

# ADVOCATE bulletin

CL:AIRE's ADVOCATE bulletins describe practical aspects of research which have direct application to the characterisation, monitoring or remediation of contaminated soil or groundwater. This bulletin describes the management of water quality on a catchment scale.

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## Water quality management on a catchment scale

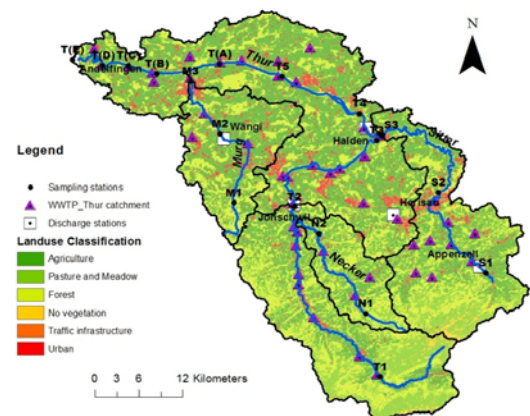
### 1. Introduction

Large catchments with varying land use patterns pose a major challenge for regulators to monitor the water quality variability in surface water bodies. The discrete sampling often carried out with significant spatial and temporal variation provides very little information about the state of water bodies. This demands an alternative approach to monitoring the major water quality parameters and identifying their source. Stable isotopes help us to better monitor and manage these challenges. Nitrate is an important water quality parameter particularly in catchments dominated by agriculture and urban water. It can thus be used as a tracer to understand the changes in water quality in large catchments, to trace the critical points of water quality change within the catchment together with other solutes like phosphate and chloride. The major anthropogenic sources of nitrate are waste water and nitrate leaching from agricultural soils which receive the input of nitrogen-based fertilizers and manure. Apart from these man-made sources there are various transformation processes that influence the production and fate of nitrate in rivers, therefore it has to be studied together with the other solutes draining into a river. Further variation in elevation in mountainous catchments can result in a dramatic change in the source of water from highlands to lowlands. Thus an understanding of the source of water, together with concentration of various solutes can give a clear insight into the changes in water quality within a large catchment. This was achieved in this study using a multi-isotope approach.

### 2. Background to Study Site

The study was conducted in the Thur catchment in north eastern Switzerland. The Thur is a pre-alpine river that originates from Mount Santis and drains into the Rhine River (Figure 1). The catchment area up to the long-term discharge monitoring station maintained by FOEN (Federal office for the Environment) at Andelfingen situated at the outlet of the catchment is 1,696 km<sup>2</sup>. The Thur catchment has varying geology from mainly limestone-dominated alpine headwaters (at 1020 m above sea level) to the lowlands (500 m above sea level) dominated by Molasse sandstones and marls as well as Pleistocene unconsolidated sediments. The average elevation of the catchment is 768 m while there is significant difference in the precipitation from the highlands (2500 mm/yr) to the lowlands (1000 mm/yr) (Seiz and Foppa, 2007). The mean annual discharge (2012) in the Thur river as measured at the Andelfingen monitoring station is 52.93 m<sup>3</sup>/s with a dynamic flow regime that varies between peak flow of 551 m<sup>3</sup>/s (10.10.2012) to low flow of 8.5 m<sup>3</sup>/s (FOEN, 2012).

The Thur river has three main tributaries namely the Murg, the Necker and the Sitter (Figure 1). The Necker (catchment area, 125 km<sup>2</sup>) and the Sitter (catchment area, 353 km<sup>2</sup>) arise from the highlands where the mean catchment elevations are 902 m and 939 m respectively. The Murg (catchment area, 197 km<sup>2</sup>) arises from the lowlands with an average catchment elevation of 590 m. The mean yearly discharge (2012) of the Murg is 4.58 m<sup>3</sup>/s contributing 8.46% of water to the lower Thur, the Necker has a mean discharge of 3.63 m<sup>3</sup>/s and contributes 15.5% of water to the Thur at the point where it joins it. The Sitter with a mean yearly discharge of 11 m<sup>3</sup>/s contributes 26% to the Thur river water. The land use in the Thur catchment is primarily agriculture (45%) followed by forest (25.4%), pasture lands (18.6%) and then a small portion of urban area (5.86%) which contributes waste water through 45 waste water treatment plants (WWTPs) situated in different parts of the catchment.



