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An integrated spatial snap-shot monitoring method for identifying seasonal changes and spatial changes in surface water quality

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SUMMARY

Integrated catchment-scale management approaches in large catchments are often hindered due to the poor understanding of the spatially and seasonally variable pathways of pollutants. High-frequency monitoring of water quality at random locations in a catchment is resource intensive and challenging. A simplified catchment-scale monitoring approach is developed in this study, for the preliminary identification of water quality changes – Integrated spatial snap-shot monitoring (ISSM). This multi-parameter monitoring approach is applied using the isotopes of water (δ^{18}O-H_2O and δD) and nitrate (δ^{15}N-NO_3^- and δ^{18}O-NO_3^-) together with the fluxes of nitrate and other solutes, which are used as chemical markers. This method involves selection of few sampling stations, which are identified as the hotspots of water quality changes within the catchment. The study was conducted in the peri-alpine Thur catchment in Switzerland, with two snap-shot campaigns (representative of two widely varying hydrological conditions), in summer 2012 (low flow) and spring 2013 (high flow). Significant spatial (varying with elevation) and seasonal changes in the sources of water were observed between the two seasons. A spatial variation of the sources of nitrate and the solute loads was observed, in tandem with the land use changes in the Thur catchment. There is a seasonal shift in the sources of nitrate, it varies from a strong treated waste water signature during the low flow season to a mixture of other sources (like soil nitrogen derived from agriculture), in the high flow season. This demonstrates the influence of other sources that override the influence of waste water treatment plants (WWTPs) during high flow in the Thur River and its tributaries. This method is expected to be a cost-effective alternative, providing snap-shots, that can help in the preliminary identification of the pathways of solutes and their seasonal/spatial changes in catchments.

1. Introduction

The European Union (EU) Water Framework Directive (European Union, 2000) calls for sustainable management of water resources on a catchment scale (Gilvear et al., 2012). This provides an impetus to understand the pathways of various pollutants, which proves to be difficult, when monitoring large catchments. Some of the more common problems in monitoring have been identified by Harmancioglu et al. (1999), which include a limited understanding of the key drivers, difficulties in selecting the appropriate sampling frequency and the lack of integration between measurement and management.

In catchments where agriculture and urban waste water are the predominant sources of pollution, nitrate contamination of surface water and groundwater was found to be the main driver that causes water quality problems (Altman and Parizek, 1995; Wassenaar, 1995, 1993; Sebilo et al., 2003). Nitrate leaching from agricultural lands in Switzerland, for example, is a significant contribution to the excessive N loads into the Rhine River, which in turn causes eutrophication problems in the North Sea (Prasuhn and Sieber, 2005; Decrem et al., 2007). From the data recorded by the International Commission for the Protection of the Rhine (ICPR), it was found that in the year 2000, around 436,000 tons of nitrogen from the entire catchment had discharged into the Rhine of which one-third was from waste water and two-thirds was from diffuse sources of pollution (ICPR, 2014).

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Nitrate in river water arises from multiple sources, namely through atmospheric deposition and by anthropogenic influences, and in very rare cases, from the catchment lithology (Berner and Berner, 1996; Jha and Masao, 2013). Stable isotopes of nitrate can be used to track the source of nitrate in rivers due to the distinct isotopic characteristics of the main sources of nitrate such as rain, chemical fertilizers, manure/human waste and nitrate derived from nitrification (Durka et al., 1994; Kendall, 1998). Transformation and reduction of nitrogen species within catchments, like nitrogen processing by headwater streams (low in oxygen), can decrease the nitrogen load in downstream systems (Starry et al., 2005; BryantMason et al., 2013). However, it is to be noted that well-oxygenated streams are not good sinks of nitrate (BryantMason et al., 2013). Since nitrate undergoes transformation processes in surface water, it is not a stable tracer and therefore nitrate is usually evaluated together with the concentration patterns of a conservative tracer like chloride (Cl^-) (Altman and Parizek, 1995; Mengis et al., 1999).

Recent studies have shown various degrees of success using dual-isotope techniques to identify the sources and transformations of nitrate in large rivers like the Mississippi River, U.S.A. (Battaglin et al., 2001; Kendall et al., 2001; Chang et al., 2002; Panno et al., 2006), the Seine River, France (Sebilo et al., 2006) and the Oldman River in Alberta, Canada (Rock and Mayer, 2004). Although it is important to understand the link between seasonal patterns of streamflow and its effect on catchment-scale processes, the source of water in these previous studies was not identified. In a recent study in the Songhua River and its tributaries in China, the sources of nitrate along with the water chemistry and water isotopes have been recommended to be analyzed together to understand the biogeochemical processes in the river (Yue et al., 2014).

Water isotopes are unique tracers that can be used to identify the hydrological responses of a river system. The isotopic composition of water is mainly determined by the composition of rainfall modified by processes in the vadose zone, tributaries and aquifers. Therefore, a spatial approach to isotope studies is necessary to not bias the specific impact of a particular sub-catchment or unique processes within it (IAEA GNIR, 2012). Seasonal shifts in the isotopic composition of water with considerable inter-annual variation have been observed in several large rivers having alpine/snowcapped mountainous head waters, like the Danube and Lena Rivers, which have recorded a depleted isotopic signature in late spring-early summer due to snow melt-water and corresponding enrichment during base flow conditions due to recession of the melt water (IAEA GNIR, 2012). Further, isotopic composition varies with altitude. The air temperature in highlands plays a significant role as there is increased fractionation between liquid and vapor at low temperatures (Ingraham, 1998; Ohlanders et al., 2013). This phenomenon has been reported in studies in the Swiss Alps by Siegenthaler and Oeschger (1980), who had reported a 0.32‰ decrease of $\delta^{18}O$ per 100 m increase in elevation.

The objective of this study is to develop an integrated spatial snap-shot catchment monitoring (ISSM) method that is demonstrated at a peri-alpine catchment in north-eastern Switzerland. In this method, the seasonal and spatial changes in the isotopic compositions of nitrate and water together with the solute fluxes are identified. This combination of isotopes and solute fluxes forms an integrated multi-parameter monitoring method. The aim of ISSM is to provide a simplified monitoring approach using only two snap-shot campaigns representative of extreme hydrological conditions to identify the critical areas spatially as well as to identify the seasonal variations in surface water quality within a catchment.

2. Study area

The study was conducted in the Thur catchment in north-eastern Switzerland as it served as a perfect case study for this integrated multi-parameter study, due to the wide variation in the catchment elevation and multiple land-uses (Fig. 1). The Thur River is a peri-alpine river (127 km long) originates from Mount Säntis and drains into the Rhine River. The catchment area (c.a.) measured till the monitoring station at Andelfingen is 1696 km^2 (Fig. 1). The Thur catchment consists of mainly limestone-dominated alpine headwaters with a high precipitation of approximately 2500 mm/yr. The lowlands are dominated by Molasse sandstones and marls as well as by Pleistocene unconsolidated sediments with a moderate precipitation of approximately 900–1000 mm/yr (Seiz and Foppa, 2007). The average elevation of the catchment is 770 m. However, there is a wide elevational variation within the catchment ranging between 356 m asl to 2504 m asl (Fuhrer and Jasper, 2012). The mean annual discharge (Q) in the Thur River as measured at the outlet of the catchment is 52.9 m^3/s (in 2012) with a dynamic flow regime that varies between 8.5 and 550 m^3/s (FOEN, 2012). The flow regime of the Thur River is nivo-pluvial (snow melt dominated).

The Thur River has three main tributaries, namely the Murg, Necker and Sitter (Fig. 1). The Necker (c.a. 125 km^2) and the Sitter (c.a. 354 km^2) arise from the highlands with the mean catchment elevation of 902 m and 939 m, respectively. The Murg (c.a. 197 km^2), arises from the lowlands with an average catchment elevation of 590 m. The mean yearly Q of the Murg River is 4.6 m^3/s, the Necker 3.6 m^3/s and the Sitter is 11.0 m^3/s (FOEN, 2012). Correspondingly, they contribute 8.5%, 15.5% and 26%, to the Thur discharge at their intersections.

