the Reppisch must have been decreasing. Both, the simulated and observed data in *Table 19* confirmed this hypothesis as now shown in *Figure 62*.

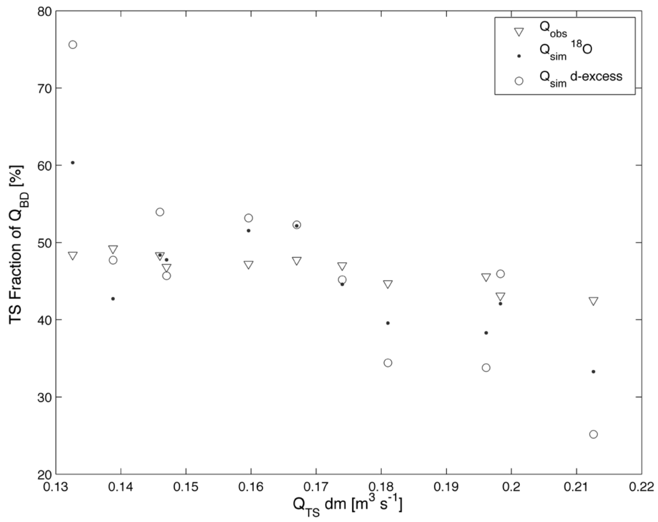

Figure 62 Türlersee fractions with daily mean discharges at the outflow of the Türlersee (data source: AWEL) for the time span of 20 - 23/09/13. The marks indicate observed and simulated Türlersee portions ($RE_{ISCO23.1}$). During this time lapse total Reppisch discharge was constantly decreasing.

Observed Türlersee fractions were increasing from 43 to 48 % during the three days. Simulated Türlersee portions (equals Q_{TS} observed of Q_{sim} simulated total Reppisch discharge) increased in *ISS* calculations with $\delta^{18}O$ from 33 to 60 % and with d-excess from 25 to 76 %. The trend of increasing Türlersee portions was given, though the ranges in the *ISS* model were too big to use these results for further estimations or for any interpretations concerning discharge portions in the Reppisch.

Anyway during the following hours, d-excess values of the other *ISCO* series samples ($RE_{ISCO23.1}$ ran out of power) rose again (*Figure 61*). This implies that Türlersee portion started to sink again, what was also confirmed by the observed discharges and in trend by *ISS* simulations.

C) Sampling Methods, Assumptions and Differently Generated Data in 2013

The following subchapters elucidate different aspects of the practical and theoretical methods used during this project. Finally, general critical reflections on some appeared uncertainties are picked out.

Comparison of WLPWS Data with Grab Samples

In order to have an idea on the sensitivity of the generated d-excess signals with samples collected by the *Water Level Proportional Water Samplers* (*WLPWS*), they were compared to the signals generated with weekly grab samples.

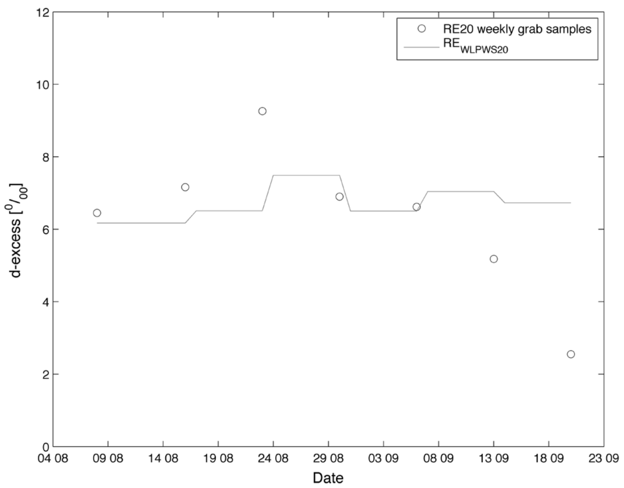

Figure 63 Time versus d-excess of collected Reppisch water at RE20 in summer 2013. Steps of the lines indicate monitoring days when *WLPWS* were emptied.

