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Effect of river restoration and hydrological changes on surface water quality – River reach-scale to catchment-scale study

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by

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Abstract

River restoration is considered as an alternative flood protection measure, to restore the native habitat in the rivers and to improve water quality. Often the restoration projects aim to achieve more than one of the objectives mentioned above as the goals are often interlinked. The effect of river restoration on water quality is seldom studied. The analysis of case studies of restoration projects from different countries forms the first part of this thesis. The case studies where water quality was the main driver for restoration were analyzed from four countries across three continents. The studies show that often a combination of restoration measures in tandem with infrastructure (like waste water treatment plant, storm sewer) up gradation or new installations need to be carried out to achieve good water quality status of the rivers. In many restoration studies, post-restoration monitoring is often not carried out due to lack of funds for carrying pre-restoration monitoring and lack of a definite protocol of indicators to be analyzed. This is an integral aim of the thesis, to define a set of parameters that could act as key water quality indicators for pre-post restoration monitoring. In the second section of this thesis, high-frequency monitoring of several parameters was done to identify key parameters and the bio-geochemical processes affecting their diurnal cycles in three different seasons. The ecosystem functioning in rivers and the theory that restoration accentuates the nutrient assimilation capacity in rivers is tested in different hydrological conditions. It was found that, the diurnal cycles of pH and DO were driven by in-stream biological processes, mainly photosynthesis and respiration. During low flow in autumn a reduction of DOC (in nighttime) and nitrate (in pre-dawn period) was observed downstream of the restored section, which is attributed to biological processes that are expected to be accentuated by increased habitat diversity post-restoration. A storm event in summer, resulted in increased nitrate and chloride accumulation at the outlet of the catchment followed by a delayed dilution, in comparison to the immediate dilution effect observed along the rest of the river stretch. This storm event also caused a reduction of dissolved organic carbon (DOC) by dilution along the entire observed river stretch. The observed reduction in the diurnal variability of dissolved oxygen (DO) in the channelized parts of the river during the storm event is an indication of higher turbidity turnover affecting the production-respiration pattern - but this does not affect the diurnal variability in the restored section. A longer restored stretch together with pre-restoration monitoring are recommended for future projects. In the final part of the thesis, a catchment-scale perspective to identify the pathways of various solutes in the catchment is presented. The simplified method - Integrated Spatial Snap-shot method (ISSM), involves the identification of few (<25) monitoring stations at critical points in the catchment and the analysis of fluxes at two contrasting discharge patterns in two extreme seasons. 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 changes were identified. This method is transferrable to different catchments under different geographical conditions and is aimed to act as a preliminary catchment-scale study to identify suitable restoration sites in large catchments.

Zusammenfassung

Die Revitalisierung von Flüssen ist eine Alternative zum herkömmlichen Hochwasserschutz. Zugleich können damit natürliche Habitate im Fluss wiederhergestellt und die Wasserqualität verbessert werden. Häufig streben Revitalisierungsprojekte mehrere der zuvor genannten Ziele an, da diese oft eng miteinander verknüpft sind. Die Auswirkungen der Flussrevitalisierung auf die Wasserqualität werden dabei jedoch eher selten untersucht.

Im ersten Teil dieser Doktorarbeit werden verschiedene Revitalisierungsprojekte, welche prioritär eine Verbesserung der Wasserqualität anstrebten, untersucht. Dabei werden Projekte aus vier Ländern dreier Kontinente berücksichtigt. Die Auswertung verdeutlicht, dass Revitalisierungsmassnahmen alleine nicht ausreichen, um die Wasserqualität zu verbessern. Zusätzliche Aufwertungen der Infrastruktur, wie beispielsweise durch Kläranlagen oder Kanalisationen, sind hierbei notwendig, um eine gute Wasserqualität zu erreichen. Häufig ist es aufgrund fehlender Kontrollen, welche vor Beginn bzw. nach Beendigung der Revitalisierung, durchgeführt werden, unmöglich festzustellen, ob das Projekt eine Verbesserung der Wasserqualität bewirkt hat. Die mangelnden Kontrollen sind, zum einen, auf ein streng limitiertes Budget, zum anderen, auf unzureichende Vorgaben bezüglich notwendiger Vor- und Nachuntersuchungen zurückzuführen. Ein wichtiges Anliegen dieser Doktorarbeit ist daher die Identifikation von chemischen Parametern, welche als Indikator der Wasserqualität dienen können. Durch Vorgabe dieser Indikatoren sollen Vor- und Nachuntersuchungen stark vereinfacht und kosteneffizienter gestaltet werden. Anhand von Vergleichsstudien an einem Feldstandort in der Nordost-Schweiz werden im zweiten Teil dieser Doktorarbeit chemische Indikatoren identifiziert. Zusätzlich werden die Auswirkungen bio-geochemische Prozesse auf die täglichen Schwankungen der zuvor genannten chemischen Indikatoren untersucht. Daten wurden hierbei während dreier verschiedener Jahreszeiten über einen Zeitraum von ca. zwei Jahren erhoben und ausgewertet. Hierbei liegt das Augenmerk der Datenauswertung auf der Funktionsfähigkeit der Flussökosysteme. Des Weiteren wird anhand verschiedener hydrogeologischer Szenarien untersucht, inwiefern Flussrevitalisierungen die Verfügbarkeit von Nährstoffen verbessern. Die Daten verdeutlichen, dass tägliche Schwankungen im pH-Wert und der Konzentration gelösten Sauerstoffs auf biologische Prozesse, d.h. Photosynthese und Respiration, zurückzuführen sind. Bei Daten der Probennahmen im Herbst zeigen sich im unterstromigen Bereich des revitalisierten Abschnittes am Feldstandort nachts und im Morgengrauen jeweils niedrigere Konzentrationen gelösten organischen Kohlenstoffs und Nitrat. Es wird vermutet, dass dies durch eine höhere biologische Aktivität, welche nach Flussrevitalisierungen erwartet wird, bedingt ist. Ein anderes Bild zeigt sich während eines Starkregenereignisses im Sommer. Hier werden am Abstrom des Einzugsgebietes erhöhte Konzentrationen an Nitrat und Chlorid gemessen. Dabei wird hier eine verzögerte Verdünnung der Konzentrationen beobachtet, die sich stark von der sofortigen Konzentrationsverringerung in den anderen Messstationen unterscheidet. Das Starkregenereignis führt

zu einer Reduktion der Konzentrationen an gelöstem organischen Kohlenstoff im gesamten Untersuchungsbereich des Flusses. Weiter zeigt sich eine Veränderung in den täglichen Schwankungen des gelösten Sauerstoffs, jedoch ausschliesslich im kanalisierten, nicht revitalisierten, Bereich des Flusses. Diese Verringerung der täglichen Schwankungen im gelösten Sauerstoff ist auf die hohe Trübung zurückzuführen, welche die biologische Aktivität, z.B. die Respiration, beeinträchtigt.

Für zukünftige Forschungsprojekte wäre es empfehlenswert bereits vor der Revitalisierung detaillierte Untersuchungen der Wasserchemie durchzuführen. Zusätzlich wäre es hilfreich für die Untersuchungen nach der Revitalisierung über einen möglichst langen revitalisierten Abschnitt zu verfügen.

Im letzten Teil dieser Doktorarbeit wird ein Vorgehen vorgeschlagen, mit welchem innerhalb eines Einzugsgebietes die Fliesspfade verschiedener gelöster Stoffe nachvollzogen werden können. Hierbei werden mit der neu entwickelten ISSM-Methode („Integrated Spatial Snap-shot“) im Einzugsgebiet eine geringe Anzahl repräsentativer Knotenpunkte für die Untersuchung der gelösten Stoffe identifiziert. Anhand dieser werden dann die Stoffflüsse bei unterschiedlichen Abflussszenarien und zu unterschiedlichen Jahreszeiten untersucht. Diese Methode wurde an verschiedenen Feldstandorten angewandt. So wurden Hotspots chemischer Indikatorspezies und deren jahreszeitlichen Schwankungen anhand der Konzentrationen gelöster Stoffe und deren Durchflussmenge sowie der Wasserstoff-/Sauerstoff- und Stickstoff-Isotopenverteilung untersucht. Es zeigt sich, dass sich diese Methode auf Einzugsgebiete mit unterschiedlichsten Topographien übertragen lässt. Auf diese Weise lassen sich in ersten Voruntersuchungen potentielle Standorte für Flussrevitalisierungen auch innerhalb grosser Einzugsgebiete identifizieren.

Résumé

La restauration des rivières est considérée comme méthode permettant d'agir sur la protection contre les crues, la reconstruction d'habitats naturels et l'amélioration de la qualité des eaux de surface. En général, les projets de restauration visent à atteindre plus d'un des objectifs précités du fait de leur connexité. L'effet de la restauration d'une rivière sur la qualité de l'eau reste relativement peu étudié. La première partie de cette thèse est vouée à l'analyse de différents cas d'études de restauration de rivière réalisés dans plusieurs pays. Nous sélectionnons et analysons des cas d'études pour lesquels la qualité de l'eau était le principal objectif visé par la restauration, pour quatre pays sur trois continents. Ces cas d'études montrent que pour atteindre un objectif de bonne qualité de l'eau au sein des rivières restaurées, il est souvent nécessaire de combiner aux mesures de restauration une amélioration (ou une installation) des infrastructures (tels que les stations d'épuration et bassins d'orage). Dans l'ensemble des études de restauration, le suivi post-restauration n'est pas souvent mené du fait d'un manque de fonds pour mener un suivi pre-restauration d'une part et d'un manque de protocole et d'indicateurs bien définis pour le contrôle de la qualité de l'eau d'autre part. L'un des buts principaux de cette thèse est de définir un jeu de paramètres afin d'offrir des indicateurs clés de la qualité de l'eau pour le suivi pre et post restauration. Dans la seconde partie de cette thèse, un suivi à haute fréquence d'un grand nombre de paramètres a été réalisé afin d'identifier les paramètres clés et les processus bio-géochimiques qui affectent leurs cycles diurne au cours de trois saisons. Le fonctionnement de l'écosystème en rivière et la théorie selon laquelle la capacité d'assimilation des nutriments des rivières est étudié et testée pour plusieurs conditions hydrologiques.

Nous montrons que les cycles diurnes du pH et de l'oxygène dissout (DO) sont dépendants des processus biologiques, principalement la photosynthèse et la respiration, en rivière. Pendant la période de basses eaux, en automne, nous avons observé une réduction du carbone organique dissous (DOC), pendant la nuit, et des nitrates, juste avant le lever du jour, à l'aval des biefs restaurés. Ceci est attribué à des processus biologiques supposés être accentués par une augmentation de la diversité des habitats post-restauration. Par ailleurs, suite à un évènement orageux d'été, nous avons pu observer une augmentation des nitrates et une accumulation du chlore à l'exutoire du bassin versant suivi par une dilution retardée comparée aux effets de dilution immédiats observés quant à eux le long du reste de la rivière. Cet évènement orageux a aussi causé une diminution du DOC par dilution le long de toute la rivière. L'observation de la diminution de la variabilité diurne du DO dans les parties chenalisées de la rivière pendant l'évènement orageux est un indicateur d'une augmentation du taux de renouvellement de la turbidité qui affecte le modèle de production-respiration - mais qui n'affecte pas la variabilité diurne de la partie restaurée. Un plus long bief restauré et un suivi pre-restauration sont recommandés pour les projets futurs. Dans la dernière partie de cette thèse, nous employons une démarche à l'échelle du bassin versant afin d'identifier les chemins de transferts des solutés. La méthode simplifiée intitulée "Integrated Spatial Snap-shot Method" (ISSM) ou Méthode d'Aperçu Spatialement Intégrée, implique l'identification d'un nombre réduit (<25) de stations de suivi à des points critiques du bassin versant et l'analyse des flux de deux modes d'écoulements contrastés, pour deux saisons extrêmes. Au travers de l'utilisation combinée des isotopes stables de l'eau et des nitrates complétée par la concentration des solutés et de leurs flux, nous identifions des hotspots de qualité des eaux de surface et les changements saisonniers associés. Cette méthode simplifiée est transposable à différents types de bassin versant situés dans différents contextes géographiques et a pour but d'offrir une étude préliminaire à l'échelle du bassin versant afin d'identifier les sites de restauration adéquats pour de grands bassins versants.

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Chapter 1 Introduction

1.1 Motivation and background

This Ph.D. thesis focusses on the investigation of the effect of river restoration and seasonal hydrological changes on surface water quality. In the following, a short introduction to river restoration and the major challenges in assessing its effectiveness is discussed. In the next part, the main water quality indicators and background information about their role in influencing in-stream processes is provided. In the last part, the challenges in scaling-up restoration projects within the context of catchment level challenges are presented.

1.1.1 River restoration - an urgent need to understand its effectiveness

Water quality deterioration in urban catchments

The “urban stream syndrome” (Meyer et al., 2005; Walsh et al., 2005) that is characterized by high peak flows, owing to dramatic increases in storm water runoff, as a result of increasing impervious surface covers (ISC) in urban catchments (Booth and Jackson, 1997), causes significant physical and biological changes in urban rivers (Paul and Meyer, 2001). The physical alterations to the river as a result of these high peak flows include homogenization of stream bed sediments, reduction of fine – and coarse-scale flow habitat variation and incision of stream channels causing disconnected riparian zones. Water quality deterioration, on the other hand is caused by the flushing of contaminants from catchment runoff directly into the receiving rivers and streams (Bernhardt et al., 2008; Sudduth et. al., 2011). Storm events induce particularly dramatic change in the hydrograph, followed by increased pollutant loads in the rivers (Paul and Meyer, 2001). Channelization of rivers was considered to be a good method to protect against physical alterations to rivers due to floods. However, the flood conveyance benefits of channelization and diversions are often offset by ecological losses resulting from increased stream velocities and reduced habitat diversity (FISRWG, 1998).