Land use in the Thur catchment is primarily agriculture (45%) followed by forest (25.4%), pasture lands (19%), and urban areas (9%), while the rest is unoccupied land (1.6%). Treated waste water discharges to the Thur and its tributaries through 45 WWTPs (Fig. 1). The contribution of agriculture (54.2%) and urban areas (6.9%) is greater in the Murg sub-catchment (sub-cat.), while the Necker sub-cat. has the most forest cover (34.9%), substantial portion of agricultural land (36.2%) and the least urban influence (4%) (FOEN, 2012). The population density (P.D.) is less than 100 people/km^2 in the upper Thur sub-cat. and Necker sub-cat., while it increases substantially in the lower Thur sub-cat. and is highest in the Murg sub-cat. (Fig. 1). The main urban centers in the catchment are the three towns of St. Gallen (Sitter sub-cat.), Frauenfeld (Murg sub-cat.) and Weinfelden (Lower Thur sub-cat.) with 72,000, 23,000 and 10,000 inhabitants, respectively. In the Murg sub-cat. there are two important WWTPs at Frauenfeld (located before M3) and at Matzingen, located up-gradient from station M2 (avg. yearly Q (2013) = 17,260 and 9740 m^3/day, respectively).

3. Materials and methods

The sampling stations were chosen along the Thur River and its main tributaries the Murg (M), the Necker (N) and the Sitter (S). The sampling stations were chosen at the headwaters of the Thur River and at its lower reach (T1)–T(E) and along its tributaries (S1–S3 along Sitter, N1–N3 along Necker, M1–M3 along Murg) (Fig. 1). The impact of the tributaries on the Thur River hydrochemistry was better analyzed by choosing sampling stations along the main river both up- and down-gradient from each tributary (Fig. 1).

The sampling for the isotope and chemical analysis was done once in summer (avg. day $Q = 31$ m^3/s, low flow) on 28-08-2012 (SC1) and once again in spring (avg. day $Q = 79$ m^3/s, high flow)

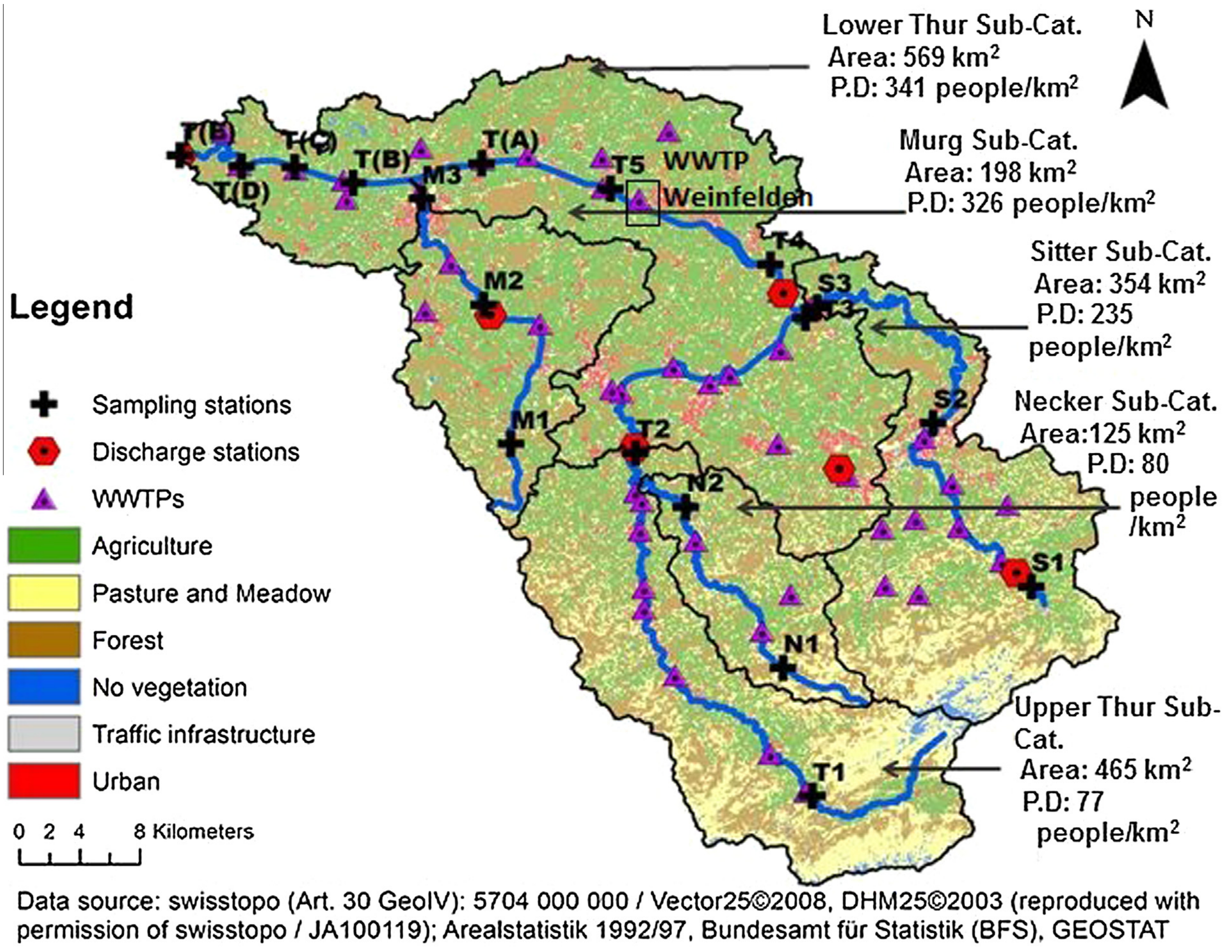

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Fig. 1. Location of the sampling sites, sub-catchments (Sub-Cat.), major discharge stations, waste water treatment plants (WWTPs) and the land use classification in the Thur catchment. The area and the population density (P.D.) of the various sub-catchments are also indicated. *Data source*: Swisstopo, Population data source: STATPOP2011, BFS GEOSTAT.

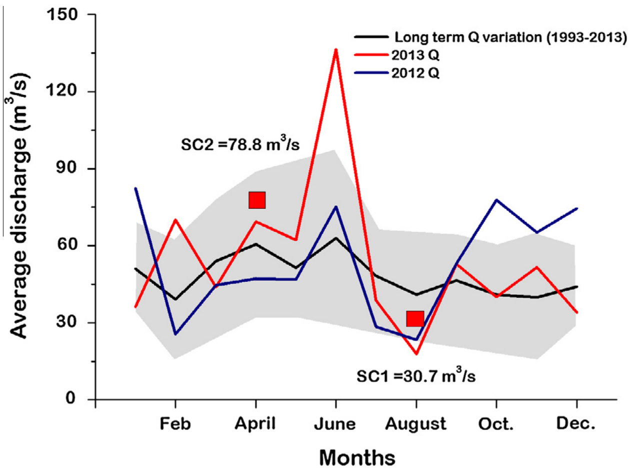

Fig. 2. Averaged discharge (for a day) during the sampling periods (SC1 and SC2) marked with shaded squares along with average monthly *Q* variation in 2012 and 2013. This is compared together with the long-term seasonal *Q* variation (1993–2013). The monthly average standard deviation in the two decades is represented in the shaded area. This data is recorded at the outlet of the catchment. *Source*: FOEN NADUF monitoring program.

on 15-04-2013 (SC2). The sampling campaigns were chosen to be representative of the extreme variation in the monthly average *Q* patterns as shown by the long-term monthly average *Q* (1993–2003) in Fig. 2.

The water samples (one grab sample per day) were collected from all stations on the same day (at different times). The samples were collected and filtered using 0.45 μm pore size cellulose nitrate filters (Sartorious AG, Göttingen, Germany) in the field. All samples were refrigerated (at 4 °C). The cooled samples were then analyzed for the isotopes of nitrate (δ^{15}N-NO_3^- and δ^{18}O-NO_3^-) and water isotopes (δ^{18}O-H_2O and δD). Isotopic analyses of nitrogen and oxygen of nitrate (δ^{15}N-NO_3^- and δ^{18}O-NO_3^-) were carried out using the denitrifier method (Sigman et al., 2001; Casciotti et al., 2002). Isotope ratios $^{18}O/^{16}O$ and $^{2}H/^{1}H$ of the water samples were determined by cavity ring-down spectroscopy (Picarro L1102-i, Santa Clara, CA) and corresponding isotope signatures δ^{18}O-H_2O and δD were conventionally expressed as a permil (‰) deviation from Vienna Standard Mean Ocean Water (VSMOW).