Deviations between the d-excess values of weekly integrated signals of water collected by *WLPWS* and of the weekly grab samples were in the range of maximal + 2.75 and – 7.1 ‰. The mean deviation lay between + 0.08 and -1.18 ‰ (*Table 20*), whereas only one mean deviation at RE19 lay in the positive range which means it had a lower d-excess value than its corresponding grab samples. In general, the *WLPWS's* samples depicted a slightly more positive isotopic signal of the streams than the grab samples. Due to bias, these means should be looked at with care. In addition, the tendencies of an increasing or decreasing d-excess were parallel, except for the sample points RE2.1, RE9 and RE15 at the end of August. Often the ranges of the grab samples were bigger than the ones of the *WLPWS*. This was also expected because *WLPWS's* samples already were a mix of water, hence their isotopic signals were averaged over time.

Table 20 Summarised comparison of mean d-excess in [‰] of all sample points where *WLPWS* were installed. Means are calculated from collected samples between 08/08/13 and 20/09/13. Differences are calculated from RE_{WLPWS} value which indicate weekly integrated signals to RE values, which indicate weekly grab samples in d-excess of the specific stream.

Sample Point	d-excess [‰] Mean 08/08/13 - 20/09/13		Difference
	RE	RE_{WLPWS}	
RE2.1, $RE_{WLPWS2.1}$	9.15	10.33	-1.18
RE7, RE_{WLPWS7}	8.18	9.32	-1.13
RE9, RE_{WLPWS9}	4.34	5.22	-0.89
RE12, $RE_{WLPWS12}$	6.56	6.76	-0.61
RE14, $RE_{WLPWS14}$	8.45	8.715	-0.27
RE15, $RE_{WLPWS15}$	6.8	7.14	-0.34
RE19, $RE_{WLPWS19}$	8.16	8.08	0.08
RE20, $RE_{WLPWS20}$	6.28	6.74	-0.46
RE23, $RE_{WLPWS23}$	6.63	7.22	-0.59

Discussion of comparison WLPWS Samples – Grab Samples

WLPWS bring along many advantages: They sample passively water level proportional stream water, no batteries or any other energy source is necessary, they are lightweight and small and they are not very vulnerable to colder conditions (Lange, 2012). Though, they are a black box. While being absent the scientist does not know whether the *WLPWS* is sampling constantly, the plug is always under water nor when the bottle was completely filled. An additional installation of water pressure logger would enhance the control.

During construction of the *WLPWS* in the laboratories difficulties appeared to manage a hermetically enclosure of all necessary parts of the sampler. Although each one was tested in the laboratories, damage during transport or installation could still have appeared. The final installation in the streams brought next difficulties: Either stream beds were filled with a very soft sediment where the armouring iron disappeared or beds were filled with stones and therefore it was difficult to dig in. Hence in advance it was obvious, the collected data by *WLPWS* should be handled cautiously.

The comparison above showed that most of the isotopic composition of *WLPWS* and grab samples did not differ a lot from each other. Though often the ranges of the grab samples were slightly bigger than the ones of the *WLPWS*. This was probably because the *WLPWS* already diminished outliers in the isotope compositions by a simple mixing of the waters.

Another observation was that mainly samples collected with *WLPWS* showed higher d-excess values than grab samples. This can simply be explained: On the day when taking the grab sample, the *WLPWS* did not sample anymore. The highest difference between grab and *WLPWS* sample was found at RE2.1 on 23/08/13. Checking back in protocols brought up that during this sampling day, most plug valves of the *WLPWS* were outside of the water (*Figure 64*), also at RE2.1. This happened mainly in inflows where stages fell unexpected low. Hence, $RE_{WLPWS2.1}$ must have sampled water of days before and generated a d-excess of 11.4 ‰, whereas the grab sample brought up one of 4.26 ‰.

Apart from measurement errors, this finding initiates two interpretations connected to different

discharge situations in the inflows: *a)* No sampling at very low stages: The *WLPWS* was filled previously to sinking discharge in the inflow. Due to lower stages the plug valve came out of the water and of course, could not suck anymore. With lower runoff amounts, the water was running slower and therefore exposed to evaporation for a longer time duration. The taken grab sample was of this low flow water. *b)* Domination of water with higher d-excess values: Slowly flowing water has less pressure, so during low flow situations less water was sucked by the *WLPWS*. If this water additionally was of lower d-excess values, then the admixture of the *WLPWS* water was dominated by water of higher d-excess values collected during high flow situations.
In the Reppisch such situations did not appear, *WLPWS's* plug valve came out of the water only once at RE12. As a result, the d-excess values of the Reppisch grab samples did vary less from the according *WLPWS's* data than it happened in the inflows.