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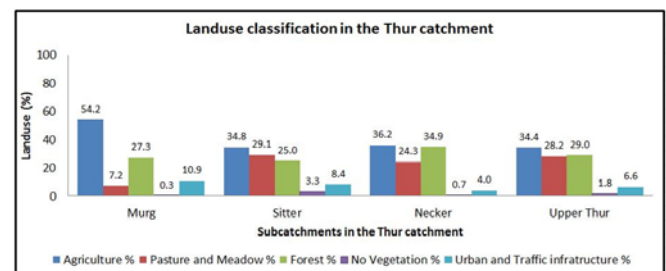


Figure 1. Location of sampling sites, wastewater treatment plants (WWTPs), discharge stations and land use classification in the Thur catchment including the sub-catchments. Copyright: EAWAG, Swiss Federal Institute of Aquatic Science and Technology.

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## 3. Background to the Technology

The stable isotopes of nitrogen and oxygen namely  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of nitrate ( $\delta^{15}\text{N-NO}_3^-$  and  $\delta^{18}\text{O-NO}_3^-$ ) are used in the dual isotope approach for the source identification and transformation of nitrate. Additionally the isotopes of hydrogen and oxygen namely  $\delta\text{D}$  and  $\delta^{18}\text{O}$  of water ( $\delta^{18}\text{O-H}_2\text{O}$ ) are also used to identify the source of water in different parts of the catchment which is expected to vary from headlands to the lowlands as well as according to the seasons. Stable isotope ratios of oxygen ( $^{18}\text{O}/^{16}\text{O}$ ) in water samples were measured with a PICARRO L1102-i isotope analyser. Isotope ratios  $^{18}\text{O}/^{16}\text{O}$  and  $^2\text{H}/^1\text{H}$  of the water samples were determined by cavity ring-down spectroscopy (Picarro L1102-i, Santa Clara, CA) against calibrations performed with water isotope standards of the International Atomic Energy Agency. The corresponding isotope signatures  $\delta^{18}\text{O}$  and  $\delta\text{D}$  are conventionally expressed as a permil deviation from Vienna Standard Mean Ocean Water (VSMOW). The overall analytical errors are 0.25‰ and 0.8‰ for  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , respectively. The local meteoric water line (LMWL) was derived from long-term precipitation measurements in the Thur catchment (Agroscope research station in Tanikon). Isotopic analyses of nitrogen and oxygen of  $\text{NO}_3^-$  were carried out using the denitrifier method (Sigman *et al.*, 2001; Casciotti *et al.*, 2002) which is based on the isotopic analysis of nitrous oxide ( $\text{N}_2\text{O}$ ) produced by denitrifying *Pseudomonas aureofaciens* (ATCC#13985) strains and *Pseudomonas chlororaphis* (ATCC #13985) strains respectively for the summer and spring measurements. The  $\text{N}_2\text{O}$  is concentrated and purified on a Gas Bench (Thermo Finnigan Gas Bench II) and the isotopic composition was determined using an isotope ratio mass spectrometer (Delta Plus XP) calibrated with ultra-high purity  $\text{N}_2$  gas against air nitrogen. Nitrogen and oxygen isotope ratios are expressed in the delta notation ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ) relative to atmospheric nitrogen and VSMOW in the conventional isotope terminology:

$$\delta(\text{‰}) = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000 \quad (1)$$

where R is  $^{15}\text{N}/^{14}\text{N}$  or  $^{18}\text{O}/^{16}\text{O}$  ratio of sample and standard, respectively. Results are given in per mil (‰). Analyses of  $\delta^{15}\text{N-NO}_3^-$  and  $\delta^{18}\text{O-NO}_3^-$  were standardised using the internationally distributed  $\text{KNO}_3$  reference material IAEA-N3 with an assigned  $\delta^{15}\text{N}$  value of 4.7‰ versus air  $\text{N}_2$  (Böhlke and Coplen, 1995) and a reported  $\delta^{18}\text{O}$  value of 22.7‰ versus VSMOW (Revesz *et al.*, 1997). Analytical precision (one standard deviation) was better than 0.2‰ for  $\delta^{15}\text{N}$  and better than 0.4‰ for  $\delta\text{O}$ , respectively.

Concentrations of Ca, Mg, Na, K and Cl were measured using ion chromatography. Alkalinity was measured by titration. Nitrate was measured photometrically (Mueller and Widemann, 1955). Orthophosphate was measured colorimetrically using the molybdenum blue method (Vogler, 1965).