In addition to this, major anions and cations were also analyzed. Since ammonium concentrations in the rivers were very low (<0.1 mg/l), we focused on nitrate, as it is the dominant inorganic nitrogen species in the Thur River. The seasonal contribution of WWTP load to the river load is calculated using data from the Matzingen WWTP (linked to 15,500 inhabitants, data from Agency for the Environment, Canton Thurgau) and from a regular discrete water quality monitoring station monitored by FOEN in the lower Murg sub-catchment (Fig. 1). A detailed method description of the measurement of the various parameters can be found in the Supplementary information.

4. Results and discussion

4.1. Seasonal and spatial changes in the hydrochemistry of the Thur River and its tributaries

The concentrations of selected major cations and anions (NO_3-N, Cl^-, Ca^{2+}, Na^+, K^+) together with total phosphorus (TP) are listed in Table S1 for SC1 and SC2.

Nitrate: Nitrate concentrations in the samples collected from the main river and the tributaries ranged between 0.2 and 5.3 mg N/l in SC1 and between 0.6 and 5.3 mg N/l in SC2. Seasonal and spatial changes were noted (although the mean value of 1.5 mg N/l over all the stations, remained the same between the two seasons). The concentrations of nitrate were lower than 1.5 mg N/l in the samples from the upper Thur SC and the headwaters of the tributaries (M1, N1, N2, S1, T1 and T2) in both seasons (Figs. 1 and 3, Table S1). However, from SC1 to SC2 there was an increase in the concentration of nitrate (0.5 mg/l increase) in the headwaters of the Thur River (samples from T1, T2) and the Murg River (sample from M2).

Total phosphorus: The mean TP concentrations over all stations were similar for both seasons (SC1 and SC2). However, there was a decrease of the concentration of TP in the headwaters of the Sitter, it increased in the headwaters of the Murg, Necker and the Thur from SC1 to SC2 (Fig. 3, Table S1). The maximum change in TP concentration was observed at M3 (with 100 μg P/l increase from SC1 to SC2). Station M3, located in the lower part of the Murg (before it joins the Thur), is critical because of the presence of WWTPs mentioned in Section 2. At M3, the increase in TP in spring (SC2) was accompanied by high concentrations of Na^+ and Cl^- as shown in Table S1 and Fig. 3.

Dilution effect in SC2: In all the stations, concentrations of Na^+ and Cl^- were lower in SC2 (mean over all stations = 6.2 mg/l for Na^+ and 8.3 mg/l for Cl^-) than in SC1 (mean over all stations = 7.3 mg/l for Na^+ and 9.9 mg/l for Cl^-), which reflects the dilution effect due to higher discharge in SC2. This is further supported by the concentrations of Ca^{2+} and K^+, which are lower in SC2 in all the stations (mean over all stations = 40.2 mg/l for Ca^{2+} and 1.5 mg/l for K^+) compared to SC1 (mean over all stations = 65.8 mg/l for Ca^{2+} and 2.2 mg/l for K^+) (Table S1, Fig. 3).

Hotspots of water quality change: As shown in Fig. 3, the water quality in the Thur River changes mainly at junctions with its primary tributaries, observed by an increase/decrease in concentration of TP, Cl^-, Na^+, Ca^{2+}, NO_3-N and K^+ at critical points like T2 (just downstream from the Necker), T4 (downstream from the Sitter), and TB (downstream from the Murg) in SC1 (Figs. 1 and 3, Table S1). Due to the higher discharge in SC2, dilution of Cl^-, Ca^{2+}, Na^+, K^+ is reflected by dips in the concentrations at the above mentioned junctions, particularly at the junctions of the head water tributaries (Necker at T2 and Sitter at T4) flowing from higher elevations. These tributaries are expected to carry comparatively more melt water and are not solute-rich like the lower tributary Murg (which is expected to be groundwater fed) as discussed in Section 2. Therefore the selection of the sampling sites at select locations including the junctions of the major tributaries with the Thur River are useful to identify the spatial changes in water quality within the catchment.

4.2. Water isotopes – δD and $\delta^{18}O$-H_2O – Capturing the seasonal and catchment elevation effect on the sources of water in the rivers

The $\delta^{18}O$-H_2O ratios varied between −10.0‰ and −8.9‰ with a mean value of −9.4‰ over all stations in SC1, and between −13.4‰ and −10.4‰ with a mean value of −12.1‰ over all stations in SC2, respectively. Significant seasonal changes in the isotopic compositions were observed from SC1 (in summer 2012) to SC2 (in spring 2013), with 2.7‰ and 23‰ decreases in the mean over all stations for $\delta^{18}O$-H_2O and δD, respectively (Table 1, Fig. 4).

The average monthly mean of groundwater isotopes (measured from a long-term monitoring well in the lower Thur catchment), varied annually between −10.4‰ and −9.8‰ for $\delta^{18}O$-H_2O (data obtained from FOEN-NAQUA monitoring program), which matches

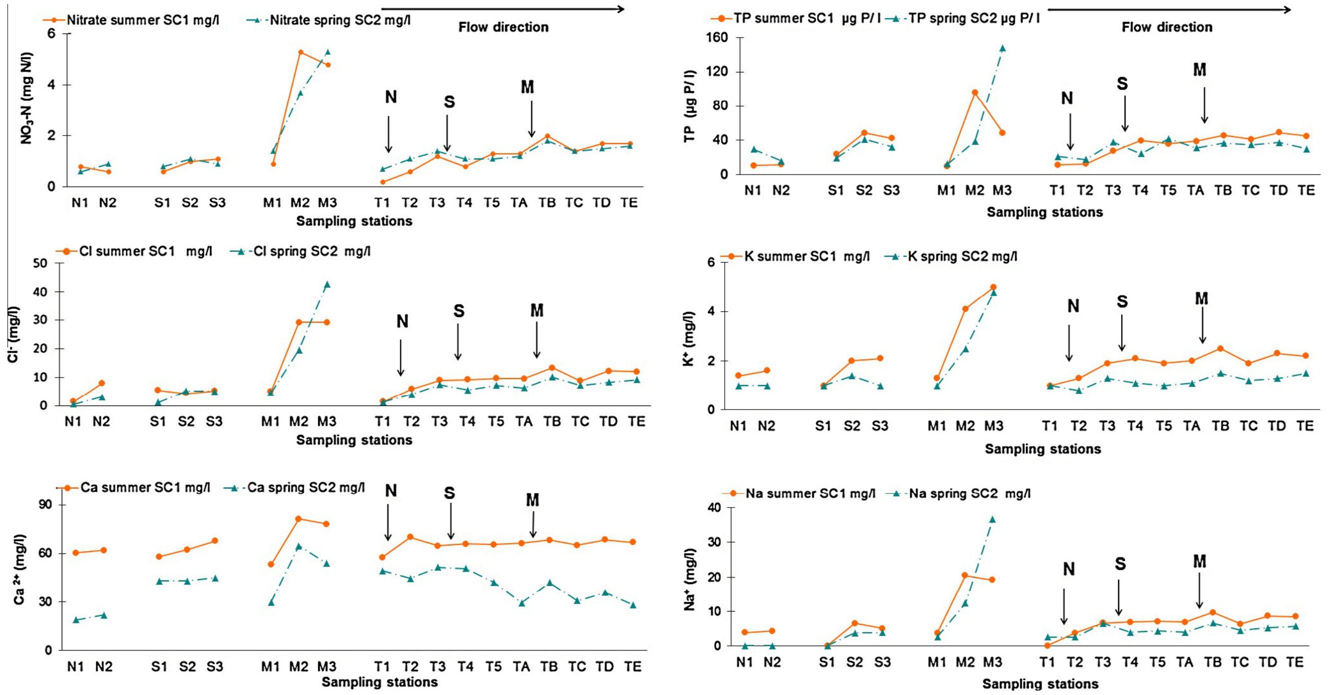

Fig. 3. Hydrochemistry variations in the Thur River and its tributaries measured at the sampling stations in summer SC1 and spring SC2. Concentrations of NO_3-N (±0.1 mg N/l), Cl^- (±0.2 mg/l), Ca^{2+} (±1.7 mg/l), K^+ (±0.3 mg/l), Na^{2+} (±0.8 mg/l), TP (±3 μg P/l) are illustrated. The hotspots of hydrochemistry variations are identified at the junctions of the tributaries Necker (N), Sitter (S) and Murg (M) joining the Thur River.