Figure 64 Plug valve of $RE_{WLPWS12}$ was out of the water after a dry spell of unexpected dimension (Photo: A. Maurer).

Discussion of different Recession Coefficient K for API/CPI for 2013
For this project, determinations of the *Recession Coefficient K* were built on instructions found in Fedora (1987), Vogel & Kroll (1996) and Tallaksen (1995).
To determine K, I firstly followed the *Correlation Method* after Langbein (1938 in Tallaksen, 1995) and Fedora (1987) with the equation:

$$K = (Q_{t+\Delta t} / Q_t) \quad [\ ] \tag{11}$$

Where the here non-dimensional K is the slope [-], Q_t discharge at one time in [$m^3\ s^{-1}$] and $Q_{t+\Delta t}$ discharge on time interval later in [$m^3\ s^{-1}$]. This determination of the slope is done for a recession limb during a dry spell. The following graph represents the recession limb of July 2013, where the discharge of two hours before the actual discharge is plotted versus the actual discharge (*Figure 65*).

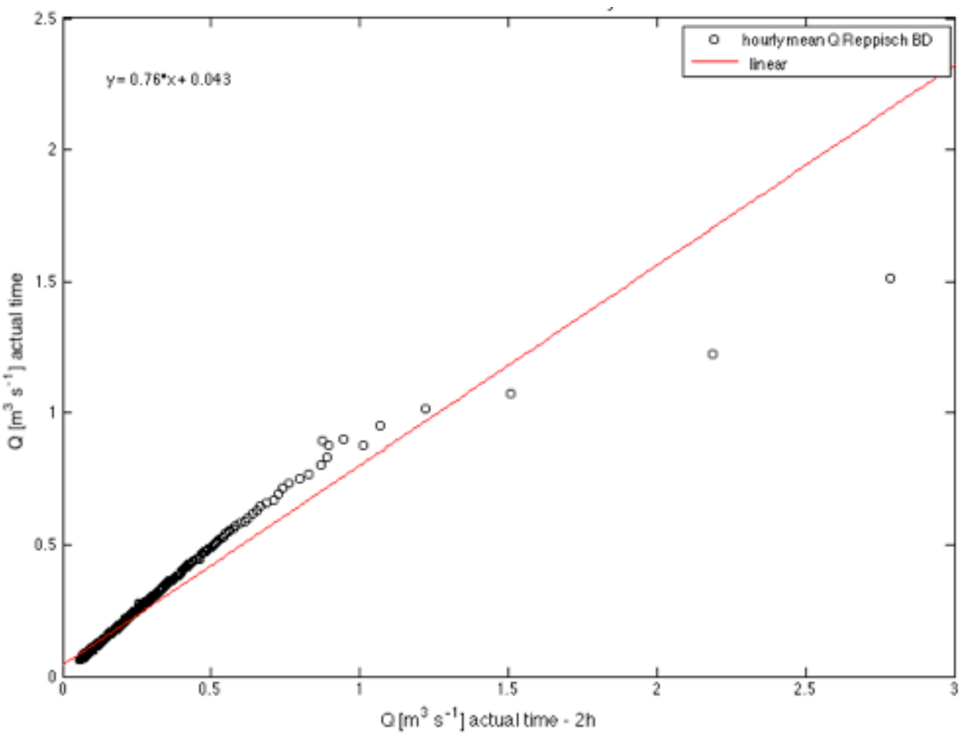

Figure 65 Daily mean discharges of the Reppisch in Birmensdorf are plotted against each other where on the x-axis the discharge values of two hours before the according actual value on y-axis is displayed (data source: AWEL). During this time lapse of 04/07 - 24/07/13 total Reppisch discharge was constantly decreasing and no precipitation was added to the basin.

With this method the received K was 0.76 and lead to very different *CPIs* than our actually used K of 0.923 1/d as shown in *Figure 66*.