The sampling stations are located along the river Thur and its main tributaries the Murg (M), the Necker (N) and the Sitter (S). The sampling stations are located at the headwater of the river Thur (T1) and its tributaries (S1,N1,M1) as well as at a station before and after the tributary joins the main river (Figure 1). Furthermore, some of the sampling stations are located near discharge measuring stations in the catchment to assess the turnover (load) of the different solutes into the river (Figure 1). In the lower reach of the river Thur, the five sampling stations are located as follows: two upstream {T(A), T(B)} of

the monitored restored section, at Niederneunforn {T(C)} and two downstream of it {T(D) and T(E)}. This covers the main influx points that can cause a change in water quality of the surface water (Figure 1). The field campaign to collect water samples for isotope analysis was conducted once in summer (SC1) on 28-08-2012 and once in spring (SC2) on 15-04-2013. The water samples were collected at all stations within the same day on both sampling campaigns. The samples were collected in 1 litre HDPE bottles and filtered into 100 ml HDPE bottles using 0.45  $\mu\text{m}$  pore size cellulose nitrate filters (Sartorius AG, Göttingen, Germany) in the field. The cooled samples were transported within a few hours and frozen on the same day. The frozen samples were sent to the Colorado Plateau Analytical Laboratory, Northern Arizona University, U.S.A for analysis of the isotopes of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of nitrate for the summer campaign and to the Helmholtz Centre for Environmental Research – UFZ Department Catchment Hydrology, Germany for the spring 2013 campaign.

## 4. Technology Description

Stable isotopic compositions of nitrate can provide useful information that can be used to track the sources of nitrate in the rivers. This is due to the distinct isotopic characteristics of the main sources of nitrate such as rain, chemical fertilizers and nitrate derived from nitrification (Durka *et al.*, 1994; Kendall 1998). Furthermore, dual isotopic models can be useful to identify de-nitrification in aquatic ecosystems because during this process  $^{15}\text{N-NO}_3^-$  and  $^{18}\text{O-NO}_3^-$  are preferentially enriched into residual nitrate (Amberger and Schmidt, 1987; Böttcher *et al.*, 1990). Recent studies have shown the various degree of success of dual isotopic techniques to identify the sources and transformation of nitrate in large rivers like the Mississippi river, U.S.A (Battaglin *et al.*, 2001; Panno *et al.*, 2006), the Seine river, France (Sebilo *et al.*, 2006) and the Oldman river, Alberta, Canada (Rock and Mayer, 2004). However, these studies did not consider the source of water within large catchments that vary significantly according to the elevation. While the higher sites have more rain/snow fed water, the lowlands are often more groundwater fed. In mountainous catchments such source separation of water is of vital importance to assess the seasonal water quality changes, as a collection of episodic events can alter the water quality significantly. Climate change can significantly affect the size and magnitude of these events, therefore a seasonal assessment of water quality change together with an understanding of the source of the water is the way forward.

## 5. Summary of Developed Research

The seasonal and spatial change in water quality in the surface waters of a large pre-alpine catchment was studied to show the effect of elevation difference and precipitation on the various solutes draining into the Thur catchment.

There is a major difference between the headwater samples and lower reach of the tributaries and the main river, clearly marking the swift change in water quality from pristine to polluted conditions where the influence of urban and agricultural water drainage is observed. Furthermore, the critical points of water quality seem to be at the influx points of the main tributaries joining the main river (Figure 2).