The increasing frequency and magnitude of storm-flows owing to ISC in urban catchments (Dunne and Leopold 1978; Walsh et al., 2005), can result in frequent bed-scouring leading to a reduction of algal biomass and productivity (Uehlinger et al., 2002; Atkinson et al., 2008) and a decrease in the retention of particulate organic matter and associated heterotrophic respiration (Meyer et al., 2005). Thus these effects can impair the natural attenuation capacity of rivers.

River restoration - a popular method to protect rivers and streams

To solve the associated problems due to modified rivers, particularly in urban catchments, legislative changes have been implemented in several countries that emphasize the need for restoration of rivers and streams. In Europe, for example, the EU Water Framework Directive (EU WFD, 2000) and Swiss Water Protection Law (GSchG, 2011; GSchV, 2011), promote engineering alterations in river courses to jointly improve flood protection, ecological status and water quality. Restoration is the process of returning a damaged ecosystem to its condition prior to disturbance (Berger 1991; Cairns 1991 and Caldwell 1991). Specifically, restoration is the re-establishment of chemical, physical, and biological components of an aquatic ecosystem that have been compromised by stressors such as point or non-point sources of pollution, habitat degradation, hydrological-modification, among others. Restoration differs from rehabilitation and reclamation, in that restoration is a holistic process not achieved through the isolated manipulation of individual elements. While restoration aims to return an ecosystem to a former natural condition, rehabilitation and reclamation imply putting a landscape to a new or altered use to serve a particular human purpose (National Research Council, 1992) (Figure 1). River restoration can be carried out at different scales and working with many different issues (such as morphological, hydrological, biological, chemical and socio-economic). Rivers and aquatic ecosystems are highly complex networks working on several spatial and temporal scales. The conceptual model of the expectations from ecosystem restoration to restore ‘degraded’ to historic ‘pristine’ conditions, and the various outcomes of the process is represented in Figure 1.

In Switzerland, an assessment of the status of rivers was made for the allocation of appropriate funds for implementation of suitable restoration measures, a standardized test - the ecomorphology module of the Modular Stepwise Procedure (Modul-Stufen-Konzept Ökomorphologie Stufe F) was applied to 24 of the 26 Swiss cantons between 1997 and 2008. The results indicated that 14,000 km, which comprises, 22 % of Swiss rivers and streams, were degraded (Zeh Weissmann et al., 2009). Following this finding, it was decided that 4,000 km of degraded rivers and streams are to be restored over the course of the next 80 years in Switzerland involving significant federal and cantonal financial investment - 40 million Swiss Francs or 44 million US Dollars are being allocated per year (BAFU, 2011). In the United States of America (U.S.A.), it has been reported that 1 billion dollars are being invested/year for restoration of rivers (Bernhardt et al., 2005).

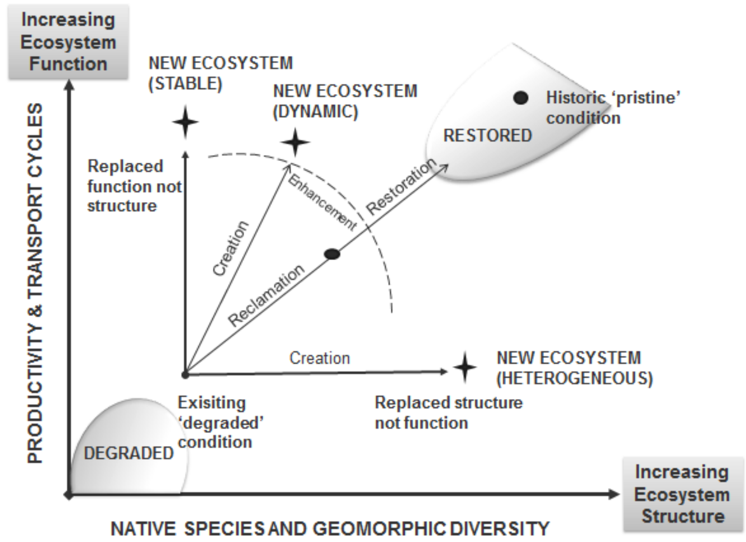

Figure 1 A conceptual model of the representation of the expectation from ecosystem restoration and the various outcomes of the process. Modified after Stockwell (2000) and Wheaton (2005).

Success evaluation of restoration projects

The large investment in river restoration projects by various governments around the world, needs to be justified by systematic evaluation of river restoration projects. This post-project evaluation is needed to not only assess the success of the projects for enhancing public support, but also to understand the reasons for failure if any, for better planning of future restoration projects (Bash and Ryan, 2002; Woolsey et al., 2007). For successful evaluation of restoration projects, a systematic definition of project objectives and identification of the indicators to be evaluated pre- and post-restoration needs to be done (Woolsey et al., 2007). Although there is a consensus among scientific, economic and political authorities involved in river restoration that the success of restoration projects needs to be evaluated, this is seldom performed (Downs and Kondolf, 2002; Woolsey et al., 2007). The identification of indicators is insufficient if they are not surveyed within on a reasonable time period after the completion of the project, but they also need to be evaluated based on inter-annual seasonal patterns or hydrological conditions (like floods) (Woolsey et al., 2007).

1.1.2 River restoration and water quality

Establishing an appropriate flow regime and geomorphology in a stream corridor may do little to ensure a healthy ecosystem if the physical and chemical characteristics of the water are inappropriate (FISRWG, 1998). In Bernhardt et al. (2007), 317 individual restoration projects (in the U.S.A.) were surveyed and practitioners were interviewed, and 27% of the restoration projects cited water quality management as their primary goal for river restoration. There is an intrinsic link between water quality deterioration and changes to habitats of different organisms. The water quality concerns particularly from non-point sources of pollution, for example have been cited as a major problem for reduction of salmonid populations in the British Isles (Hendry et al., 2003).

A recommendation for prioritizing water quality management, for improvement of the habitat for salmonids and a few guidelines for water quality requirements in rivers is made by Hendry et al. (2003):

• 'Well oxygenated water with natural nutrient content and temperature range, typically of upland or spring origin.'

• 'Suitably buffered water to prevent sustained variations in pH outside of the normal range.'

• 'Water devoid of significant chemical contaminants.'

• 'A naturally low silt/fines content within the normal sediment matrix.'

Water quality is an important consideration for river restoration projects. Herricks and Osborne (1985) have defined water quality restoration as: *'Restoration of water quality can be defined as returning the concentration of substances to values typical of undisturbed conditions.'* The knowledge of pre-existing water quality concentrations is implicit in implementing water quality restoration. A selection of suitable water quality indicators is important to follow up the changes pre-post restoration.

Main water quality indicators

Dissolved oxygen (DO) – There are two main routes for oxygen input in surface waters: transfer of oxygen directly from the atmosphere (a process called reaeration), and from plants as a result of photosynthesis. Reaeration is the primary route for introducing oxygen into most waters. Oxygen gas (O_2) constitutes about 21% of the atmosphere and readily dissolves in water (FISRWG, 1998). The ability of water to hold oxygen is influenced by temperature and salinity. The saturation concentration of DO in water is a measure of the maximum amount of oxygen that water can hold at a given temperature. As the salinity of water increases, the saturation concentration decreases (FISRWG, 1998).
When oxygen is below the saturation concentration, it tends to diffuse from the atmosphere to water. Apart from these physical processes that influence the DO concentration in surface waters, biological processes like photosynthesis and respiration also influence the DO content. Daytime photosynthesis, influenced by the solar photo cycle, increases the productivity of autotrophs causing the increase of oxygen. In the nighttime, in the absence of photosynthesis, respiration is active in the streams causing the removal of oxygen (FISRWG, 1998). Shallow depth in rivers and large surface exposure to air, cause abundant DO supply in undisturbed streams. However, external loading of nutrients (which are oxygen demanding) as well as excessive plant growth (eutrophication) can cause depletion of DO (FISRWG, 1998). Some fish and aquatic organisms, such as carp and sludge worms, are adapted to

low oxygen conditions, but most fish species, such as trout and salmon, suffer if DO concentrations fall below 3 to 4 mg/l. Larvae and juvenile fish are more sensitive and require even higher concentrations of DO (USEPA, 1997).

Temperature – Temperature-dependent solubility affects the DO levels in streams. Temperature governs many biochemical and physiological processes in aquatic organisms and increases metabolic and reproductive rates throughout the flood chain. Temperature also affects abiotic chemical processes, such as reaeration rate, sorption of organic chemicals to particulate matter, and volatilization rates (FISRWG, 1998).

pH – The acidity of rivers is quantified by the logarithm of the hydrogen ion concentration or pH. Many biological processes, such as reproduction, cannot function in acidic or alkaline waters. In particular, aquatic organisms may suffer an osmotic imbalance under sustained exposure to low pH (acidic waters. In poorly buffered streams and rivers, high daily variability is due to the abundance of aquatic vegetation, that affects the carbonate buffering system attributable to biological processes (FISRWG, 1998). Uptake of carbon dioxide by plants during photosynthesis removes carbonic acid from the water, which can increase pH by several units. Conversely, pH levels may fall by several units during the night in the absence of photosynthesis and can cause subsequent release of carbon di oxide by plants during respiration (FISRWG, 1998).

***Nutrients* -** The primary producers (aquatic plants, algae etc.), require a variety of elements to support their bodily structures and metabolism. Among these elements, nitrogen and phosphorus are the most important nutrients (FISRWG, 1998). Human activities have increased the inflow of these nutrients into surface waters, from both point sources (treated waste water from waste water treatment plants (WWTPs) and combined sewer outflows (CSOs)) and from non-point sources (like agricultural inputs from manure and fertilizers, runoff from catchments) (FISRWG, 1998). Nitrogen exists in several forms in the aquatic environment, as dissolved nitrogen gas (N_2), ammonia and ammonium ions (NH_3 and NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), and organic nitrogen in dissolved or particulate phases. Among these, the readily available ammonia ions, nitrites, and nitrates have significant immediate impacts on water quality, as they need to be converted (broken down) more available forms to be usable for the nutrient intake of primary producers (FISRWG, 1998). Dissolved organic phosphorus includes organic phosphorus excreted by organisms and colloidal phosphorus compounds. The soluble inorganic phosphate forms $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}, collectively known as soluble reactive phosphorus (SRP) are readily available to plants. The SRP (usually as orthophosphate) is assimilated by aquatic plants and converted to organic phosphorus (FISRWG, 1998). The above-described water quality parameters are modified by in-stream bio-chemical processes and variations occur on a daytime/nighttime basis leading to diurnal cycles of the water quality parameters, which are useful for understanding the underlying processes in aquatic environments (Figure 2) (Nimick et. al., 2011).

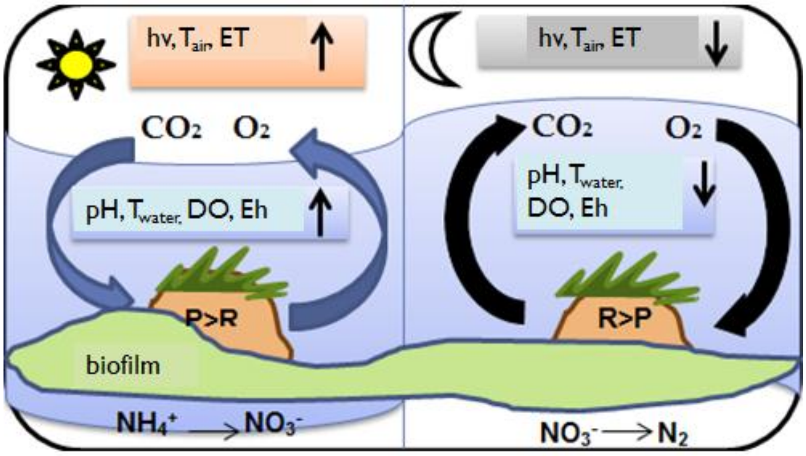

Figure 2 The diurnal variation of the bio-chemical processes affecting the various water quality indicators in an aquatic system. P-photosynthesis; R-respiration; hv-Light photon; ET-Evapotranspiration; Eh-oxidation-reduction potential; DO-dissolved oxygen; increase (↑) decrease (↓), T-temperature. Source: Modified after Nimick et. al. (2011).

Carbonate system - The carbonate species and its associated ions form the carbonate system, which is the major factor controlling pH of fresh waters (Butler, 1982). The stream geochemistry is affected by the presence of particulate and dissolved organic matter and dissolved carbonates. The sources of carbon in the stream can be differentiated as: a. Derived from terrestrial organic matter; b. From in-situ biological production; and c. Derived from anthropogenic sources like agriculture, domestic and industrial processes (Degens, 1982).

