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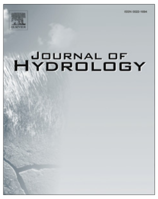

An integrated spatial snap-shot monitoring method for identifying seasonal changes and spatial changes in surface water quality

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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 ($\delta^{18}O\text{-}H_2O$ and δD) and nitrate ($\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$) 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 meltwater 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)