Table 1
Measured isotopic values of water (δD ‰ ± 0.4‰ and δ^{18}O-H_2O ‰ ± 0.25‰) and nitrate (δ^{15}N ‰ ± 0.2‰ and δ^{18}O ‰ ± 0.4‰) and the calculated theoretical values of δ^{18}O-NO_3 ‰.

Sampling stations	$\delta^{15}N_{NO3}$ (‰)		$\delta^{18}O_{NO3}$ (‰)		δ^{18}O-H_2O (‰)		δD-H_2O (‰)		δ^{18}O-NO_3 (‰)	δ^{18}O-NO_3 (‰)
	SC1	SC2	SC1	SC2	SC1	SC2	SC1	SC2	Summer (Theoretical)	Spring (Theoretical)
M1	6.8	2.5	1.1	−3.7	−9.5	−11.2	−66.1	−77.3	1.5	0.4
M2	11.3	10.8	1.6	5.7	−9.1	−10.4	−64.6	−73.7	1.8	0.9
M3	12.0	21.6	2.7	4.5	−9.1	−10.5	−63.7	−74.4	1.8	0.8
N1	6.1	−3.3	0.3	3.7	−9.7	−13.4	−65.8	−96.2	1.4	−1.1
N2	7.0	2.2	1.5	0.1	−9.5	−12.4	−65.0	−88.7	1.5	−0.4
S1	3.4	−0.2	1.3	3.2	−10.0	−13.4	−68.9	−94.6	1.2	−1.1
S2	9.9	4.2	0.5	2.2	−9.5	−12.7	−64.4	−92.9	1.5	−0.6
S3	9.1	5.3	1.5	2.2	−9.1	−12.7	−62.9	−92.1	1.8	−0.6
T1	3.0	0.7	1.5	−4.6	−9.8	−13.0	−66.6	−95.9	1.3	−0.8
T2	6.0	2.8	1.4	−3.1	−9.8	−11.3	−68.3	−84.2	1.3	0.3
T3	8.5	5.8	1.5	−2.7	−9.4	−12.9	−64.2	−91.8	1.6	−0.8
T4	9.2	4.6	1.5	−2.5	−9.4	−12.8	−64.7	−92.1	1.6	−0.7
T5	8.4	5.7	0.1	−2.2	−9.2	−12.5	−62.7	−90.1	1.7	−0.5
TA	9.5	5.1	1.5	−0.9	−9.3	−12.3	−63.0	−88.2	1.7	−0.4
TB	10.6	8.4	2.5	−0.1	−9.2	−11.2	−63.3	−84.1	1.7	0.4
TC	8.6	6.5	1.0	−1.0	−8.9	−10.8	−61.7	−84.0	1.9	0.6
TD	11.4	6.9	2.4	−1.9	−9.1	−12.4	−62.1	−87.8	1.8	−0.4
TE	11.0	7.5	3.5	−0.4	−9.3	−12.0	−62.8	−86.5	1.7	−0.2
Mean	8.4	5.4	1.5	−0.08	−9.4	−12.1	−64.5	−87.5	1.6	−0.2

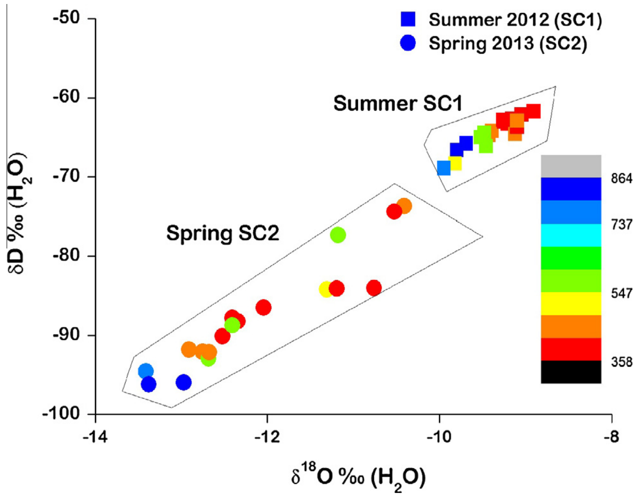

Fig. 4. The isotopic composition of water (δD and δ^{18}O-H_2O) and its variability with elevation in summer 2012 (SC1) and spring 2013 (SC2) in the Thur catchment. Legend shows the color map of the catchment elevation (m).

with the SC1 (summer during low flow) isotopic composition in the Thur River and its tributaries (Fig. S2). This indicates that the Thur River and its tributaries are mainly fed by groundwater during low flow.

During high flow as in SC2, the water isotopes were influenced by the changes in the isotopic composition of precipitation indicated with the lighter isotopic composition in all the stations compared to SC1 (Table 1, Fig. 4). It is to be noted that the monthly mean water isotopic values in the catchment precipitation over the past decade (2004–2014) (measured by FOEN-ISOT monitoring at St. Gallen) varied seasonally (showing depleted signatures from January–April and enriched signatures in July–August), with 8‰ annual variations in δ^{18}O-H_2O (Fig. S2).

The changes in catchment elevation and its effect on the water isotopes, was evident along the Thur River, with an enrichment of the water isotopes with decreasing elevation from T1 to TE (Fig. 1). In SC1, there was an increase in both δD (3.8‰ increase) and in δ^{18}O-H_2O (0.5‰ increase) from T1 to TE. In SC2 also, there was an increase of δD (9.4‰ increase) and in δ^{18}O-H_2O (1‰ increase) from T1 to TE (Table 1, Fig. 4). Significant elevational changes (when the highest station located at Grimsel-1950 m is compared with that in the lowest station located in Bern-511 m) in δ^{18}O-H_2O (nearly 4‰ change in the winter and spring months from February to April) was observed in the long-term averaged monthly samples of precipitation collected at various stations in Switzerland (Fig. S2). Thus, the seasonal effect on the isotopic composition change with elevation is evident with a higher change observed in spring (SC2) when compared to summer (SC1).

4.3. Nitrate isotopes – Tracking nitrate sources using a dual isotope approach

In each season, the isotopes of nitrate (δ^{15}N-NO_3^- and δ^{18}O-NO_3^-) had an increasing trend from upstream to downstream in the Thur River and its tributaries (Fig. S3, Table 1). The dual isotopic model of nitrate was applied to trace the sources of nitrate in the catchment.

Nitrate (measured as NO_3-N) in the river may be derived from rain, synthetic fertilizer, manure, nitrification of soil organic nitrogen and sewage effluents. Atmospheric deposition of nitrate through precipitation exhibits a large variation in nitrogen isotopic composition, with δ^{15}N-NO_3^- ranging between −15‰ and +15‰ (Kendall et al., 1995, 2007; Kendall, 1998; Elliott et al., 2007). The δ^{15}N-NO_3^- of synthetic/inorganic fertilizers (usually ammonium fertilizers) varies between −8‰ and +7‰ (Kendall et al., 2007; Hübner, 1986; Macko and Ostrom, 1994; Vitoria et al., 2004). Nitrogen fertilizers that are organic and derived from plant composts, liquid and solid animal waste have a higher δ^{15}N-NO_3^- range between +2‰ to +30‰ when compared to inorganic fertilizers (Kendall et al., 2007). Since the range of atmospheric deposition of nitrate has an overlapping signature of δ^{15}N-NO_3^- with synthetic fertilizer, the δ^{18}O-NO_3^- is used additionally. Nitrate derived from nitrification of ammonium fertilizers and ammonium from precipitation has lower δ^{18}O values (in the range of −5‰ to +15‰) when compared to those of direct deposition of nitrate from rain (+63‰ to +94‰) and from chemical nitrogen fertilizers (+17‰ to 25‰) (Amberger and Schmidt, 1987; Elliott et al., 2007).