There are two types of organic carbon in the river, namely particulate organic matter (POM) and dissolved organic matter (measured as dissolved organic carbon – DOC), which are mainly classified based on whether they pass through a 0.45-0.5 µm filter or not (Thurman, 1985). On the other hand there is dissolved inorganic carbon (DIC), which occurs in ionic form as CO_3^{2-}, HCO_3^-, H_2CO_3 or also as dissolved CO_2. Biological processes like photosynthesis, respiration and decomposition alter the inorganically derived HCO_3^- ions in water, which in turn affects the flux of CO_2 in the water (Stumm and Morgen, 1981). The export of carbon and changes in the carbon fluxes in the river are governed by several processes that include *in situ* biological processes and geological conditions, land use in the catchment, seasonal fluctuations, varying discharge conditions and so on. Biological processes like breaking down of particulate matter by stream biota causes degradation of organic matter, which causes the mineralization of nutrients, and may contribute significant amounts of DOC to stream water (Meyer and Tate, 1983). Catchment processes like discharge, soil type and the hydrological flow paths influence the concentrations and fluxes of carbon transport in the river draining a catchment. The discharge of a number of major ionic species and the concentration of inorganic carbon is inversely proportional to the discharge in a river (Reid et al., 1981). However, the export of organic carbon has a positive correlation with discharge (Schlesinger and Melack, 1981). The relationship between stream discharge and DOC concentrations was observed to be improved when base flow and storm flow data were treated separately (Reid et al., 1980; Moore and Jackson, 1989). The concentrations of POM increase during storm events, but showed a tendency of peaking before the peak discharge which shows the influence of rainfall directly on the formation of POM which should also be considered to assess the seasonal trends in DOC export (Hope et al., 1994).

Stream ecosystem functioning

Ecosystem function metrics synthesize complex biogeochemical interactions with implications for nutrient cycling and water quality (Sudduth et. al., 2011). Some of the ecosystem functions and their associated biogeochemical activity are illustrated in Figure 3. Gross primary production (GPP) is the total production of energy in a stream, usually expressed in units of grams of oxygen or carbon/m^2/day (Odum, 1956; Bott, 2006). It is primarily driven by nutrient and light availability to stream autotrophs (Hill et al., 2001; Mulholland et al., 2001; Flecker et al., 2002), and may be limited by the availability of stable habitats (Grimm and Fisher, 1989; Uehlinger, 2002).

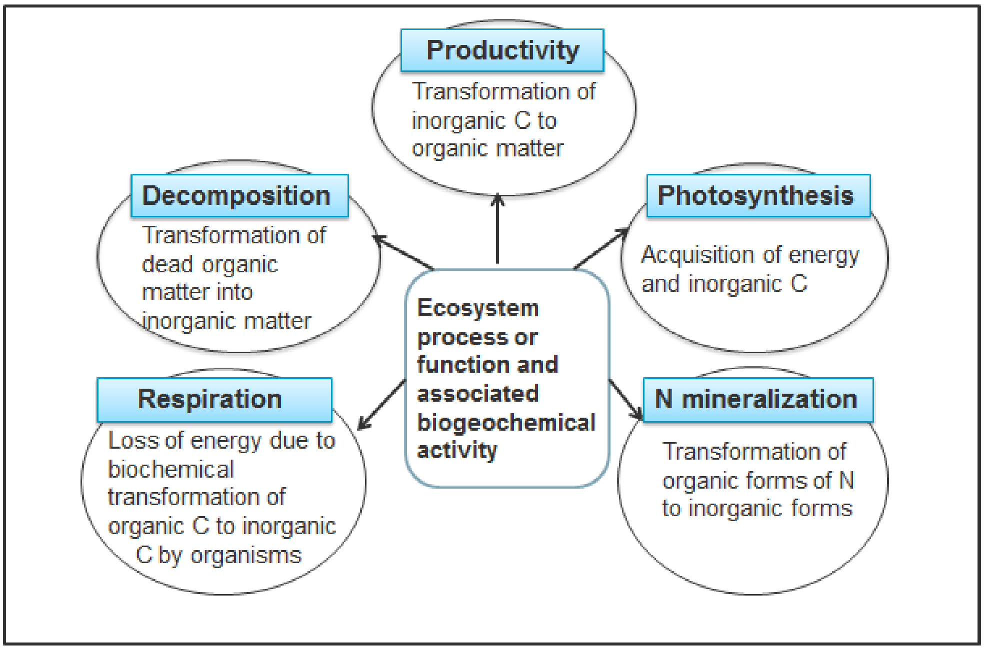

Figure 3 Ecosystem processes/functions and associated biogeochemical activities – the transformation of carbon (C) and nitrogen (N) through the biogeochemical processes is shown. Adapted from Naeem (2006).

Ecosystem respiration (ER) can include autotrophic respiration as well as heterotrophic respiration, which is largely dependent upon supply and retention of benthic organic matter (BOM) and dissolved organic carbon (DOC) (Webster and Benfield, 1986; Wallace et al., 1997). The decomposition of organic matter can be further limited by nutrient availability or by instability of habitats that are incapable of retaining BOM (Webster et al., 1999; Small et al., 2008). A complex relationship exists between urbanization and nutrient uptake functions. Urban stream nutrient uptake experiments indicate reduced nutrient uptake efficiencies in urban streams as shown by Grimm et. al. (2005), Meyer et al. (2005) and Mulholland et al. (2008). Urbanization and its associated problems like increased ISC, leading to increased frequency and magnitude of stormflows (Dunne and Leopold, 1978; Walsh et al., 2005) can result in frequent bed-scouring disturbances that reduce algal biomass and productivity (Uehlinger et al., 2002; Atkinson et al., 2008). This will also decrease the retention of particulate organic matter and associated heterotrophic respiration (Meyer et al., 2005).

The reach-scale restoration projects aim to increase habitat heterogeneity and successful restoration projects aim to reduce storm-flow disturbances and promote organic matter retention. Although most urban stream restoration focuses on reach-scale habitat complexity, the causative relationship between habitat complexity and ecosystem function is poorly researched (Sudduth et al., 2011). There are many links in our conceptual model on the path between habitat restoration and nutrient uptake (Figure 4).

Several previous studies have observed enhanced nutrient uptake rates as a result of channel restoration, which have been attributed to increased transient storage, stimulation of metabolism, and hydrologic reconnection of riparian soils (Bukaveckas, 2007; Roberts et al., 2007; Kaushal et al., 2008). Further, there is an expectation for dampening of storm flows and reduced storm scour in restored urban streams, and they are expected to have less variable rates of GPP than their unrestored counterparts (Figure 4) (Sudduth et al., 2011).

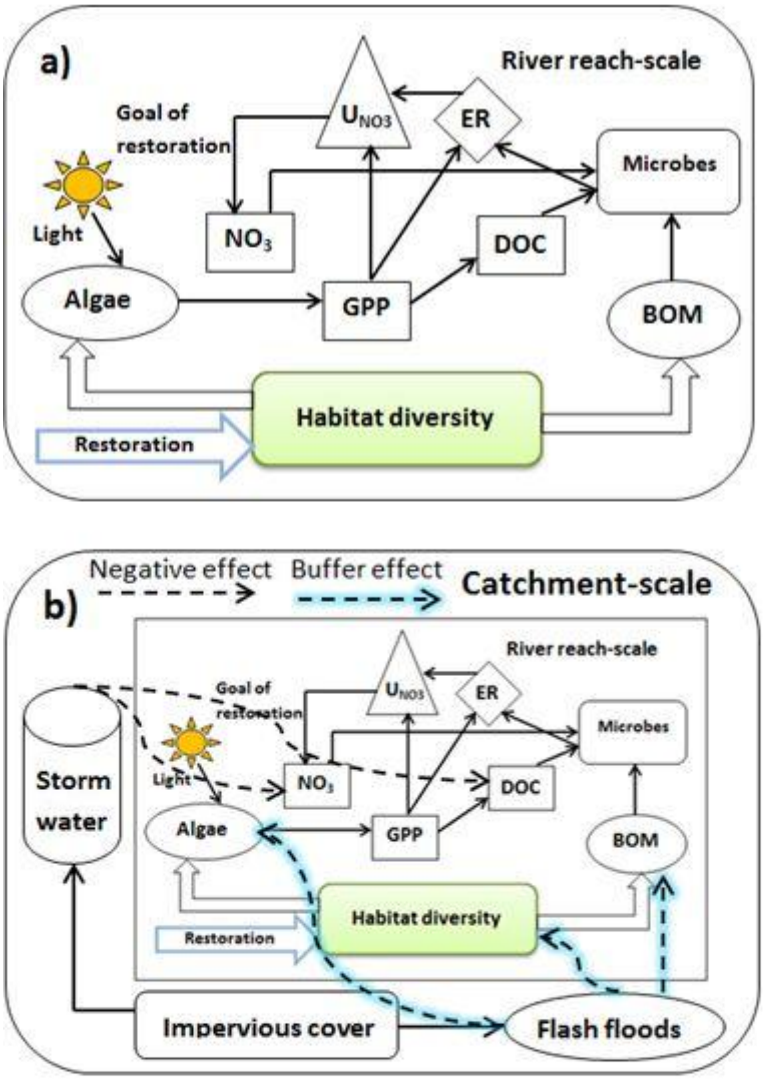

Figure 4 Model of stream ecosystem function (modified after Hall et al., 2009). (a) Reach-scale controls on gross primary productivity (GPP), ecosystem respiration (ER), and nitrate uptake, indicating the management practice (habitat diversity) and the goal (water quality improvement by nitrate concentration reduction) of many stream restoration projects. (b) Catchment-scale effects of urbanization and their proposed reach-scale effects on ecosystem function. Variables are U_{NO3} - nutrient uptake areal rate; DOC-dissolved oxygen content; BOM-benthic organic matter. Black dashed arrows indicate that a variable has a negative effect, and the shaded broken arrows indicate the expected buffering effect of river restoration over these negative effects.

1.1.3 Scaling up of restoration projects – reach scale to catchment-wide planning

The River Restoration Centre (RRC), U.K. has defined catchment scale river restoration as:

“River and floodplain-focused enhancement that considers catchment scale hydrological, ecological, morphological processes and associated land management pressures.”

There is a growing consensus that a catchment scale perspective (incorporating the complete fluvial landscape) is critical for successful river restoration (Logan and Furze, 2002; Kondolf et al., 2007; Nilsson et al., 2007; Benda et al., 2011). A catchment-scale perspective provides a larger frame of reference for smaller scale projects, particularly the influence of geomorphology, river network structure and natural disturbances (floods, landslides) on restored corridors are better understood (Benda et al., 2011). The adverse catchment-scale impacts on water quality can include runoff from treated waste water, diffuse inputs of nutrients from agricultural areas and an absence of upstream riparian buffers, which can have an impact on downstream water quality in a higher-order river (Figure 5).

Local restoration projects can be more effective if they are designed and strategically placed using a catchment context for the greatest ecological benefit (Thoms and Parsons, 2002; Gilvear and Casas, 2008; Benda et al., 2011). Restoration activities with a catchment perspective include measures such as channel re-meandering, flood embankment removal, buffer strip creation, reconnection of side channels, and wetland development, that have an influence on the nutrient inputs into the rivers and can affect the biogeochemical processes in the river (Gilvear and Casas, 2008).

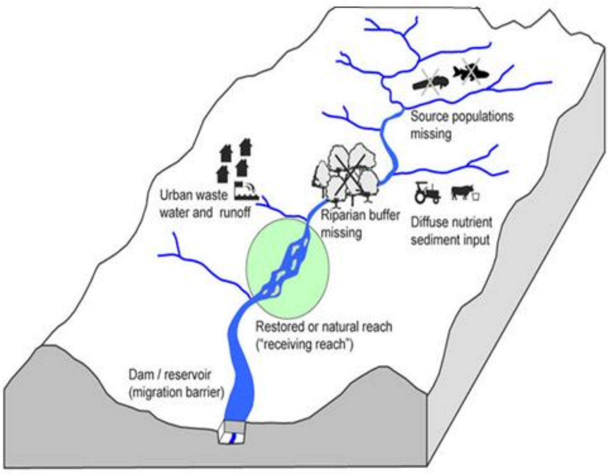

Figure 5 Catchment-scale processes that can affect reach-scale restoration.

Source: http://www.wiser.eu

This raises the main motivations for this thesis:

1. There is an urgent need for mechanistic understanding of underlying processes to make an unbiased evaluation of the success/failure of restoration projects. This is to justify the heavy investments in restoration projects as well as to better plan future projects.
2. A systematic evaluation of indicators that can be transcended across different restoration projects that have similar goals is essential.

3. Thorough assessment of the indicators under various hydrological and seasonal conditions is needed to capture sensitivity, dynamics and trajectories of change.
4. Post-project evaluation of river restoration success/failure in different scales, to act as an inventory for future restoration projects is the needed.
5. Restoration projects need to be placed in a catchment context, to capture the impacts of catchment scale processes and human interventions.

1.2 Objectives and structure of this thesis

The overall goal of this Ph.D. thesis is to deepen the understanding of the effect of river restoration and hydrological changes on the biogeochemical processes affecting river water quality and comparing the effects on different spatial and temporal scales. To achieve this extensive field investigations and lab measurements were conducted to assess several water quality indicators and the processes that affect them on a river reach and catchment scale. The field investigations were carried out at the Thur catchment in north-eastern Switzerland as described in detail in Chapters 3.2 and 4.2 in this thesis.

The objectives are defined to focus on the main motivations of this thesis, which are to:

1. Analyse the important considerations for achieving water quality improvement by investigating other restoration projects.
2. Identify a set of water quality indicators on a river reach-scale, to make an inventory for future projects.
3. Perform post-restoration evaluation of the selected water quality indicators and analyse the bio-geochemical processes that affect them, to test the ecosystem functioning expectations out of restoration.
4. Develop a simplified method to identify the hotspots of water quality change in the catchment and to estimate the seasonal changes to the fluxes.