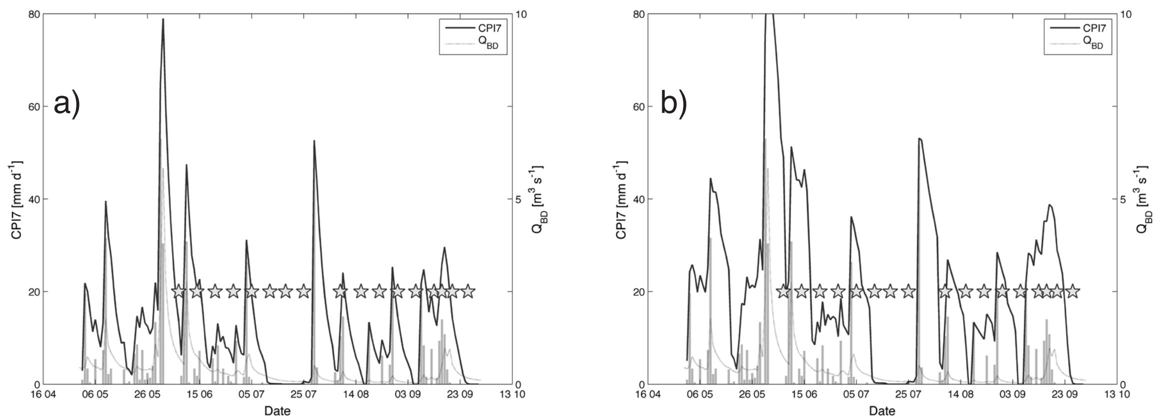

Figure 66 CPI7 conditions, precipitation and discharge during May to September 2013. CPI7 is determined with a K *a)* of 0.76 (derived by Q at t-2h versus actual Q at t) and *b)* of 0.923 [1 d^{-1}] (derived by time step versus LogQ). Stars represent the positioning of the sampling days during monitoring period 2013.

It is of big importance, if K is 0.76 or 0.923 like the *Figures 67 a)* and *b)* show. I decided to use K of 0.923 1/d received by the time step versus LogQ method, it seemed to model more realistic *CPI7* scenarios.

Comparing the two and many other Ks led to very different antecedent conditions as for example for 09 July where with K 0.76 *CPI7* is 6.13 mm/d and with K 0.923 *CPI7* is 18.7 mm/d. In gen-

eral, with a smaller K antecedent wetness in the area will stay for a shorter time duration, show quick peaks, decrease rapidly and in a more u-curve shaped way than with a higher K value (more n-curve shaped). With a higher K value the wetness reaches higher levels and lasts longer. Its decrease though is more straight and vertical. If K would be even higher, like 0.998, then once reached peaks appear as tables for some days before the curves start to slowly drop. Such a high K value seemed to be very unrealistic for the Reppisch basin in summer 2013 because some inflows that fell dry would have fallen into periods of *CPI7* situations with quite high values.
Moreover, the determined parameter K for monitoring period 2013 might of course not be the optimum for another period (see also Beven, 2012).

Discussion of CPI Moving Window of 7, 14 or 30 days
If a chosen *CPI* moving window is one of 7, 14 or even 30 days is an arbitrary decision. I made this decision by keeping the observed behaviour of the Reppisch and its inflows during summer 2013 in mind. Hence, this may of course be completely different in another time span with different meteorological conditions or just with another observer making his subjective interpretations to the system. To have an idea of how *CPI* would have been if a longer moving windows was chosen, *Table 21* summarises all sampling days of 2013 additionally with *CPI14* and *CPI30*. For the two days with lowest *CPI7* (18/07/13 and 06/09/13) *CPI14* would only have fit better to the observed runoff of 18/07/13. There *CPI14* was 0.72 mm/d, no inflow felt dry for that day. Whereas for the 06/09/13 when two inflows felt dry, *CPI14* still simulated 13.87 mm/d.

Table 21 Monitoring days of summer 2013 with the according observed precipitation (data source: METEOCENTRALE) and *CPI* scenarios with different moving windows of 7, 14 and 30 days.