The range of the δ^{15}N-NO_3^- of soil organic nitrogen ranges from 0 to +8‰, with most soils having a range of 2–5‰ (Kendall, 1998; Bedard-Haughn et al., 2003; Spoelstra et al., 2007; Singleton et al., 2007; Xue et al., 2009). The nitrate-nitrogen derived from manure or sewage is isotopically distinct and is usually characterized by high δ^{15}N-NO_3^-, which is from +9‰ to more than +20‰ (Heaton, 1986; Widory et al., 2004, 2005; Choi et al., 2007; Xue et al., 2009).

In the head waters of the Thur (T1, T2), Murg (M1), Sitter (S1) rivers and Necker (N1, N2), the isotopic composition of δ^{15}N-NO_3^- was lower varying between 3‰ and 7‰, during SC1 and varying between −3.3‰ and 2.8‰ in SC2. The δ^{18}O-NO_3^- values, in all the samples are in the range of 0.1–3.5‰ in SC1 and between −4.6% and 5.7‰ in SC2 (Table 1, Fig. 5). Thus, the combination of the ranges of the signatures of both the isotopes indicate the sources of nitrate can be from nitrified ammonium in synthetic fertilizers and precipitation/soil organic nitrogen in SC1 and SC2. It is to be noted that the concentration of nitrate in the headwaters of the Thur and the Necker in both SC1 and SC2 was lower than 1.5 mg N/l as discussed in Section 4.1. This low concentration could be as a result of oxidation of soil organic nitrogen or derived directly from precipitation.

However, in the lower Thur (from T3 to T(E)), Sitter (S2, S3) and Murg (M2, M3) there was an enrichment of δ^{15}N-NO_3^-, varying between 8‰ and 13‰ in SC1, which falls within the theoretical isotopic range of nitrate derived from soil organic nitrogen and sewage effluent or manure (Table 1, Fig. 5). In SC2, in the lower Thur (from T3 to T(E)) and Sitter (S2, S3), the δ^{15}N-NO_3^- varies between 4.2‰ and 8.4‰, this lower range (as compared to SC1) is indicative of a mixing effect of the precipitation derived nitrate and soil nitrogen source in the upper regions with the waste water derived source of nitrate in the lower regions of these rivers. However, it is to be noted that at the lower Murg, the δ^{15}N-NO_3^- in SC2 had enriched signatures of 10.8‰ and 21.6‰ at M2 and M3, respectively, showing an isotopic signature of nitrate derived from manure or from treated waste water, which is likely due to the presence of WWTPs as described in Section 2 (Table 1, Fig. 5).

Effect of nitrification in the river: In theory, the δ^{18}O values of nitrate produced by microbial nitrification would have approximately one-third of the oxygen in NO_3^- derived from oxygen in the air (δ^{18}O-O_2) that has a value of +23.5‰ (Kroopnick and Craig, 1972), while two-thirds should be derived from ambient water oxygen (δ^{18}O-H_2O) (Andersson and Hooper, 1983). Therefore, based on this assumption, the calculated δ^{18}O-NO_3^- in the Thur River from nitrification is with a mean value of 1.58‰ across all stations in SC1 and is with a mean value of −0.23‰ across all stations in SC2 (Table 1). This calculated mean nitrate value matches very well with the mean measured δ^{18}O-NO_3^- value of 1.53‰ in SC1 but is different from the mean of −0.08‰ in SC2 in the Thur River and its tributaries. This shift of measured value from the calculated δ^{18}O-NO_3^- in SC2, can result from mixing processes during infiltration through soil. Thus, microbial nitrification of ammonium from precipitation and soil nitrogen is identified as the main transformation process aiding additional nitrate production in the river (other than direct input from treated waste water) in both the seasons. Additionally, a positive linear correlation was observed between chloride (a conservative tracer) and nitrate concentrations (r^2 = 0.95) in both the seasons, indicating that both are derived from the same source (e.g. treated waste water) (Yue et al., 2014) (Fig. S1). There is a very small positive correlation between the isotopes of nitrate in all the samples obtained from the Thur River and its main tributaries in both seasons (the slope of the linear regression between δ^{15}N-NO_3^- and δ^{18}O-NO_3^- was 0.23 (R^2 = 0.14) in SC1 and 1.3 (R^2 = 0.25) in SC2). Further, the overall increase of δ^{15}N-NO_3^- and δ^{18}O-NO_3^- from upstream to downstream in SC1 and SC2 (Table 1), suggests that de-nitrification had not predominantly occurred in the well oxygenated Thur River during both the sampling days.

Seasonally, there is a pattern of nitrate isotopic values which become lighter in the Thur River from SC1 to SC2. This is indicative of the role of precipitation and soil flushing in the overriding of the dominant waste-water signature in the lower parts of the catchment. The seasonal contribution of WWTPs is discussed in Section 4.4 to clarify this finding further. Additionally, when monthly average ammonium concentrations in rain samples were compared in 2012 and 2013 from an industrial area (<50 km from the study catchment) in Switzerland, the concentration were highest (nearly 1 mg/l) during the spring season (March and April) (Fig. S4). Such seasonal increase of ammonium in the precipitation samples in spring have also been observed in δ^{15}N-NH_4, reported by Russel et al. (1998) in the Chesapeake Bay region in the U.S.A., who attributed it to increased spring-time agricultural emissions. The additional input of ammonium from precipitation has a greater influence in SC2 (in spring during high flow) than during SC1 (during low flow in summer).

4.4. Tracking the seasonal contribution from the various tributaries and WWTP using solute loads

The total load (kg/day) was calculated for the different solutes (Table 2, Fig. 6) showing that discharge is higher during spring in SC2 in comparison to summer SC1 in all stations. The increase was between 150% and 200% higher in SC2 in most stations, while the Necker (at N2) recorded a nearly 400% higher discharge, which is reflected in the upper Thur at T2. The higher nitrate load in SC2 (when compared to the load in SC1) is comparable to the increase

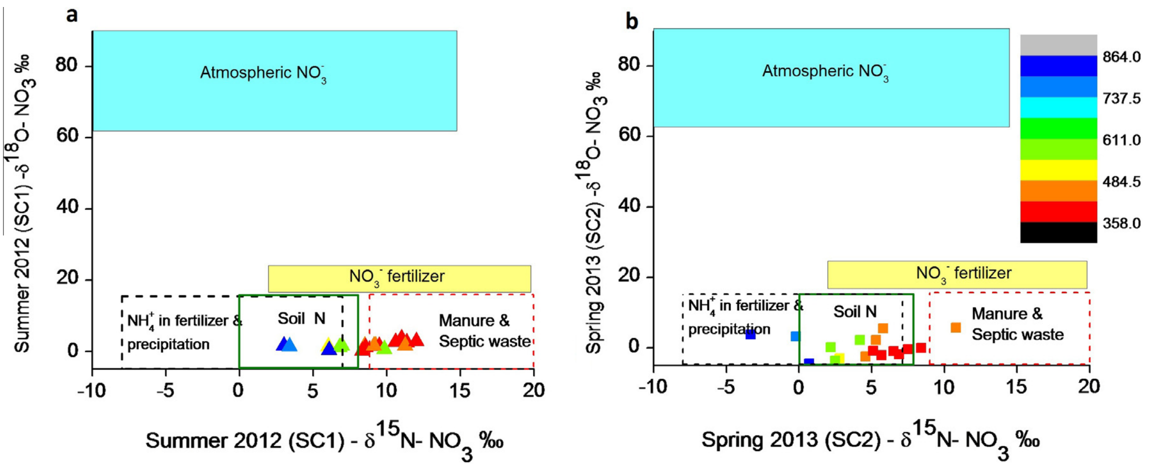

Fig. 5. Relationships between δ^{15}N and δ^{18}O of nitrate in the Thur River and its tributaries in summer SC1 (a) and spring SC2 (b). The isotopic composition of various sources is also provided in the diagram (modified after Kendall et al., 2007).

Table 2
Total solute loads (TN, TP, NO_3-N,Cl) in the Thur River and its tributaries, the Murg, the Necker and the Sitter in SC1 and SC2.