The thesis is structured in the following way:

Chapter 2 contains a detailed review of case studies of restoration projects from different parts of the world. The case studies of those projects that had water quality deterioration as the main driver for river restoration were selected from three different continents – Asia, Europe and North America. In the case studies selected, the drivers, the methods of restoration and indicators of success measurement were analysed. Lessons learned from the considered restoration projects, is summarized to act as an inventory for future restoration projects that would aim to achieve water quality amelioration through river restoration.

Chapter 3 compiles the post-restoration spatial assessment of the effect of river restoration on water quality changes in the Thur River. An identification of a sub-set of critical water quality parameters is done. The bio-geochemical processes that affect their daily changes and alter their inter-relationships seasonally is presented. The stream ecosystem functioning expected to be altered by river restoration is tested.

Chapter 4 summarizes a simplified catchment-scale monitoring method – called the Integrated Spatial Snap-shot method (ISSM), to identify the pathways of various solutes in the catchment. The hotspots of water quality change in the Thur catchment are identified. The seasonal changes to catchment fluxes are recorded. Identification of the major sources of the nitrate in the catchment is done using nitrate isotopes. The simplified method involves the identification of select (<25) monitoring stations at critical points in the catchment and the analysis of solute fluxes at two contrasting discharge patterns in two extreme seasons.

Chapter 5 includes the important conclusions drawn from this thesis.

Chapter 6 is an outlook that summarizes some additional studies conducted during the course of the thesis. These studies are presented together with a rudimentary analysis of the data collected. This chapter is intended to be a summary of the initial promising findings to make recommendations for further studies on these topics.

Chapter 2 Water quality deterioration as a driver for river restoration – A review of case studies from Asia, Europe and North America

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Abstract

River restoration projects are carried out actively in several countries as an alternative flood protection measure, also to improve/restore water quality and habitat diversity. The implication of various river restoration measures on water quality is seldom studied. In this review, case studies of restoration projects that aimed at water quality improvement, were selected from four industrialized countries in three continents. The water quality concerns and the systematic development of legislative policies towards better water quality management in the different countries considered were assessed. The best management practices (BMP's) for river restoration with respect to water quality amelioration were evaluated with the perspective of the case studies considered. In the various case studies discussed, a combination of different restoration measures were implemented in tandem. The restoration measures were adapted to suit the local conditions and problems. A pre- and post-restoration investigation of the main success indicators was found to be an important criterion for the evaluation of the outcome of restoration projects. Successful restoration projects were found to focus on reduction of pollutant/nutrient input to the rivers, in addition to the implementation of suitable restoration measures. This has been achieved by public infrastructure development (like installation of storm water controls and sewage treatment plants). This review is aimed to act as an inventory for future restoration projects with water quality amelioration as their main target.

Keywords *River restoration, Water quality, Case studies, Laws and policies, BMPs*

2.1 Introduction

Rivers are naturally dynamic, they flood adjacent lands, erode their banks and bed, and move sediment around. Urban development and historical engineering activities can affect this natural balance and result in morphological damage. This can lead to loss of important habitats, cause changes to rates of erosion or sediment deposition and pose an increased risk of flooding elsewhere in the catchment (SEPA, 2007). Degraded streams and rivers that drain urban areas are not only characterized by high nutrient loads and concentrations of contaminants, but they also have altered stream morphology and reduced biodiversity (Meyer et al., 2005; Zhou et. al., 2012). In recent times, river restoration is globally accepted as an alternative way to protect ecosystem health, preserve water resources and provide flood protection (Palmer et al., 2005; Andrea et al., 2012; Wortley et al., 2013; Kurth and Schirmer, 2014). Increased funds are available for restoration projects in various countries through systematic changes in government policies that are now focusing more on river restoration (EU WFD, 2000; SEPA, 2007). This has resulted in an increase in the number of restoration projects around the world (Wortley et al., 2013; Kurth and Schirmer, 2014; Schirmer et. al., 2014).

The evaluation of stream corridor restoration is an important step that is often omitted in restoration projects (Kondolf and Micheli, 1995; FISRWG, 1998). The ability to evaluate the success (or failure) of management schemes must rely on data that track a system's response to management. Thus, post-restoration monitoring is necessary to provide valuable information (through 'lessons learned') for the management of restoration projects in the future. It shall also be useful for promoting future restoration projects by using previous examples to clearly demonstrate strengths and weaknesses of different scenarios (Palmer et al., 2005; UNEP, 2008). In recent literature there has been reportage of the assessment of the performance of various hydromorphological alterations in the rivers with specific regional context. In Miller and Kochel (2010, 2013), the performance of various in-stream structures have been evaluated across various river basins in North Carolina, U.S.A.. Kurth and Schirmer (2014) and González del Tánago et. al. (2012), have investigated the merits of the various restoration measures employed in Switzerland and Spain respectively. However, the effect of the hydromorphological alterations on water quality in rivers (with pre – post-restoration quantitative sampling) have seldom been studied (Bernhardt and Palmer, 2011).

This review is aimed at transferring lessons learned from various restoration projects focusing on water quality improvement from different parts of the world. To achieve this, restoration projects aimed at water quality amelioration through river restoration are chosen from four countries across three continents (Europe, Asia and North America).

2.2 Overview of the countries selected – the water use, reasons for deterioration of water quality and chronological development of legislative policies for better water quality management

Water use varies significantly at a global level. In 2006, the withdrawal was largely for agricultural followed by industrial and municipal sectors. The proportion of water withdrawn, varies according to the regional context, as shown in Figure 1. The water withdrawal per sector varies largely based on the major occupation in the region; it is withdrawn mainly for agriculture in Asia, for industrial sector in Europe and is equally used for both agricultural and industrial sectors in North America (FAO, AQUASTAT, 2015).

Some of the features of the countries chosen like country size, amount of internal renewable freshwater (surface + groundwater) available and the water use by sector are tabulated in Table 1. The trend of higher water use for agriculture in Asia and for municipal water use in Europe (Figure 1) is also reflected in the data from the countries selected (Table 1).

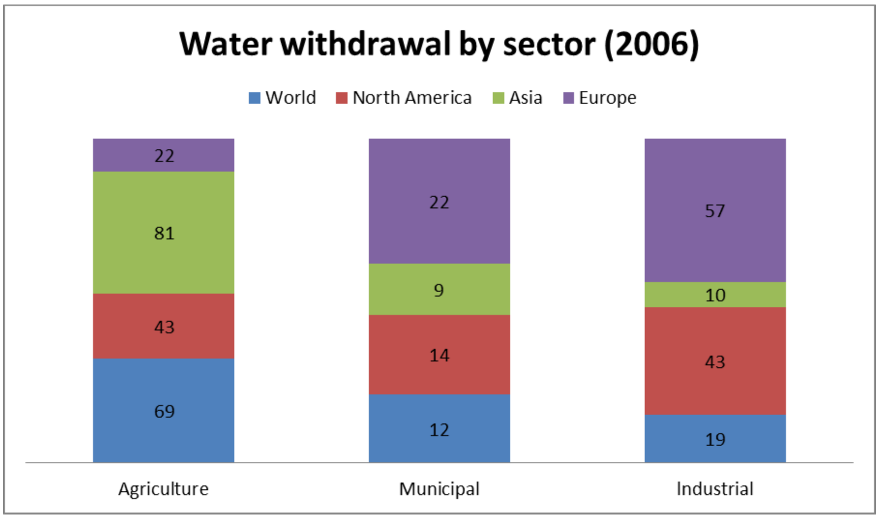

Figure 1 The water withdrawal by sector (in %) globally and in the three continents Asia, Europe and North America are shown. (Data Source: FAO AQUASTAT, 2012: AQUASTAT database, http://www.fao.org/nr/aquastat)

Table 1 The characteristics of the countries considered - land area, annual average precipitation, amount of internal renewable resources, total and per capita freshwater withdrawal and water use by sector are summarized.

Countries selected	Land Area (x1000 ha) (FAO, AQUASTAT 2012)	Average annual precipitation (mm/year) (FAO, AQUASTAT 2012)	Total average internal renewable resources (km^3/year) (FAO, AQUASTAT 2012)	Total freshwater withdrawal (km^3/year)/per capita consumption (m^3/year) (CIA WORLD FACTBOOK, 2015)	Water use by sector domestic/ industrial/ agricultural (%) (CIA WORLD FACTBOOK, 2015)
Japan	37 796	1 668	430	90/714 (in 2007)	20/18/62
South Korea	10 015	1 274	65	26/549 (in 2003)	26/12/62
United Kingdom (U.K.)	24 361	1 220	145	13/213 (in 2008)	58/33/9
United States of America (U.S.A.)	983 151	715	2 818	478/1583 (in 2005)	14/ 46/40

2.2.1 Water quality status of the rivers in the countries selected

Japan: Most of the Japanese cities are susceptible to floods because they lie in the lowland, which are below the flood water level of rivers. River engineering has been carried out extensively to protect the rivers from floods. However, water circulation is poor in these channelized rivers. Nitrogen, phosphorus, and other nutrients cause rapid proliferation of algae. The progressive worsening of water quality has led to eutrophication, which causes red tides, which are toxic and harmful to the local fish and other aquatic life (World Bank, 2006). River and lake restoration in Japan is extensive and many successes have been documented even in heavily urbanized areas with high population densities (Nakamura et al., 2006).

South Korea: Apart from an unequal distribution of water resources seasonally and regionally, the rapid industrialization and urbanization since 1960s, has polluted many water bodies in South Korea. The major pollution sources that influence the quality of surface waters used for irrigation are wastewater from industries, livestock, sewage and acid mine drainage. This pollution problem continues to grow as both the human and livestock populations steadily increase over the years (FAO, 2000).

U.K. (Scotland): The water quality problems in Scotland are mainly around urban areas, particularly around the populated cities of Glasgow and Edinburgh. Although many large rivers and estuaries, such as the Clyde in the west and the Forth in the east, have seen marked improvements over the last 20 years, water quality problems still remain. Land use in the northeastern part of the river basin district is mainly agricultural, which can give rise to a range of environmental problems (SEPA, 2007). Assessments indicate that about 40% of Scottish waters fail to meet the environmental standards required to support good ecology (SEPA, 2007). This is because of the pollution of the water bodies by diffuse agricultural pollution along the east coast, central belt and southwest; the pollution of the urban rivers by sewer overflows and contaminated runoff from roads in the highlands owing to the construction of hydropower dams; in the lowlands mainly due to urban and agricultural intensification (SEPA, 2007).

U.S.A.: During the summers of 2008 and 2009, 1,924 river and stream sites across the country were monitored by the U.S. Environmental protection Agency (EPA) under the National Rivers and Streams Assessment 2008–2009 program.

The following water quality assessment was made:

40% of the nation’s river and stream miles have high levels of phosphorus. 27% have high levels of nitrogen. Biological communities are at an increased risk when the phosphorus and nitrogen pollution levels are high in the rivers and streams. Phosphorus and nitrogen pollution is caused by the use of excess fertilizers, from wastewater and other sources, and can cause algae blooms, low oxygen levels, and more. A substantial portion of the nation’s river and stream miles comprise of poor vegetative cover (24%) and human disturbances (20%) near the surface water bodies. These degraded habitat conditions make the rivers and streams more vulnerable to flooding, which in turn contribute to erosion and increased inflow of pollutants into them. In addition to this, the excess levels of streambed sediments, which can affect the habitat of aquatic organisms, were reported in 15% of the rivers and streams (EPA, 2014 a).

2.2.2 The history of legislation for Water quality improvement in Japan, South Korea, U.K. (Scotland) and U.S.A.

Many industrialized countries in the world have often gone through a series of legislative reforms over the last 70 years to steer their policies towards being more environment friendly. The legislative time frame among the countries selected have similarities. The policies have changed from focusing on water quality management mainly by pollution prevention towards adopting an integrated catchment-scale planning approach, with an emphasis on ecological protection as shown in Table 2.

Table 2 An overview of some of the legislative changes and policies related to water quality improvement in Japan, South Korea, U.K. (Scotland) and U.S.A. in the chronological order.