Date	P [mm d^{-1}]	CPI7 [mm d^{-1}]	CPI14 [mm d^{-1}]	CPI30 [mm d^{-1}]
07/06/13	0	49.03	61.70	71.58
14/06/13	1.8	42.51	70.48	80.64
21/06/13	0.6	11.25	34.47	55.43
28/06/13	0.2	10.29	16.36	39.95
05/07/13	0	31.15	36.90	47.93
12/07/13	0	0.31	18.09	23.68
18/07/13	0	0.00	0.72	13.80
25/07/13	0.6	0.60	0.60	7.22
08/08/13	10.4	13.35	38.94	38.98
16/08/13	0	8.33	15.36	28.83
23/08/13	0	9.72	14.48	26.17
30/08/13	0	24.31	29.85	34.85
06/09/13	0	0.00	13.87	19.67
13/09/13	0	28.83	28.83	38.55
16/09/13	14	35.16	46.54	54.18
20/09/13	0	28.91	45.36	49.87
26/09/13	0	0.23	20.34	30.37

For the monitoring day of 12/07/13 *CPI7* classified the area to dry conditions, but discharges in Reppisch were still higher than our threshold of 0.0894 m^3/s (see also *Figure 38*). The moving window of seven days already left the precipitation that has fallen more than seven days before, otherwise 12/07/13 would have been classified to be humid.

Critical Reflections on different points of this project

At different steps during this project insecurities, uncertainties, difficulties or obvious discrepancies appeared. In this section some of them are picked out and shortly described. This chapter is not exhaustive.

Groundwater

Groundwater may play a significant role in a watershed's behaviour (BUTTLE, 2006). Though this component of the Reppisch basin was not subject to sampling or any other examinations. According to SCHERRER (2006) *Deep Percolation* (*DP*) is not an important part in the research area, nevertheless the importance of shallow groundwater - Reppisch interactions remains unknown. Sampling the inflows to the Reppisch and Türlersee gave an idea of possible isotopic compositions of groundwater, because especially the little inflows' springs often were not far away from the sampling point and their isotopic compositions sometimes seemed to reflect the one of precipitation. This closeness can often be assumed (GENEREUX & HOOPER, 1998). Some remaining open questions might be answered by additional research around groundwater, riparian zones and stream interactions.

Uncertainties in Data Generation

Discharge Measurements

Discharge measurement were undertaken mainly with the bucket method for the inflows and salt dilution method for the Reppisch and for the inflows when their discharges were more than estimated 5 l/s. Several times discharges were so low that the bucket method was more an estimation method where the cross section and runoff speed were estimated and as a resultant mean discharge calculated. These discharge measurements, or estimations, come with uncertainties that have to be kept in mind. For the salt dilution method precision of within 5 % can be reached under good conditions (Day, 1977 and Johnstone, 1988 in Moore, 2004). Especially during low flow conditions they were surely not always reached in the Reppisch.

Sample Numeration

For sample processing in the laboratories samples had to have a continuing numeration, therefore new numbers were given to all samples. Many new possible steps where mistakes could have happened emerged:

- Transcribing new numbers to existing sample number and date
- Mixing of samples during pipetting into vials
- Mixing of vials when feeding *Picarro* and labelling them to the *Picarro* system
- Transcribing back the continuous numbers to sample number and date (copy paste in *Excel*, ordering dates and data)

ISCO Samplers

Programmed and realised end times often did not match: e.g. 16/09/13 $RE_{ISCO23.1}$ finished with bottle 24 at 05:07 p.m. (displayed in *ISCO*), but bottle number 19 was filled at 09:07 a.m.. So with hourly time steps the programme should have finished at 02:07 p.m.. Hence it was not clear when the programme really finished and if it really took the samples hourly and half hourly as programmed. Here many imprecisions appeared, probably mainly due to battery weaknesses.

Uncertainties in adopting historical data

As discussed in section 4.1.1, sampling point RE4 was not located at the same position for the three monitoring periods. Though, thanks to clearly distinctive signals of the lake and the inflows, samples could be allocated to their sources.