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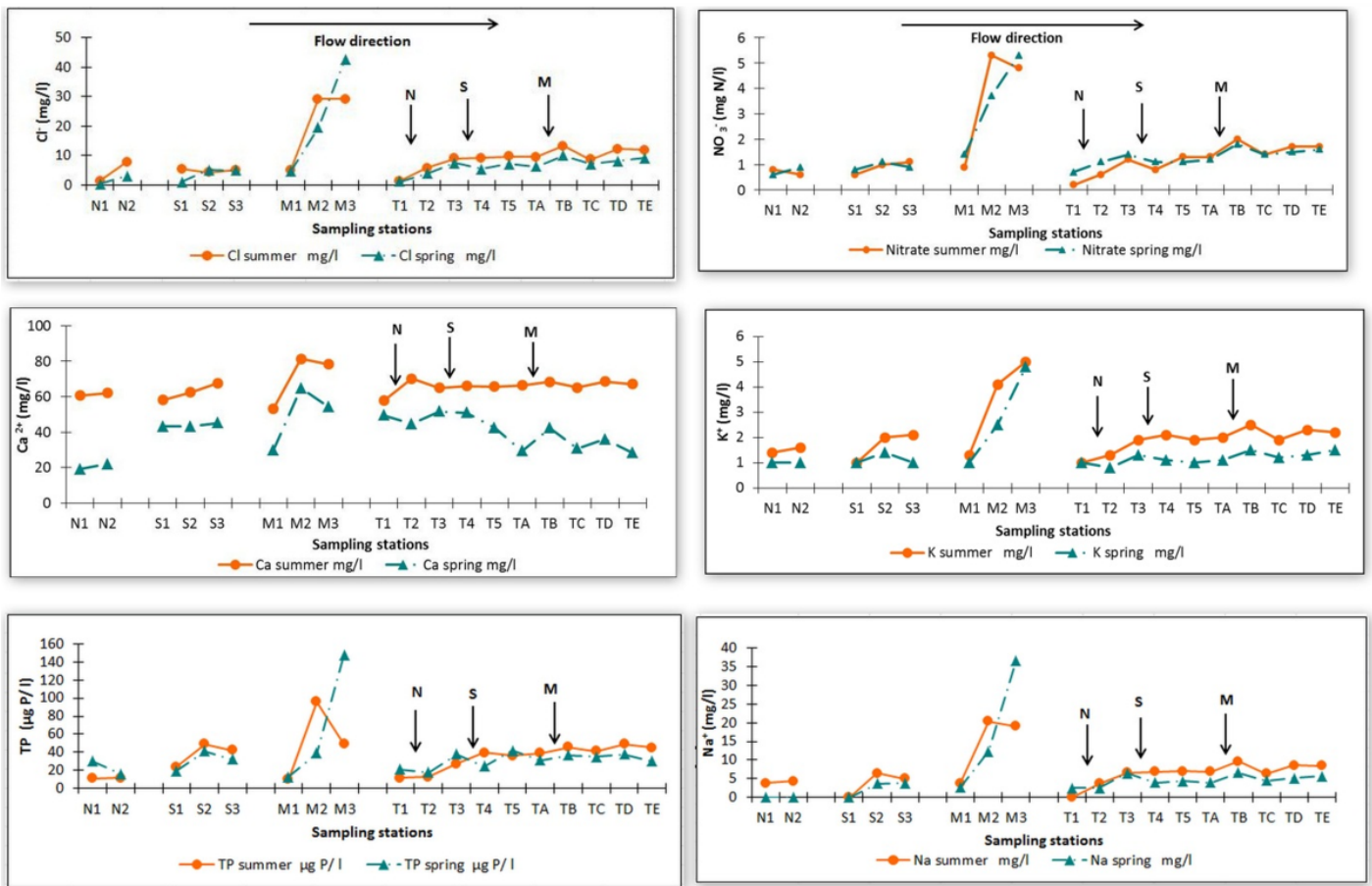


Figure 2. Hydrochemical variations of the Thur river water and major tributaries in the summer 2012 and spring 2013 seasons, along with the hotspots of water quality change at the influx points of the tributaries Murg (M), Sitter (S) and the Necker (N). Copyright: EAWAG, Swiss Federal Institute of Aquatic Science and Technology.

The major source of nitrate in the catchment is identified as urban waste water and nitrate nitrogen that leaches from agricultural soil, with microbial nitrification contributing to the nitrate content in the rivers (Figure 3).

Seasonally, there is a greater contribution of precipitation to the river water in spring, which is indicated by the lighter isotopes of water corresponding with the increase in discharge. This contributes to the dilution of all the major solutes. Spatially, there is a greater contribution from precipitation in the headwater than in the lower reach, indicated by the lighter isotopic composition of the water upstream (Figure 4).

The increase in the nitrogen load in spring corresponds to the corresponding increase in discharge, whereas the phosphorus loading is higher in the lower part of the tributaries - the Sitter and the Murg. This shows the additional influence of a non-point phosphorus source other than the point source of waste water discharge in the lower part of Sitter. The lower part of the Murg also has a higher chloride loading, indicating a higher contribution from waste water in spring.

## 6. Acknowledgements

The authors would like to thank the Federal Office of Environment for providing archived and forecast hydrological and chemical data (NADUF); Andreas Scholtis (Amt für Umwelt, Canton Thurgau) and Ulrich Göttelmann (Amt für Umwelt, Canton Thurgau) for their support and close cooperation; the members of the hydrogeology group at EAWAG (Samuel Diem, Jana von Freyberg, Anne-Marie Kurth, Behnam Doulatyari and Mehdi Ghasemizade) for their active involvement during the field campaigns. The authors would further like to thank the AuA lab at EAWAG (Madeleine Langmeier, Denise Freudemann and Samuel Derrer) for their support in the laboratory analysis.