Stations	Q SC1 (m^3/s)	Q SC2 (m^3/s)	% increase	Nitrate load (kg/day)		% increase	Total phosphorus load (kg/day)		% increase	Chloride load (kg/day)		% increase
(ID)	Mean	Mean	SC1 to SC2	SC1	SC2	SC1 to SC2	SC1	SC2	SC1 to SC2	SC1	SC2	SC1 to SC2
T2	12.3	50	307	638	4960	677	13	77	492	6300	17,400	176
T4	23.2	71.7	209	1600	6860	328	79	152	92	18,400	34,400	88
T(E)	30.7	78.8	157	4510	11,000	144	119	204	71	31,800	63,000	98
M2	0.6	1.8	203	284	590	106	5	6	20	1500	3000	98
M3	1.5	4	167	639	1860	191	7	52	767	3800	15,000	288
S1	2.1	8.1	287	109	535	391	4	14	250	280	820	194
S2	6.8	18.7	175	588	1750	199	29	67	131	4700	8400	82
N2	1.6	7.8	388	82	590	611	2	11	450	700	2100	190

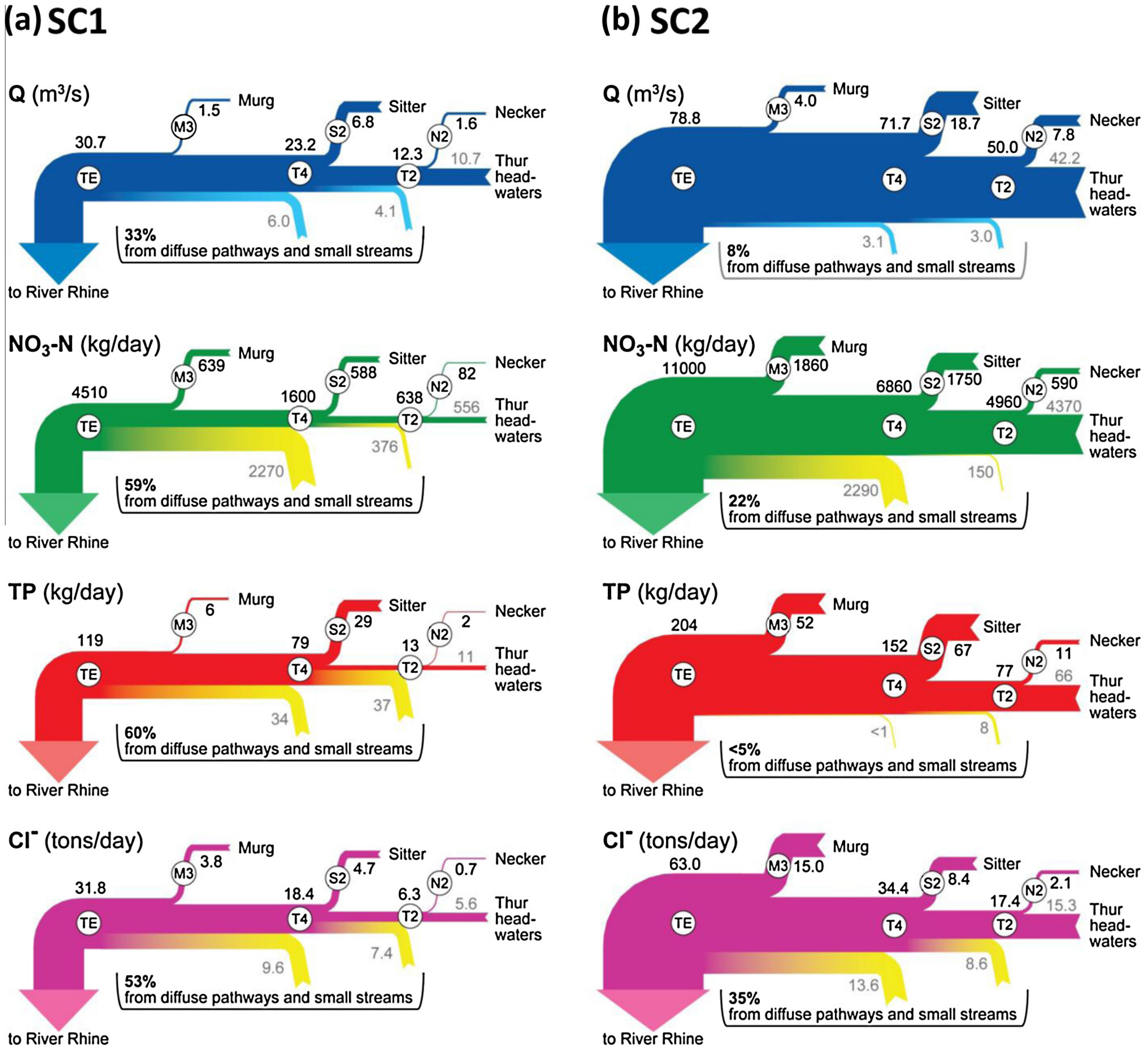

Fig. 6. Flow diagrams of water discharge (Q), NO_3-N, TP, and chloride along the course of the River Thur in (a) summer 2012, and (b) spring 2013. Encircled numbers refer to the monitoring stations labeled in Fig. 1. The gray shaded (or: yellow colored) inputs were calculated to match the observed mass flows at sites T4 and TE. The inputs represent small tributaries and diffuse input pathways, such as drainage, groundwater infiltration, or runoff in the indicated sections. In August 2012, diffuse pathways accounted for >50% of the NO_3-N, TP, and chloride loads. Note that the diagrams are not exactly to scale.

in discharge at the outlet of the catchment (at T(E)). However, the nitrate load varies significantly between the two sampling campaigns in the lower part of the Necker (600% higher during SC2 at N2), which is also reflected in the upper Thur sub-cat. (677% higher during SC2 at T2). Thus it is clear that there is a greater contribution of nitrate load from the headwaters of the Thur and Necker in SC2 compared to SC1, accompanied by a nitrate concentration increase in the upper Thur (at T1 and T2) as discussed in

Section 4.1 (Table 2, Fig. 6). This is attributed to manure application in spring leading to leaching of nitrate from soil especially during rains in addition to direct contribution from precipitation. Although the headwaters of the Thur and Necker have low population density owing to less urban areas, there is substantial agriculture and pasture land in this area as shown in Fig. 1.

The contribution of the various tributaries to the total discharge of the Thur River was also calculated at the junctions where the tributaries join the Thur River. Accordingly, the contribution of the Necker is calculated at station T2, the Sitter's contribution at T4 and the Murg's contribution is calculated at T(E). We found that the contribution from the Murg to the Thur River's discharge in both seasons remained the same at 5%. However, the Necker and Sitter contribute 3% more discharge to the Thur in SC2 compared to SC1. There is a higher contribution (10% higher) of the nitrate load from the Sitter in SC1 compared to SC2. This is further substantiated with an increase in the concentration of nitrate along the Sitter in SC1 compared to SC2.

However, the TP load contribution from the Sitter (8% more) and the Murg (20% more) is higher in SC2. Therefore, it is hypothesized that there is higher contribution of runoff from agricultural lands (where phosphorus is used as an important fertilizer in these regions) and from urban sources in the lower Thur catchment during SC2. Both the nitrate and phosphate loads (at the outlet of the catchment T(E)) in SC1 and SC2 are consistent with the average monthly load variation observed over the past two decades (from FOEN data) as shown in Fig. S5.

The next step was to seasonally differentiate the contribution of the diffuse sources (agricultural runoff) from the point sources (WWTPs). This was done by comparing the solute loads (calculated from the daily concentrations of the individual solutes and the daily discharge recorded) from the Matzingen WWTP (L_{WWTP}) with the loads from a water quality monitoring station at the Murg River (L_{MURG}) located 7 km downstream of the WWTP in the lower Murg sub-cat., as described in Section 3. The method discussed previously in Heeb et al. (2012), is employed wherein the ratio of the waste-water loads is compared to that of the river loads which is (L_{WWTP}/L_{MURG}). When this ratio is >1, there is a transformation of the solute released from the waste water, while it travels in the river. If this ratio is <1 then there is additional loading of the solute into the river other than from the WWTP. The ratio of the daily WWTP loads to the river loads are compared monthly for 2012 and 2013 (Table S2). It was found that the ratio was <1 for nitrate and phosphate for all months in both years indicating an additional contribution of these solutes from the catchment throughout the year.