Japan (ARRN, 2009)	**South Korea (ARRN, 2009; UNDESA, 2004)**	**United States of America (EPA, 2014 b)**	**U.K. (Scotland) (SEPA, 2007; www.evolvingmedia.co.uk, 2014)**
Water Pollution Control law 1970, controls water quality of freshwater and groundwater.	River Act 1961, basic principles of river basin management defined.	Federal Water Pollution Control Act 1948, first major water pollution law in U.S.A. (later amended as Clean Water Act)	Sewage (Scotland) Act 1968, Scottish Water as the water supply and sewerage authority for the whole of Scotland
		Water Quality Act of 1965, States were directed to develop water quality standards establishing water quality goals for interstate waters	
1990, beginning of national census on river environment.	Water Supply and Waterworks Installation Act 1961 and the Sewerage Act 1966, cover water use by industry and households	National Environmental Policy Act of 1969 (NEPA) NEPA is the basic national charter for protection of the environment. It establishes policy, sets goals, and provides means for carrying out the policy.	Water (Scotland) Act 1980
Basic environment law 1993, direction for developing measures from the viewpoint of environmental conservation	Management of Drinking Water Act 1965, addresses issues related to the control of drinking water quality	Federal Water Pollution Control Act Amendments of 1972, each point source discharger to waters of the U.S. was required to obtain a discharge permit, wastewater standards for industry setup	Environment Act 1995, Creation of Scottish Environment Protection Agency
Amendment to River law 1997, river management such as flood control water use and environment, strong stakeholder engagement encouraged	The Agriculture and Fishery Improvement Act 1997, covers the use of water by agriculture	Safe Drinking Water Act (SDWA) 1974, to protect public health amended twice in 1986 and 1996 to protect drinking water and its sources: rivers, lakes, reservoirs, springs, and ground water wells.	Scotland Act 1998, Water and sewage disposal legislation moved from London to Scottish parliament at Edinburgh
Law for environmental impact assessment, 1998	Water Quality Conservation Act 1990, Ground Water Act 1993, and Dam Construction and Support Act 1999; comprise the general legal and regulatory framework for water resource management and development in South Korea.	The Clean Water Act (CWA) 1977, is an amendment to the Federal Water Pollution Control Act of 1972, which set the basic structure for regulating discharges of pollutants to waters of the United States.	Water Environment and Water Services (Scotland) Act 2003
Law for Promotion of Natural restoration, 2003	Water Quality Conservation Act 1997, the government established the Special Comprehensive Measures for Han River Water Quality (1998), followed by similar measures for the Nakdong River (1999), Geum River (2000), and Yeongsan River (2000)	Water Quality Act of 1987, development of numeric criteria for those water body segments where toxic pollutants were likely to adversely affect designated uses	Water Services (Scotland) Act 2005, separation of Scottish Water's operational and retail functions to promote competition for retail in water supply and sewage disposal services
Rules for permitting use of river zones, 2004 (Citizen based planning of rivers for practical use.)	Creation of eco-friendly river reach in 50 sites, 2005-2011	1990 National Guidance: Wetlands and Non-Point Source Control - describes how State non-point source programs can use the protection of existing wetlands and the restoration of previously lost or degraded wetlands to meet the water quality objectives of adjacent or downstream water bodies.	River Basin Management Plan 2009, environmental management by reduction of diffuse pollution into rivers.
Invasive alien species act and landscape law, 2004 , to eradicate certain invasive species.			Water Environment (controlled activities) regulation 2011, prevent new damage to the water environment from engineering works on rivers (including from maintenance regimes).
Amendment to Nature oriented river work (beginning of nature oriented river management), 2006	Establishing comprehensive river management plan (4 major rivers), 2010		European Union's Water Framework Directive (EU WFD, 2000) requires incorporation of new 'hydrogeomorphological, chemical and ecological factors' into water quality assessment standards. It states that by 2015 member states must ensure all water bodies reach 'good' ecological status by 2027.

2.3 Description of the selected case studies with water quality deterioration as a driver for river restoration

2.3.1 Cheonggyecheon River – South Korea

The Cheonggyecheon River in Seoul, was originally developed from a brook into 14 waterways by King Taejong in 1412. Following this, the river was covered between 1958-1978 (Figure 2a). The Cheonggye highway (5.84 km long) built over this covered river between 1967-1976 had been a symbol of Korean development for many years (Hwang, 2004).

2.3.1.1 Drivers

The elevated highway built over the covered stream was causing air pollution (emission of benzene and nitrous oxide). The population in the Cheonggyecheon area decreased from 66% to 14.9% in the two decades since the construction of the highway. The covered river was heavily polluted with lack of plant and animal life due to decreased dissolved oxygen (DO) owing to excessive nutrient input (Hwang, 2004).

2.3.1.2 Solutions

Demolition of the highway was the first restoration measure. Following the demolition, the urban stream was redesigned from a tributary of the Han River to include flood protection measures with the construction of an embankment to protect the banks from a 200 year return period of flood (Hwang, 2004). Terraces and sidewalks were built in the upper and lower reaches of the stream to make the river accessible to the public. Additionally, intercept sewage lines were also designed in the upper reach to control the inflow of nutrients into the river. Further, a uniform supply of water to maintain a maximum depth of 40 cm was maintained by redirecting water from the Han River. Jungang sewage treatment plant was upgraded to treat three times the sewage generated in the region, this treated water drains into the river. The opening up of the river and its beautification has resulted in it becoming a serene getaway for the residents of Seoul and tourists alike (Figure 2b) (Hwang, 2004).

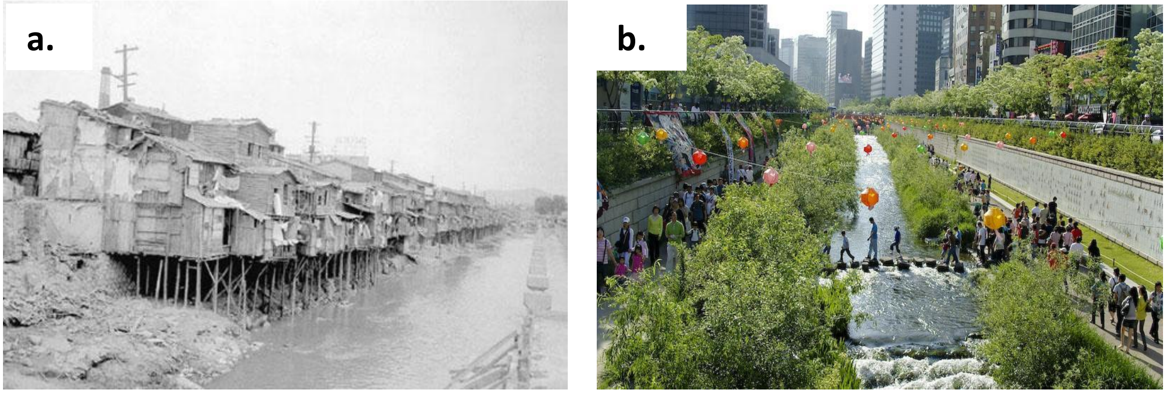

Figure 2 a. Chonggyecheon River in the 1950's b. the river post-restoration in 2008 in downtown Seoul **Source:** Wikimedia.org

2.3.1.3 Success monitoring

Monitoring of water quality parameters like DO, biological oxygen demand (BOD), and suspended solids (SS) in the larger Jungnancheon River, which is fed by the (Cheonggycheon River) was carried out pre- and post-restoration. The air quality was measured by nitrous oxide levels and particulate organic matter (POM) in the vicinity of the Cheonggycheon River and the neighbouring regions (Lee and Anderson, 2013).

The Cheonggycheon River acts as a ventilation mechanism restoring cool winds. Therefore, a reduction in the air temperature from 30 to 26.6 ℃ was achieved in the surrounding areas. The wind-speed in these areas has increased from 2.2 to 7.8 % which explains the temperature reductions (Holzer et al., 2011). Pre-restoration delivery of waste to the river has been replaced by cleaner runoff and recycled water. Therefore a noticeable change in some of the major water quality indicators was observed from 2002 to 2011, decrease in the SS (> 16 ppm to <10 ppm), decrease in BOD (>12 ppm to <5 ppm) and increasing levels of DO (< 4 ppm to > 6 ppm) post-restoration has been achieved (Lee and Anderson, 2013). There was an increase in the overall biodiversity observed in the river between pre-restoration observation in 2003 and post-restoration in 2008. The diversity of plant species have increased from 62 to 308, fish species from 4 to 25, insect species from 15 to 192, aquatic invertebrate species from 5 to 53 and bird species from 6 to 36 (Landscape performance, 2015).

2.3.2 Izumi River – Japan

The Izumi River is a small river (9.5 km long), flowing at the bottom of a ravine lying between a plateau in the west side of Yokohama City in the Sakai Rawa River basin (Figure 3a). The urbanization of the basin has advanced rapidly near the centre of Yokohama. Farmlands occupy middle and lower part of the basin (ARRN, 2009).

2.3.2.1 Drivers

In the 1970s, following a flash flood, there was an urgent need to implement flood control measures. Therefore, the shore of the Izumi River was covered by steel sheet piles and the river bed was dredged, making it hard for the residents to approach the riverside. After the river was altered, the water quality began deteriorating and it was soon called the “Sewage River” (ARRN, 2009).

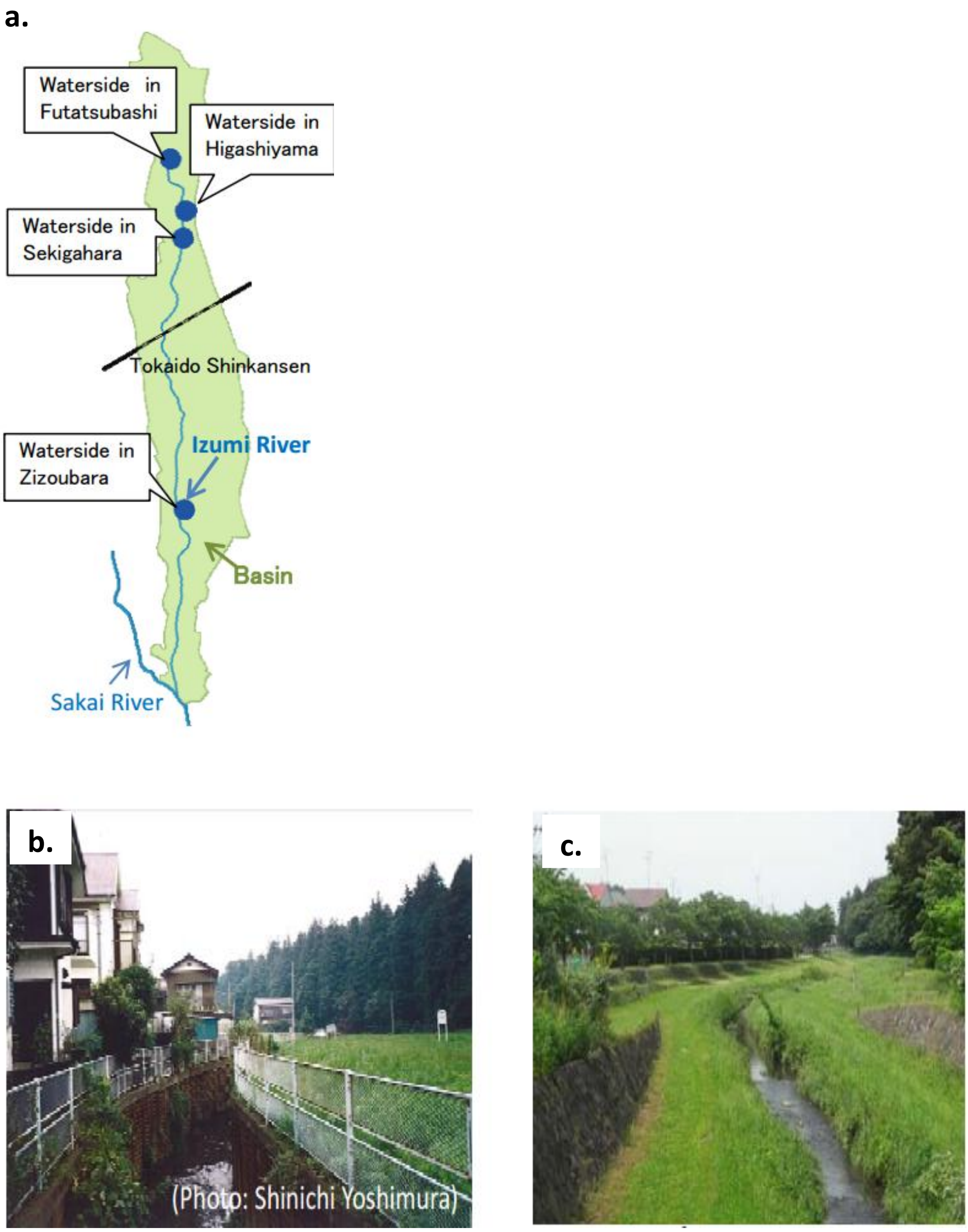

Figure 3 a. The location of the restoration sites along the Izumi River b. pre - restoration c. post-restoration of the water side Higashiyama along the Izumi River. **Source:** Modified after Asian River Restoration Network - ARRN (2009).

2.3.2.2 Solutions

The Izumi River restoration was implemented in several steps. The first step was with the formation of the “Izumi River environmental improvement basic plan", which started in 1987. This involved the local community, particularly the students from the elementary schools in the basin to effectively use the river basin through activities like park and green space conservation. Following this, the implementation of stream reach-scale restoration projects were carried out like: "Waterside in Zizoubara" in 1994, "Waterside in Higashiyama" in 1996, "Waterside in Sekigahara" in 1997 and "Waterside in Futatsubashi” in 1998 (Figure 3). The stream reach-scale restoration measures included reconstruction of the flow paths by widening the river bed and improvement of the river connectivity. Additionally, river bank restoration through slope stabilization and creation of green spaces in the banks were also carried out (ARRN, 2009).

2.3.2.3 Success monitoring

There are eight watershed protection agencies located in the watershed, which involve local citizen participation in the clean-up of the river. During a monitoring survey conducted in 2005-2006, it was noted that the water quality of the river had improved significantly, the BOD decreased from 10 ppm (in 1993) to <5 ppm (since 1996). Additionally, fish like *Carassius* and *Loach* were found in the river for the first time in 1996, these fish had not been found before due to their sensitivity to pollution. 18 species of fish were also found post-restoration in the Izumi River (ARRN, 2009).