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013 under grant agreement n°265063). Additionally funding for the field installation and the logistics was provided by the Competence Center Environment and Sustainability (CCES) in the framework of the RECORD and RECORD Catchment projects.

The results of this bulletin are discussed in full detail in the Journal of Hydrology with the following reference: Viswanathan, V.C., Jiang, Y., Berg, M., Hunkeler, D., Schirmer, M. An integrated spatial snap-shot monitoring method for identifying seasonal changes and spatial changes in surface water quality., J. Hydrol. 539, 567–576. <http://dx.doi.org/10.1016/j.jhydrol.2016.05.017>



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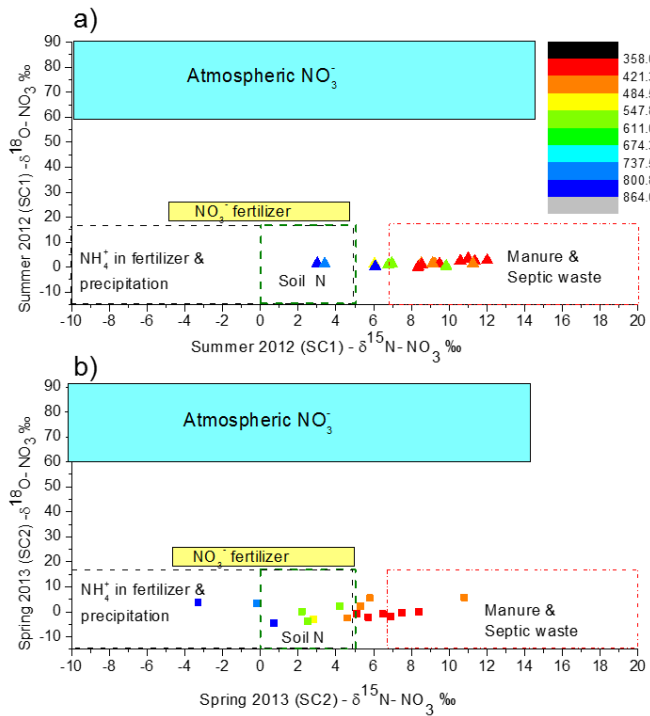


Figure 3. Relationship between  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of nitrate in the Thur River and its tributaries during summer 2012 (SC1) and spring 2013 (SC2). Applying the dual isotope approach of source identification, modified after Kendall *et al.* (2007). Copyright: EAWAG, Swiss Federal Institute of Aquatic Science and Technology.

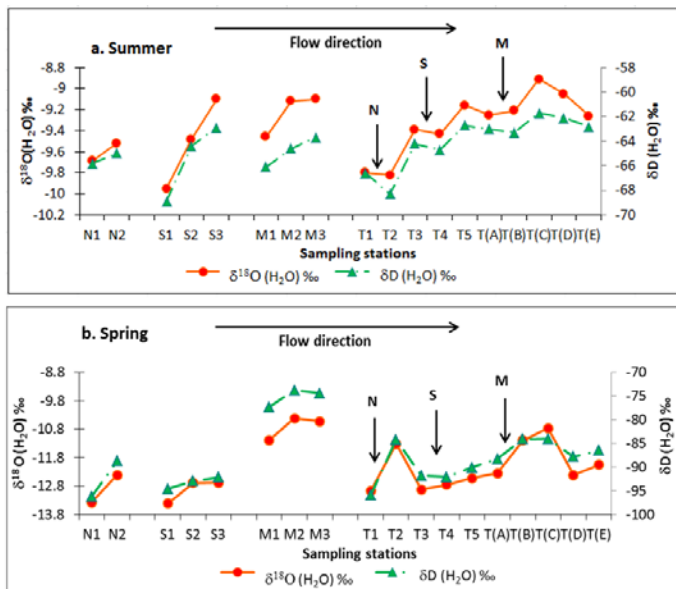


Figure 4. Isotopic composition of water  $\delta\text{D}$  and  $\delta^{18}\text{O}$  together with flow direction in summer 2012 (SC1) and spring 2013 (SC2) (4a and 3b), and identification of critical points of water composition change at influx points of the tributaries. Copyright: EAWAG, Swiss Federal Institute of Aquatic Science and Technology.

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