The load contribution (%) from the WWTP varied every month, from 4% to 24% in 2012 and from 5% to 30% in 2013 for nitrate and from 4% to 94% in 2012 and 4–70% in 2013 for TP. It was found that both nitrate and TP contributions from the WWTP were lowest in December 2012 and January 2013. It is to be noted that there was very high flow in December 2012 and January 2013 with respective discharges at the Murg River of 941,800 m^3/day and 642,000 m^3/day (40% and 44% higher than the average yearly Q, respectively). Additionally, while the average yearly Q contribution from the WWTP to the total Q in the Murg River was 2.8% and 3.4% in 2012 and 2013, respectively, it was reduced to 2.5% and 2.7% during the high flow season in December 2012 and January 2013. However, in the low flow summer months of May 2012 and July 2013, there was a higher contribution of treated WWTP effluent (3.6% and 4.3%, respectively) to the river Q. Therefore, in the months when there is very high Q in the river, there is a lower contribution of treated waste water in the lower Murg River and vice-versa.

To get an idea of the total nitrate load contribution (kg/day) from waste water in the entire catchment, one of the largest WWTPs in the Thur catchment at Weinfelden (avg. Q = 14,617 m^3/-day in 2013) is taken into consideration. The total nitrate load from the WWTP is compared to the population it serves (29,480) and extrapolated to the entire population of the urban areas within the whole catchment (1,210,000). Thus the estimated loads from the WWTP considering the entire population of the Thur catchment were 3400 kg/day and 3860 kg/day (due to difference in the amount of effluent released on both the sampling days), respectively in SC1 and SC2. The WWTP contribution to the total nitrate load calculated at the catchment outlet (at T(E)) was 76% in SC1 and 35% in SC2. This is consistent with the earlier finding that during low-flow periods, there is a higher relative contribution of nitrate from the WWTP compared to the high flow season. This is also consistent with the conclusion obtained from Section 4.3 that there is clearly a nitrate isotopic signature of soil nitrogen in the samples from SC2, while samples from SC1 had a distinct waste-water signature.

5. Conclusion

An integrated catchment monitoring method was developed in this study – Integrated spatial snap-shot monitoring (ISSM). It involves a multi-parameter approach, using a combination of solute fluxes and isotopes. The selected parameters were measured in two representative campaigns (in low flow and high flow seasons), with few sampling stations at select locations. By using a combination of water and nitrate isotopes together with the concentration of solutes and their fluxes, hotspots of surface water quality and the associated seasonal/spatial changes were identified in the catchment. The isotopes of water give an overview of the contribution of the various sources of water that vary seasonally (with varying hydrological conditions) and spatially (with varying elevation). The influence of precipitation is significant in the highlands, while the river is predominantly groundwater fed in the lowlands. The isotopes of nitrate indicate changes in the influence of the various sources of nitrate spatially and seasonally. The land use changes have significant effect on the river water chemistry, the urban areas have higher waste water influence particularly in the lowlands. During high flow, the strong waste water nitrate signature in the lowlands, is overridden by the influence of soil nitrogen flushed from the agricultural areas in the catchment. Flow diagrams indicating the various solute loads draining from the tributaries and other diffuse sources were constructed. The net turnover of the nutrients draining from the catchment varies significantly between the two sampling days. Thus, in this study it is shown that a good understanding of nutrient pathways and the identification of the hotspots of water quality changes can be obtained with the help of the ISSM method. This method is particularly effective when the snap-shot campaigns are representative of the major hydrological changes in the catchment. This method can be further enhanced using additional isotopes like boron and with bacterial source tracking to differentiate between sewage and manure signatures. The limitations of this method over high-frequency sampling is the lack of data to verify pollutant peaks and to estimate the rapid mobilization of solutes especially during storm events. Thus, this is recommended as a preliminary method to identify the critical areas in a large catchment, which can then be routinely monitored to obtain further insights.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhydrol.2016.05.017.

References

Altman, S.J., Parizek, R.R., 1995. Dilution of non-point source nitrate in groundwater. J. Environ. Qual. 24 (4), 707–718.

Amberger, A., Schmidt, H., 1987. Natürliche isotopengehalte von Nitrat als Indikatoren für dessen herkunft. Geochim. Cosmochim. Acta 51 (10), 2699–2705.

Andersson, K.K., Hooper, A.B., 1983. O_2 and H_2O are each the source of one O in NO_2^- produced from NH_3 by Nitrosomonas: ^{15}NNMR evidence. FEBS – Lett. 164 (2), 236–240.

Battaglin, W.A., Kendall, C., Chang, C.C.Y., Silva, S.R., Campbell, D.H., 2001. Chemical and isotopic evidence of nitrogen transformation in the Mississippi River, 1997–98. Hydrol. Process. 15 (7), 1285–1300.

Bedard-Haughn, A., van Groenigen, J.W., van Kessel, C., 2003. Tracing ^{15}N through landscapes: potential uses and precautions. J. Hydrol. 272 (1–4), 175–190.

Berner, R.A., Berner, R.A., 1996. Global Environment: Water, Air and Geochemical Cycles. Prentice Hall, Upper Saddle River, NJ, p. 376.

BryantMason, A., Xu, Y.J., Altabet, M., 2013. Isotopic signature of nitrate in river waters of the lower Mississippi and its distributary, the Atchafalaya. Hydrol Process 27, 2840–2850. http://dx.doi.org/10.1002/hyp.9420.

Casciotti, K.L., Sigman, D.M., Hastings, M.G., Bohlke, J.K., Hilkert, A., 2002. Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. Anal. Chem. 74 (19), 4905–4912.

Chang, C.C.Y., Kendall, C., Silva, S.R., Battaglin, W.A., Campbell, D.H., 2002. Nitrate stable isotopes: tools for determining nitrate sources among different land uses in the Mississippi River basin. Can. J. Fish. Aquat. Sci. 59 (12), 1874–1885. http://dx.doi.org/10.1139/f02-153.

Choi, W.J., Han, G.H., Lee, S.M., Lee, G.T., Yoon, K.S., Choi, S.M., Ro, H.M., 2007. Impact of land-use types on nitrate concentration and δ^{15}N in unconfined ground water in rural areas of Korea. Agric. Ecosyst. Environ. 120 (2–4), 259–268.

Decrem, M., Spiess, E., Richner, W., Herzog, F., 2007. Impact of Swiss agricultural policies on nitrate leaching from arable land. Agron. Sustain. Dev. 27 (3), 243–253.

Durka, W., Schulze, E., Gebauer, G., Voerkelius, S., 1994. Effects of forest decline on uptake and leaching of deposited nitrate determined from 15N and 18O measurements. Nature 372 (6508), 765–767.

Elliott, E.M., Kendall, C., Wankel, S.D., Burns, D.A., Boyer, E.W., Harlin, K., Bain, D.J., Butler, T.J., 2007. Nitrogen isotopes as indicators of NO_3 source contributions to atmospheric nitrate deposition across the Midwestern and Northeastern United States. Environ. Sci. Technol. 41 (22), 7661–7667.

European Union, 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy ("Water Framework Directive"). Off. J. Eur. Commun. 327 (1), 1–72.

FOEN, 2012. Federal Office for the Environment, Switzerland – <http://www.hydrodaten.admin.ch> (accessed online on 30.06.2013).

Fuhrer, J., Jasper, K., 2012. Demand and supply of water for agriculture: influence of topography and climate in pre-alpine, mesoscale catchments. Natural Resources 3 (3), 145–155. http://dx.doi.org/10.4236/nr.2012.33019.

Gilvear, D.J., Casas-Mulet, R., Spray, C.J., 2012. Trends and issues in delivery of integrated catchment scale river restoration: lessons learned from a national river restoration survey within Scotland. River Res. Appl. 28 (2), 234–246.

Harmancioglu, N.B., Fistikoglu, O., Ozkul, D., Singh, V.P., Alpaslan, M.N., 1999. Water Quality Monitoring Network Design. Kluwer Academic Publishers, Dordrecht.

Heaton, T.H.E., 1986. Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: a review. Chem. Geol. 59 (1), 87–102.