2.3.3 Ythan river – Scotland

Ythan River Catchment (680 km^2) is an agricultural catchment situated in Aberdeenshire, East Scotland, the river has a low flow of around 6 m^3/s. The Ythan River drains into the North Sea. The river channel is flanked by an intertidal area of approximately 2 km^2 and the mouth is constricted by a sand bar. Landuse in the catchment is dominated by agriculture (90% of the total area), which comprises of a mix of arable land and livestock (Balls et. al., 1995).

2.3.3.1 Drivers

The Ythan catchment was declared the first large scale Nitrate Vulnerable Zone (in 2000) in Scotland (OSPAR, 2006). As the Ythen River suffered from several water quality issues that resulted in the eutrophication of the Ythen estuary (a Ramsar wetland and site of special scientific interest), which in turn impacted the waterfowl population in the natural reserve (OSPAR, 2006). The Ythan River is the main source of nitrogen to the estuary in the form of total oxidised nitrogen. The concentration of total oxidised nitrogen in the river increased from ca. 100-150 µM in the early 1960s to ca. 500-550 µM in the 1990s as a result of changing land use patterns in the catchment (OSPAR, 2006).

2.3.3.2 Solutions

Restoration was carried out at 6 sites along the Ythan River, which were selected by the public from12 potential sites.

The restoration involved several measures like:

removal of non-native over shadowing dense conifer trees from 1.75 km of the river bank, replanting native trees at 35 sites along the river, creation of buffer strips of 70 km along the river and its tributaries. In addition to this, creation of nutrient budgeting software and production of nutrient budgets for 62 farms to measure nutrient efficiency in the farms were carried out (Ythan project, 2014).

Incentives were given to farmers for the creation of the buffer strips (where no nutrient application was done) close to the river through agri-environment schemes. Flow diversification was accomplished on the Burn of Keithfield (a small stream that joins the Ythen River) in September 2004. Small rocks and boulders were placed at strategic locations to create pools and eddies in the flow that create turbulence effects. These hydrologic features increase the variety of flow patterns in the river, thereby creating a greater habitat variety for insects and fish. Bank stabilisation was also carried out using felled conifer trees and native plants that were grown on the banks like in Chapelhaugh near Methlick (Figure 4) (Ythan project, 2014).

2.3.3.3 Success monitoring

Eutrophication assessment was carried out between 2001-2005 in the Ythan estuary. Additionally, 25 km of the Ythan River was surveyed with the help of local volunteers and 240 samples were collected during the project duration and after the completion of the project (Ythan project, 2014).

Figure 4 Fencing and bank restoration at Chapelhaugh near Methlick in the Ythan catchment. The banks had been heavily eroded pre-restoration. a. Fencing and bank restoration done using felled conifer logs b. regrowth of native vegetation and stabilized banks **Source:** Ythan project, retrieved from [ythan.org.uk on August 4, 2014.](ythan.org.uk)

In the river the following indicators were considered: SS - decrease in SS was noted in the buffer strips (created in farmlands in the vicinity of the river as described in 3.2.2) when compared to the other parts; nitrate – no appreciable difference was noted between the buffer strips and the other monitoring sites; orthophosphate (OP) - decrease in concentration downstream of the buffer strip was observed in a certain section.

In the estuary the following indicators were considered: Algal cover - there was overall reduction in the algal cover from 31.4 % in 2000 to around 15 % in 2003; Oxidised nitrogen - the oxidised nitrogen did not show any increase from 2000 in the estuary (Dunne, 2003); Biodiversity – large sea trout have been seen upstream, indicating that the fish pass is working as expected. No correlation between the bird count and algal extent was noted (Dunne, 2003; Ythan project, 2014).

2.3.4 Kissimmee River - Florida, U.S.A.

The lower Kissimmee River is located between Lake Kissimmee and Lake Okeechobee in Florida (Figure 5). The lower Kissimmee basin has a catchment area of 7804 km^2. The regional climate is humid, sub-tropical with an average rainfall of 135 cm/year (Colangelo and Jones, 2005; Colangelo, 2014).

2.3.4.1 Drivers

In response to prolonged flooding, the 166 km naturally meandering lower Kissimmee River flowing between Lake Kissimmee and Lake Okeechobee, was channelized from 1962 to 1971 into a 90 km (l) x 100 m (b) x 9 m (h) flood control canal called as C-38 (Figure 5, Figure 6a). The free flowing river was then transformed into a series of impounded reservoirs or pools separated by water control structures (Colangelo and Jones, 2005).

The channelization resulted in the elimination of 12000-14000 ha of floodplain wetlands leading to the degradation of wild life habitat structure and water quality (Colangelo and Jones, 2005; Toth, 1993). The new flood control canal eliminated the flow of water into the natural river channel due to its high conveyance capacity, resulting in little or no flow into the natural river channel. In addition to this, the river got disconnected from the floodplain (Colangelo and Jones, 2005; Colangelo, 2014). The low or no flow in the remnant river channels resulted in vegetation encroachment of floating species like *Pistia stratiotes* [water lettuce] and *Eichhornia crassipes* [water hyacinth]. This resulted in organic matter accumulation up to 3 m in the river bed causing eutrophication and consumption of DO in the river leading to a chronic reduction of DO (Toth, 1990). The altered low flow conditions and low DO led to the replacement of local fish like largemouth bass to species tolerant of low DO regimes (such as *Lepisosteus platyrahincus* [Florida gar] and *Amia calva* [bowfin]) (Toth, 1993). Diverse and abundant wading bird populations declined and were largely replaced by *Bubulcus ibis* [cattle egret], a species generally associated with upland, terrestrial habitats (Perrin et al., 1982). In addition, there was a high nutrient contribution from the lower Kissimmee river to the Lake Okeechobee, delivering 20% of total phosphorus (TP) and 31% of total nitrogen (TN) of the inflow to the lake. Channelization is believed to have facilitated nutrient transport from agricultural watersheds downstream to Lake Okeechobee (Ritter and Flaig, 1987).

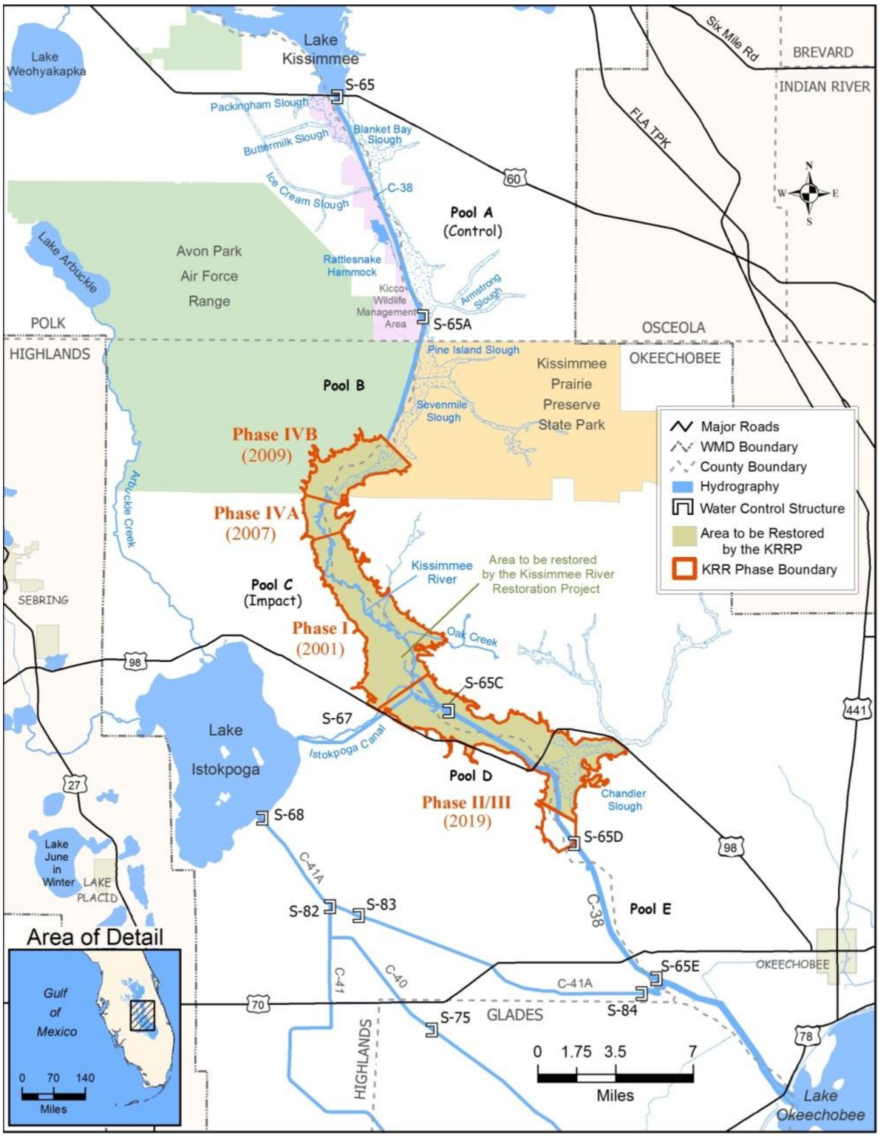

Figure 5 The extent of the lower Kissimmee River with the various phases of restoration. The various restoration phases (I, 1V A,B, II/III) are marked along with the year of completion. Source: Modified after South Florida Environment Report 2015, (Map courtesy: South Florida Water Management District)

2.3.4.2 Solutions

The Kissimmee River restoration project aims to restore the pre-channelization habitat structure and function of the floodplain ecosystem by including seasonal inflow patterns and improvement of river channel-flood plain connectivity disrupted by channelization.

In the Phase I of restoration (Figure 5) (completed in 2001) the following measures were done: backfilling was done in the C-38 canal (for 12 km of the canal), grading the spoil areas to original channel elevations, recarving and reconnecting sections of the river destroyed during channelization. In addition, one water control structure was removed, two new river sections (2.4 km) were constructed and flow was restored to 24 km of the natural river channel (Figure 6b). In this phase, 2344 ha of wetlands were restored (Colangelo and Jones, 2005).

In Phase IV a and IV b (Figure 5) (completed in 2007), 9 km of the canal was back filled and 8 km of river channel was recarved. An additional 776 ha of wetlands are expected to be restored owing to these changes (Figure 6b). Additional Phase II/III stages of restoration are to begin in 2017 to backfill more canal sections, recarve additional river sections and restore more wetlands (Koebel and Bousquin, 2014).

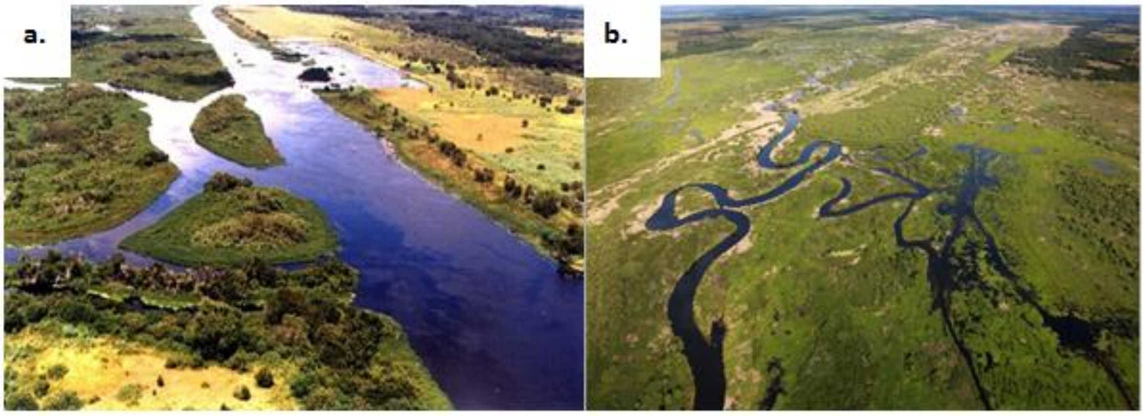

Fig.6 a. The channelized pre-restoration Kissimmee River, C-38 canal in 1995. b. Meandering river channel post-restoration (of phases I, IVa and IVb), photo from April, 2014.**Source:** a. U.S. Army Corps of Engineers Digital Visual Library [Public domain], via Wikimedia Commons. b. Photo courtesy: South Florida Water Management District (SFWMD).

In addition to the restoration measures in the Kissimmee River, BMPs in agriculture and Storm Water Treatment Areas (STAs) have been extensively applied to control the inflow of nutrients from the catchment (SFWMD, 2015).

2.3.4.3 Success monitoring

DO: The pre-restoration monitoring of the lower Kissimmee River was carried out 3 years before phase I of the construction and post-restoration monitoring was done for 8 years after phase I. There was significant recovery of mean DO increasing from 2.3 to 4.9 ppm in the impacted areas. The regulated flow and subsequent removal of submergent vegetation in the post – restoration phase resulting in increased re-aeration rates in the river is attributed to be the reason for the increased DO levels post restoration (Colangelo, 2014).

Nutrients: The TP loading post restoration is expected to be lower as the channelized C-38 was flushing high nutrient loads and the increased wetland area is expected to have increased nutrient retention. Although, total loading in the last five years (2007-2011) has been over 50 % lower than loading in the previous five years (2002-2006), the reduction cannot be directly attributed to restoration and is dependent on hydrological conditions and land use in the catchment (Jones et.al., 2012).