Discharge measurements in the Reppisch of 25/08/11 did evidently not agree with *AWEL* data (five minutes interval) of the lake outflow and of the runoff in Birmensdorf. In measurement protocols discharges were lying between 1.3 and 5.6 l/s, *AWEL* data showed a decrease of discharges in Birmensdorf from 1350 to 250 l/s within 24 hours. This situation must have made field measurements difficult. Nevertheless, even wrong indices do not explain these values.

Used salt masses, as written in protocols, were lying between 10 and 52 g (for the Reppisch and inflows respectively), this is not adequate for discharges around several 100 l/s and background electrical conductivity around 500 µS/cm anyway (Moore, 2005). Trust in discharge measurements of the other two monitoring days in 2011 disappeared and a further use of these data was abandonned. Generally the adoption of data generated by other researchers in summers 2010 and 2011 was afflicted with a lot of uncertainty. Protocols, where available, were a great support.

Uncertainties in processing actual data
Uncertainties though appear of course also with data generated by oneself. Uncountable steps appear while data processing where confusion and mistakes could emerge. If they generate too unreal results, they are often detected.
However, there are also uncertainties which are simply a lack of knowledge. Beven (2012) discussed them as *epistemic uncertainties* in the context of rainfall-runoff modelling. In this project they especially revealed with the poorly performing *ISS* model and determinations of antecedent conditions.

Geographic Information Systems
An inconspicuous, even though not unimportant or small part of this project was the generation of geographic data in particular catchment sizes and stream lengths. Therefore *Geographic Information Systems* (*GIS*) were used and different algorithms implemented. The following two paragraphs describe some critical steps with *Whitebox* and *ArcGIS*.

Whitebox
Stream Network Analysis: To extract streams different thresholds could be used, different ones were tested. For example if it was 1800 or 2000 led to a stream length of RE9.2 of 180 m longer or shorter.

ArcGIS
Stream artefacts: When determining stream length in the *Digital Elevation Map* (*DEM*) in depressions some parts of the streams appeared that do not exist in reality whereas others, existing ones, were not displayed in the *GIS* model. A comparison of the streams in *ArcGIS* with the ones mapped by Swisstopo and a separation of artificially connected streams became necessary. Finally only the lengths of existing ones were calculated.

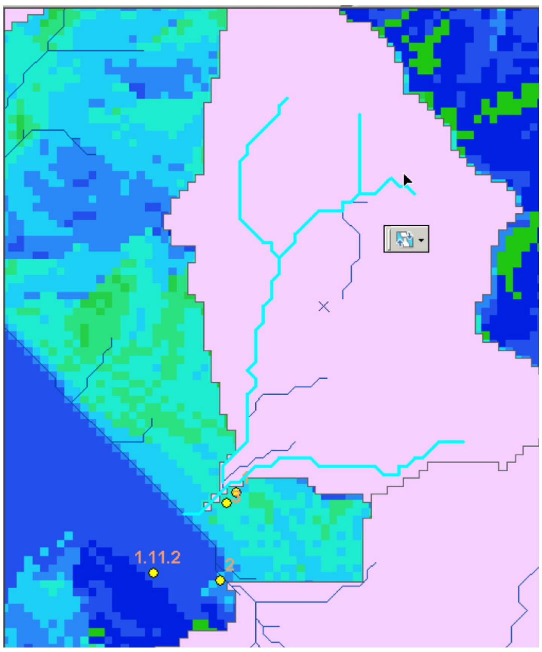

Figure 67 Example in *ArcGIS* of artefacts in stream determination at RE3: some tributary flows are linear, others are not mapped by Swisstopo (map.geo.admin.ch, 2013).

In some cases even distances between streams were not as expected by referencing Swisstopo maps. Initially streams were derived point by point in *Whitebox* with flow algorithms called *Rho8 flow pointer (Whitebox:* Fairfield & Leymarie, 1991). One was just not derivable, so it had to be drawn by hand in *ArcGIS*. This of course had no more the same construction criteria like the ones derived with the flow algorithm.
Polygons of subcatchment areas sometimes also had to be adjusted by hand.
However, in this project geographic data were determined by best practice, it may though be that some streams differentiate in few metres.

Personal Declaration

I hereby declare that the submitted thesis is the result of my own, independent, work. All external sources are explicitly acknowledged in the thesis.

Biberstein, 25 March 2014 Alexandra Chevrolet