Heeb, F., Singer, H., Pernet-Coudrier, B., Qi, W., Liu, H., Longree, P., Müller, B., Berg, M., 2012. Organic micropollutants in rivers downstream of the megacity Beijing: sources and mass fluxes in a large-scale wastewater irrigation system. Environ. Sci. Technol. 46 (16), 8680–8688. http://dx.doi.org/10.1021/es301912q.

Hübner, H., 1986. Isotope effects of nitrogen in the soil and biosphere. In: Fritz, P., Fontes, J.C. (Eds.), Handbook of Environmental Isotope Geochemistry, vol. 2b, The Terrestrial Environment, Elsevier, Amsterdam, pp. 361–425.

IAEA GNIR 2012. Monitoring Isotopes in Rivers: Creation of the Global Network of Isotopes in Rivers (GNIR) IAEA-TECDOC-1673, ISBN 978-92-0-126810-5, ISSN 1011-4289.

ICPR, 2014. International Commission for the Protection of the Rhine. <http://www.iksr.org/index.php?id=88andL=3> (accessed online on 20.05.2014).

Ingraham, N.L., 1998. Isotopic variation in precipitation. In: Kendall, C., McDonnell, J.J. (Eds.), Isotope tracers in catchment hydrology. Elsevier, Amsterdam, The Netherlands and Oxford, UK.

Jha, P.K., Masao, M., 2013. Factors Affecting nutrient concentration and stable carbon and nitrogen isotope Ratio of Particulate organic matter in the Ishikari River System, Japan. Water, Air, Soil Pollut. J. 224 (5), 1551. http://dx.doi.org/10.1007/s11270-013-1551-z.

Kendall, C., 1998. Tracing sources and cycling of nitrate in catchments. In: Kendall, C., McDonnell, J.J. (Eds.), Isotope Tracers in Catchment Hydrology. Elsevier Science BV, New York.

Kendall, C., Campbell, D.H., Burns, D.A., Shanley, J.B., Silva, S.R., Chang, C.C.Y., 1995. Tracing sources of nitrate in snowmelt runoff using the oxygen and nitrogen isotopic compositions of nitrate. In: Biogeochemistry of Seasonally Snow-Covered Catchments, Proceedings of a Boulder Symposium, vol. 228, pp. 339–347.

Kendall, C., Elliott, E.M., Wankel, S.D., 2007. Tracing anthropogenic inputs of nitrogen to ecosystems. In: Michener, R., Lajtha, K. (Eds.), Stable Isotopes In Ecology and Environmental Science, second ed., Blackwell Publishing, pp. 375–449.

Kendall, C., Silva, S.R., Kelly, V.J., 2001. Carbon and nitrogen isotopic compositions of particulate organic matter in four large river systems across the United States. Hydrol. Process. 15 (7), 1301–1346.

Kroopnick, P., Craig, H., 1972. Atmospheric oxygen: Isotopic composition and solubility fractionation. Science 175 (4017), 54–55.

Macko, S.A., Ostrom, N.E., 1994. Pollution studies using nitrogen isotopes. In: Lajtha, K., Michener, R.M. (Eds.), Stable Isotopes in Ecology and Environmental Science. Blackwell Scientific Publishers, Oxford, pp. 45–62.

Mengis, M., Schiff, S.L., Harris, M., English, M.C., Aravena, R., Elgood, R.J., MacLean, A., 1999. Multiple geochemical and isotopic approaches for assessing ground water NO_3^- elimination in a riparian zone. Ground Water 37 (3), 448–457.

Ohlanders, N., Rodriguez, M., McPhee, J., 2013. Stable water isotope variation in a Central Andean watershed dominated by glacier and snowmelt. Hydrol Earth Syst. Sci. 17, 1035–1050. http://dx.doi.org/10.5194/hess-17-1035-2013.

Panno, S.V., Hackley, K.C., Kelly, W.R., Hwang, H., 2006. Isotopic evidence of nitrate sources and denitrification in the Mississippi River, Illinois. J. Environ. Qual. 35 (2), 495–504. http://dx.doi.org/10.1002/hyp.5576.

Prasuhn, V., Sieber, U., 2005. Changes in diffuse phosphorus and nitrogen inputs into surface waters in the Rhine watershed in Switzerland. Aquat. Sci. 67 (3), 363–371. http://dx.doi.org/10.1007/s00027-005-0774-5.

Rock, L., Mayer, B., 2004. Isotopic assessment of sources of surface water nitrate within the Oldman River basin, southern Alberta, Canada. Water Air Soil Pollut. Focus 4 (2–3), 545–562.

Russel, K.M., Gallowy, J.N., Macko, S.A., Moody, J.L., Schuldark, J.R., 1998. Sources of nitrogen in wet deposition to the Chesapeake Bay region. Atmos. Environ. 32, 2453–2465.

Sebilo, M., Billen, G., Grably, M., Mariotti, A., 2003. Isotopic composition of nitrate-nitrogen as a marker of riparian and benthic denitrification at the scale of the whole Seine River system. Biogeochemistry 63 (1), 35–51.

Sebilo, M., Billen, G., Mayer, B., Billiou, D., Grably, M., Garnier, J., Mariotti, A., 2006. Assessing nitrification and denitrification in the Seine River and estuary using chemical and isotopic techniques. Ecosystems 9 (4), 564–577.

Seiz, G., Foppa, N., 2007. Nationales Klima-Beobachtungssystem (GCOS Schweiz). Bundesamt für Meteorologie und Klimatologie, MeteoSchweiz und ProClim, Bern.

Siegenthaler, U., Oeschger, H., 1980. Correlation of ^{18}O in precipitation with temperature and altitude. Nature 285, 314–317.

Sigman, D.M., Casciotti, K.L., Andreani, M., Barford, C., Galanter, M., Bohlke, J.K., 2001. A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. Anal. Chem. 73 (17), 4145–4153.

Singleton, M.J., Esser, B.K., Moran, J.E., Hudson, G.B., Mcnab, W.W., Harter, T., 2007. Saturated zone denitrification: potential for natural attenuation of nitrate contamination in shallow groundwater under dairy operations. Environ. Sci. Technol. 41 (3), 759–765.

Spoelstra, J., Schiff, S.L., Hazlett, P.W., Jeffries, D.S., Semkin, R.G., 2007. The isotopic composition of nitrate produced from nitrification in a hardwood forest floor. Geochim. Cosmochim. Acta 71 (15), 3757–3771.

Starry, O.S., Valett, H.M., Schreiber, M.E., 2005. Nitrification rates in a headwater stream: influences of seasonal variation in C and N supply. J. North Am. Benthol. Soc. 24 (4), 753–768.

Vitoria, L., Otero, N., Soler, A., Canals, A., 2004. Fertilizer characterization: Isotopic data (N, S, O, C, and Sr). Environ. Sci. Technol. 38 (12), 3254–3262.

Wassenaar, L.I., 1995. Evaluation of the origin and fate of nitrate in the Abbotsford aquifer using the isotopes of ^{15}N and ^{18}O in NO_3^-. Appl. Geochem. 10 (4), 391–405.

Widory, D., Kloppmann, W., Chery, L., Bonnin, J., Rochdi, H., Guinamant, J.L., 2004. Nitrate in groundwater: an isotopic multi-tracer approach. J. Contam. Hydrol. 72 (1–4), 165–188.

Widory, D., Petelet-Giraud, E., Négrel, P., Ladouche, B., 2005. Tracking the sources of nitrate in groundwater using coupled nitrogen and boron isotopes: a synthesis. Environ. Sci. Technol. 39 (2), 539–548.

Xue, D., Botte, J., Baets, B., Accoe, F., Nestler, A., Taylor, P., Cleemput, O., Berglund, M., Boeckx, P., 2009. Present limitations and future prospects of stable isotope methods for nitrate source identification in surface- and groundwater. Water Res. 43 (5), 1159–1170.

Yue, F.J., Liu, C.Q., Li, S.L., Zhao, Z.Q., Liu, X.L., Ding, H., Liu, B.J., Zhong, J., 2014. Analysis of δ15N and δ18O to identify nitrate sources and transformations in Songhua River, Northeast China. J. Hydrol. 519, 329–339. http://dx.doi.org/10.1016/j.jhydrol.2014.07.026.