In addition, the BMPs and STAs, have removed more than 4582 metric tons of TP from water entering the Everglades Protection Area. Two decades ago, before STAs were constructed, phosphorus concentrations in Everglades-bound waters averaged 170 parts per billion (ppb). Today, the concentrations in discharges to the Everglades have been as low as 12 ppb (SFMD, 2015).

Fish: In the restored area after Phase I, the relative abundance of invasive fish like bowfin and gar declined from 2004 onwards and reached expected levels in 2010. Fish like centrarchids met the expected levels in 2004-2007 but fell below the 58% expectation level in 2010 which is attributed to the growth and abundance of other fish as well as to droughts and low flow conditions (Jones et.al., 2012).

Birds: After phase I of construction in 2001, the foraging wading birds population began to meet restoration target of 30.6 birds/km^2 (three year running average), except for the drier periods in 2007–2009 and 2009–2011 when this count fell. During 2009–2011, there was a waterfowl abundance exceeding the restoration expectation of 3.9 ducks/km^2 (Jones et. al., 2012).

The summary of all the case studies discussed can be found in Table 3.

Table 3 Table with the summary of the various case studies, reason for water quality degradation, river restoration measures implemented and goals achieved

River Name, Country	Catchment area km²/ River length	Project duration	Main drivers for river restoration	Reasons for water quality degradation	Methods of river restoration	Special techniques used in the project	Success indicators
Cheonggyecheon River, South Korea	61 km²/ 13.7 km (total length) 5.8 km (restored length)	2000-2005	Polluted river, lack of plant and animal life	The river was culverted and buried underneath a 12 lane highway, urban activities	The highway was de-commissioned, the new river channel was excavated, water supply from Han river maintenance of minimum flow of 40 cm depth, creation of combined sewer	New green belt with waterfront: West to East, Creation of ecological biotope and environment Thematic places: waterfall and fountains	Water quality improvement, species richness BOD > 12 ppm reduced to < 5 ppm, DO increase < 4 ppm to > 6 ppm, SS (Monitoring period January 2003 (before)-2011 (after))
Izumi River, Japan	Data unavailable / 11.5 km	1987-1998	Water quality deterioration in the 1970s, was called 'sewage river'	Shore covered by steel sheet piles and river bed dug deep due to frequent floods.	Widening of the river and reconstruction of the flow path and waterside were implemented, an integral improvement by growing woods in slopes on the left bank side with the whole river space was carried out.	Involving public participation in the clean-up activities through 8 watershed protection associations, improving sewerage coverage and creating environment friendly path to rivers	BOD >10 ppm until 1993 to < 5 ppm since 1996. Fish like *Carassius* and *Loach* found in the river again.
Kissimmee River, Florida, U.S.A.	7804 km² /166 km (pre-channelized) reduced to 90 km channelized river	1999- 2019 (expected)	Eutrophication in the remnant river after channelization, lack of oxygen leading to ecological concern	Channelization of the River led to low flow to no flow conditions in the remnant river, this led to encroachment of vegetation, reduction of oxygen levels	Canal backfilling, removal of water control structures, restoring flow and floodplain connectivity by channel recarving. Wetland restoration is also carried out.	Creation of Storm water treatment areas and adopting best management practices in agriculture to remove the excess nutrients entering the water	DO increase (2.3 to 4.9 ppm) after Phase I of restoration in impacted areas, abundance of water fowl and wading birds increased, invasive fish like bowfin and gar reduced in number.
Ythan River, Scotland, U.K.	680 km²/ 60 km (river length)	2001-2005	Eutrophication of estuary waters, degradation of critical habitat of migratory birds, declared first nitrate vulnerable zone in Scotland (in 2000)	Discharges from sewage treatment facilities, diffuse pollution from agricultural runoff	Felling of non-native conifer, creation of variable flow through eddies and ripples, flow diversification, erosion control through re-vegetation (riparian fencing), and redesign of existing weirs, creation of wetlands and buffer strips.	Creation of a simple software for nutrient budgeting of fields, financial incentive for farmers to create buffer strips, Involving public participation in monitoring and clean-up activities.	Decrease in suspended solids was noted in the buffer strips, decrease of phosphate was noted downstream of the buffer strips.

2.4 Best Management practices (BMPs) for water quality improvement through river restoration

Restoration of the physical features of a river cannot guarantee a positive effect on the ecological integrity of the system if there are water quality constraints (FISRWG, 1998). In Table 4, it is shown that various restoration activities can affect the different water quality stressors simultaneously. While on one hand, the limitation of impervious cover and land disturbing activities reduce the nutrient, toxics and fine sediment runoff from the catchment, thereby increasing the DO in the river. On the other hand, creation of drop structures (created to pass water to a lower elevation, which can control its velocity especially in streams with steep gradients) can result in the decrease of sediment loads along with an increase in the DO in the river.

Table 4 The potential water quality impacts of selected stream restoration and catchment best management practices (BMPs) (FISRWG, 1998)

Restoration activities	Fine sediment Loads	Water temperature	Salinity	pH	Dissolved oxygen (DO)	Nutrients	Toxics
Reduce land disturbing activities	Decrease	Decrease	Decrease	Decrease/ Increase	Increase	Decrease	Decrease
Limit impervious area in watershed	Decrease	Decrease	Negligible effect	Increase	Increase	Decrease	Decrease
Restore riparian vegetation	Decrease	Decrease	Decrease	Decrease	Increase	Decrease	Decrease
Restore wetlands	Decrease	Decrease/Increase	Decrease/ Increase	Decrease/ Increase	Decrease	Increase	Increase
Stabilize channel and restore under-cut banks	Decrease	Decrease	Decrease	Decrease	Increase	Decrease	Negligible effect
Create drop structures	Increase	Negligible effect	Negligible effect	Decrease/ Increase	Increase	Negligible effect	Decrease
Re-establish riffle substrate	Negligible effect	Negligible effect	Negligible effect	Decrease/ Increase	Increase	Negligible effect	Negligible effect

From the various case studies discussed above, it is clear that a combination of different restoration measures can simultaneously improve the water quality status of the river. Like in the case of the Izumi River, the deterioration of the river water quality was tackled with a combination of restoration measures like widening the river bed and reconstruction of the flow paths, improvement of the bank stability by growing wood along with creation of green spaces near the stream. This was backed by improvement of sewage treatment facilities in the catchment. These measures not only protect the river from floods but also help improve the water quality by decreasing the BOD in the river. In addition to this, the involvement of the public in the clean-up and monitoring activities only increased the sustainability of the restoration measures.

In the Kissimmee River restoration project, in addition to restoring the flow in the remnant river channels; additional catchment wide measures like creation of STAs and adoption of BMPs in agriculture management has helped reduce the nutrient levels in the river.

In the case of the Ythan River restoration, it was found that the restoration measures like flow diversification by placing boulders in the river was supplemented with community wide actions like creation of buffer strips and nutrient budget in farms. In this project, there was active public participation in the selection of the sites pre-restoration and in post-restoration monitoring as well.

Therefore, it is important to consider the local conditions in the catchment and identify the critical parameters that are affected before choosing the appropriate restoration measures. It is observed that application of morphological alterations in isolation cannot work wonders to rectify the water quality problems in deteriorated streams without fixing the source of the pollutant (like runoff from agriculture, sewage treatment plants), through infrastructural interventions, as emphasized earlier by Bernhardt and Palmer (2011).

2.5 Conclusion

In this chapter, an assessment of four river restoration projects that had water quality deterioration as the major driver for river restoration has been done. The projects were chosen from industrialized countries, located in three different continents. Although geographically different, the countries selected have faced similar problems (increased agriculture and urban areas) that have caused water quality deterioration and in turn habitat destruction in their surface water bodies. To address this, the changes to water management policies have evolved with time. They have periodically changed from primarily addressing pollution related problems to a more holistic approach, by adopting integrated river basin management.

In the various case studies considered, the water quality deterioration occurred due to different reasons like narrowing of river bed due to canalisation (often as a flood protection measure), rapid urbanization leading to increased sewage discharge and covering the river to develop urban infrastructure like roads and bridges. The improvement of water quality was carried out by adopting a combination of various river restoration measures like widening of the river bed, improvement of stream bank stability with vegetation, creation of wetlands and improving the variability of flow through the creation of pools, riffles and eddies. These restoration measures were often implemented in tandem with engineering alterations to the public infrastructure in the catchment like creating new/up-grading the storm water controls, sewage treatment plants and decommissioning of highways that covered the river.

In successful restoration projects, it is often noted that along with the engineering solutions there was also an emphasis on involving active public participation. These included not only measures like the creation of nutrient budgets for farmers, creation of river fronts and beautification of rivers to improve the public access to the rivers, but also the involvement of the public in the monitoring surveys. The BMPs for river restoration are often carried out in combination as they simultaneously affect more than one parameter. Therefore, it is important to select the appropriate restoration measure in accordance to the local conditions. The success indicators used are often basic water quality parameters like BOD, DO, nutrients and sometimes biological indicators in addition, which are indicative of long term status recovery.

Thus, the main points learned from the case studies, for water quality amelioration through river restoration are:

a. Selection of appropriate site specific restoration measures (often in combination) by pre-restoration identification of the critical parameters that are to be rectified.

b. Involvement of public is encouraged at various phases of the restoration project, in the planning phase as well as in the pre - and post-restoration monitoring phases.

c. Having a designated post-restoration success monitoring period with specific budget allocation.

d. Reducing the pollutant source by the creation of buffer strips in agricultural areas and up-gradation/installation of necessary public infrastructure.

The changes to the water management policies in the industrialized nations discussed in this review are also a big factor in the realization of successful restoration projects in these countries. They have achieved this by adopting a holistic approach to river basin management. Additional changes to these policies are desired that lay more emphasis on public participation and promoting catchment wide pollution prevention in tandem with the river reach-scale measures.

Acknowledgements

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Chapter 3 Does river restoration affect diurnal and seasonal changes to surface water quality? A study along the Thur River, Switzerland

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Abstract

Changes in river water quality were investigated along the lower reach of the Thur River, Switzerland, following river restoration and a summer storm event. River restoration and hydrological storm events can each cause dramatic changes to water quality by affecting various bio-geochemical processes in the river, but have to date not been well documented, especially in combination. Evaluating the success of river restoration is often restricted in large catchments due to a lack of high frequency water quality data, which are needed for process understanding. These challenges were addressed in this study by measuring water quality parameters including dissolved oxygen (DO), temperature, pH, electrical conductivity (EC), nitrate and dissolved organic carbon (DOC) with a high temporal frequency (15 minutes - 1 hour) over selected time scales. In addition, the stable isotopes of water (δD and δ^{18}O-H_2O) as well as those of nitrate (δ^{15}N-NO_3^- and δ^{18}O-NO_3^-) were measured to follow changes in water quality in response to the hydrological changes in the river. To compare the spatial distribution of pre- and post-restoration water quality, the sampling stations were chosen upstream and downstream of the restored section. The diurnal and seasonal changes were monitored by conducting 24-hour campaigns in three seasons (winter, summer and autumn) in 2012 and 2013. The amplitude of the diurnal changes of the various observed parameters showed significant seasonal and spatial variability. Biological processes - mainly photosynthesis and respiration - were found to be the major drivers of these diurnal cycles. During low flow in autumn, a reduction of nitrate (attributed to assimilation by autotrophs) in the pre-dawn period and a production of DOC during the daytime (attributed to photosynthesis) was observed downstream of the restored site. Further, a summer storm event was found to override the influence of these biological processes that control the diurnal changes. High frequency daily monitoring of key water quality parameters over different seasons is shown to be essential in evaluating river restoration success.

Keywords: *River restoration; Water quality; Summer storm event; Diurnal cycles; Seasonal changes*

3.1 Introduction

River water quality is typically characterized by significant diurnal, seasonal, and event-driven variations (Brezonik and Stadelmann, 2002; Henjum et.al, 2010; Hessen et.al., 1997). Bio-geochemical processes affecting river water quality, for example, occur on a diurnal timescale in response to the solar photo cycle. The amplitude of some of these diurnal processes can be as large as the changes occurring on annual and seasonal time scales (Nimick et al., 2005; Parker et al., 2005). In many urban rivers, the diurnal fluctuations are found to be more important than the seasonal variations (Fogle et al., 2003).

Diurnal changes of dissolved oxygen (DO) and pH are due to photosynthesis of autotrophs including aquatic plants, phytoplankton and periphytons, which drive oxygen production during the day and its consumption overnight, and vice-versa for carbon dioxide (CO_2) thereby affecting the carbonate equilibrium (Odum, 1956). These biological processes can also cause a diurnal change in nutrients like nitrate in clear, unpolluted rivers and streams. Being the primary nutrient for photosynthesis, nitrate uptake has been observed during the daytime, while nitrate is subsequently released back into the water column during overnight respiration (oxidative decay of organic matter) (Gammons et al., 2005, 2011). Dissolved organic carbon (DOC) has also been found to exhibit diurnal changes in response to photosynthesis, in which autotrophs produce DOC in the form of carbohydrates during the daytime and hetrotrophs consume it overnight (Hood et al., 2003; Kaplan and Bott, 1989; Parker et al., 2010; Rier and Stevenson, 2002; Westhorpe and Mitrovic, 2012).

During storm events, an increase in river discharge in turn decreases the nutrient and DOC concentrations due to dilution. Flashiness due to large impervious covers in urban catchments can result in scouring and removal of benthic organic matter (BOM) and algae (Sudduth et al., 2011).

Since river water quality parameters can vary rapidly in space and time, random intermittent sampling will fail to capture the extremes and can obscure the complex hydrochemical signals within the river (Brick and Moore, 1996; Halliday et al., 2012; Kirchner et al., 2000, 2004; Madrid and Zayas, 2007). Therefore, in order to fully understand the processes that link catchment hydrology to the hydrochemistry, the measurement frequency has to coincide with the hydrological response time of the river, which often ranges from minutes to hours, depending on the catchment size and other local factors (Halliday et al., 2012; Kirchner, 2006; Kirchner et al., 2004; Moraetis et al., 2010; Scholefield et al., 2005).

The aim of many river restoration projects is to increase the hyporheic exchange between the river and the subsurface by structural changes like widening the riverbed, remeandering river reaches, developing gravel bars, or by side-arm reconnections (Battin et al., 2007; Kasahara and Wondzell, 2003). The positive influence that river restoration has on the water quality at the river reach scale is often attributed to the increase in the natural attenuation processes in the river, due to the increase in hyporheic exchange (Cha et al., 2009; Johnston, 1991). This is expected to create thermal refugia for aquatic biota (Acuña and Tockner, 2009) and hotspots of biogeochemical processing (Lautz and Fanelli, 2008; McClain et al., 2003, Vogt et. al., 2010).

Additionally, river restoration is also expected to cause habitat diversity in the river reach leading to increased primary productivity and a subsequent increase of DO during daytime. Simultaneously, it can also result in increased nutrient uptake by primary producers during photosynthesis (Mulholland et. al., 2009 and Sudduth et. al., 2011). This enhanced nutrient uptake due to ecosystem stimulation by river restoration has been documented and analysed in only a few studies (i.e., Bukaveckas, 2007; Kaushal et al., 2008; Roberts and Mulholland, 2007; Sudduth et al., 2011).

This study aims to verify whether river restoration indeed increases nutrient uptake in a river and whether this effect is unique to certain seasons or hydrological conditions. Further, it aims to study the effect of a summer storm event on the river water quality. To verify if the restored site can act as a buffer to nullify the catchment flashiness effect, especially on the post-flood removal of BOM cover in the river bed and the excess solute and DOC turnover. A post-restoration spatial and diurnal water quality study is thus carried out in three seasons along the lower stretch of the Thur River, Switzerland.

3.2 Study Area

The study was conducted along the Thur River in northeastern Switzerland, which arises from Mt. Santis (2502 masl), and flows into the Rhine River (Figure 1). The catchment area (extending to the outlet of the catchment at Andelfingen as shown in Figure 1) is 1,696 km^2. The main characteristic of the Thur catchment is the absence of a reservoir or a lake in the entire catchment, making it the largest river without a retention basin in Switzerland (Schirmer et al., 2014). The river is characterized by dynamic discharge patterns varying between 15 and 552 m^3/s in 2012. The dynamic discharge pattern can further be characterized by the flashiness index of the catchment defined by a ratio of discharge quantiles (Q5/Q95) calculated from a long-term discharge data set available from Andelfingen (Table S1 in supplementary information). Annual mean discharge in 2012 was 53 m^3/s (Federal Office for the Environment [FOEN], 2012). The Thur River has three main tributaries, namely the Murg, the Necker and the Sitter. The Niederneunforn restored site is located 8.5 km downstream of the confluence with the Murg River (Figure 1).

The Thur catchment consists mainly of limestone-dominated alpine headwaters. Precipitation varies between 900 and 2500 mm/yr from the lowlands to highlands (Seiz and Foppa, 2007). The Thur valley aquifer consists of fluvial sandy gravels overlaying impervious lacustrine clays and has an approximate extent of 70 km^2 and a thickness of 5-20 m in the lower part of the catchment as indicated in Figure 1 (Schneider et al., 2011).

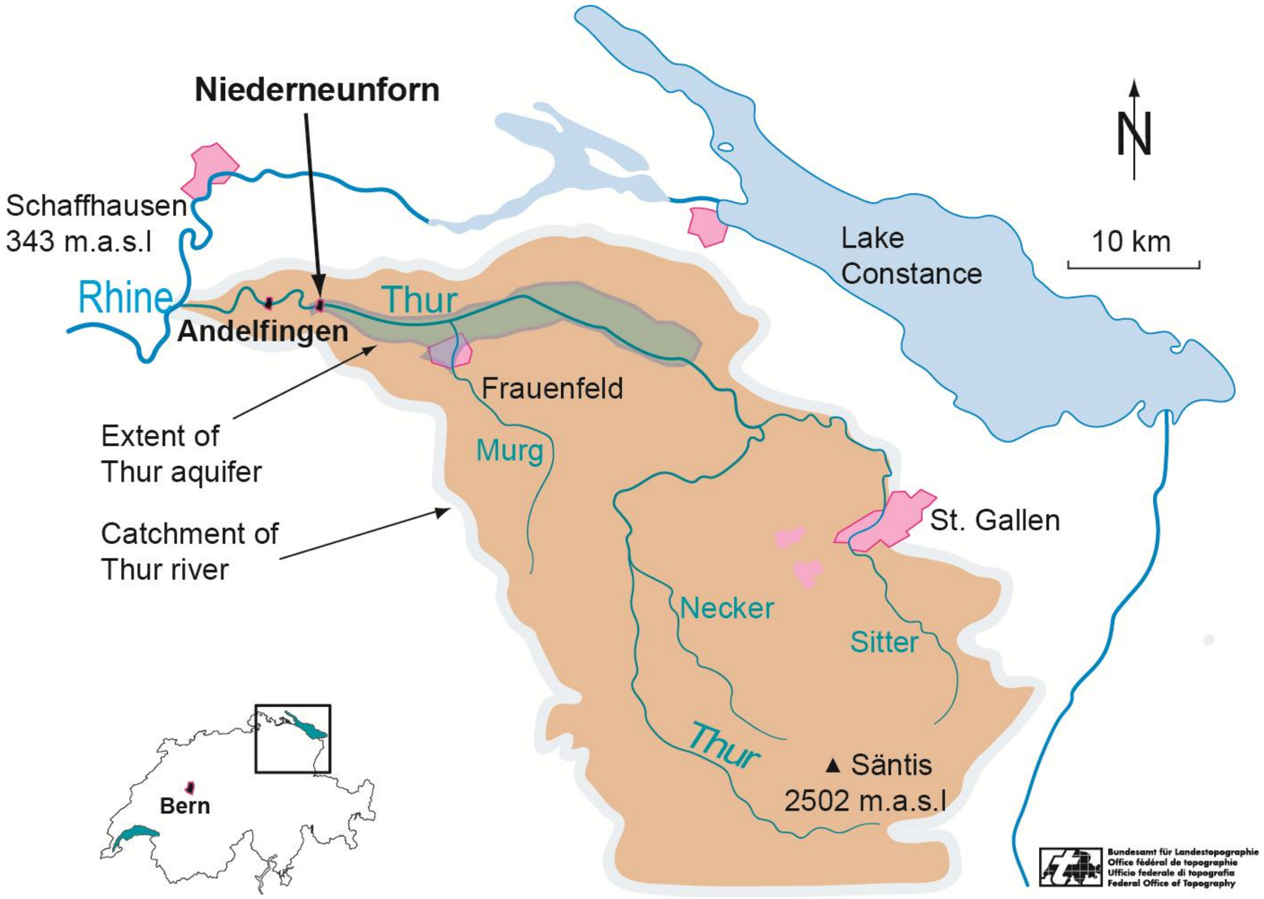

Figure 1 The Thur catchment in northeastern Switzerland with the three main tributaries – the Murg River, the Necker River and the Sitter River. The extent of the alluvial aquifer and the restored section at the lower reach at Niederneunforn and the FOEN monitoring Station at the outlet of the catchment at Andelfingen are indicated. **Copyright:** Swiss Federal Office of Topography.

In the 1890's the meandering Thur River was straightened and confined to a narrow channel (45 m wide) bordered by 50-150 m wide overbanks defined by a levee as a flood-protection measure (Vogt et al., 2010). After a series of large floods between 1960 and 1980, there was a consensus that the flood protection measures were inadequete (Vogt et al., 2010). As part of a river restoration initiative, the river reach at Niederneunforn (Figure 1) was restored between 2002 and 2003 to mimic pre-channelization conditions, which resulted in a riverbed width of 50-100 m (Vogt et al., 2010). The river has maintained naturally meandering channels between Niederneunforn and Andelfingen (Hayashi et al., 2012; Schneider et al., 2011). The restoration activities included channel bed remodelling, lowering and restructing the river banks to improve flow connectivity, habitat provision by introducing deadwood and root stools, aiding the creation of natural gravel bars and in-stream islands through re-introduction of eroded materials thereby promoting new habitat development in these parts (Kurth and Schirmer, 2014).

3.3 Methods

Three 24-hour field sampling campaigns (SCs) were conducted at the Thur River: in winter (SC1 on 28.02.2012-29.02.2012), in summer (SC2 on 07.08.2012-08.08.2012), and in autumn (SC3 on 08.10.2013-09.10.2013), when the average daily discharges recorded at Station E (Figure 2) were 50.4, 43 and 20.7 m^3/s, respectively (FOEN, 2012, 2013). The sampling locations were at two upstream stations, namely A-Pfyn (47°35'20.4"N 8°56'51.7"E) and B-Uesslingen (47°34'43"N 8°50'03"E), while the monitored restored river corridor (2 km long) is located at Station C-Niederneunforn (47°35'19.0"N 8°46'57.4"E), and two stations were selected further downstream of the restored corridor, D-Guetighausen (47°35'22.6"N 8°44'09.6"E) and E-Andelfingen (47°35'44.1"N 8°39'06.6"E) (Figure 2). The Murg River has an average yearly (2012) mean discharge of 4.5 m^3/s (FOEN, 2012) and joins the Thur between stations A and B (Figure 2). No tributary drains into the Thur River between the Murg confluence and the catchment outlet, except for a few first-order streams and side channels. The lower reach is interspersed with six waste-water treatment plants (WWTPs) of which the Frauenfeld WWTP is the largest (average outflow = 17,262 m^3/day (in 2012)), discharging into the Murg River, which then joins the Thur River (Figure 2). The 24-hour sampling campaigns were conducted at all five stations in summer (SC2) and winter (SC1). In autumn (SC3), monitoring was restricted to stations B, C and D to limit the detailed study (together with nitrate isotopes) to a shorter stretch.

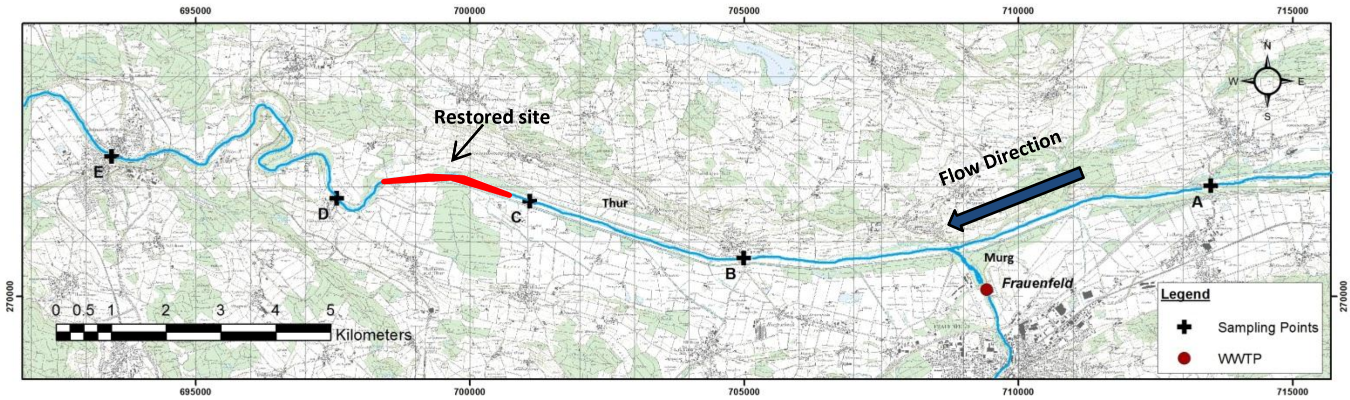

Figure 2 Lower reach of the Thur River showing the locations of the study stations from upstream to downstream: A-Pfyn, B-Uesslingen, C-Niederneunforn, D-Guetighausen and E-Andelfingen. The location of the largest waste-water treatment plant (WWTP) releasing treated effluent into the Murg (WWTP Frauenfeld) is also indicated.

High frequency monitoring of EC, temperature, pH, pressure and DO (in 15 minute intervals) was carried out using *in-situ* loggers. Samples for measurement of nitrate, DOC and the isotopes of water (δD and $\delta^{18}O\text{-}H_2O$) and nitrate ($\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$) were collected using auto samplers (24-hour sampling). Additionally, a 1D hydraulic model using HEC-RAS was developed to compute the velocity of the river at average base flow (28 m^3/s) and during a summer storm event in order to compute the travel times between the stations and to calculate the discharge at each sampling station. Detailed explanations of the field installation, the analytical methods for sample analysis and the HEC-RAS model set-up can be found in the supplementary information. The interrelationship among mutually linked parameters are expressed using the Pearson correlation coefficient ‘r’ by applying a two-tailed Pearson correlation test at a 5% significance level. The variation is described with the standard deviation (σ). Hypothesis testing was carried out by a paired student t-test.

3.4 Results and Discussion

3.4.1 Diurnal changes to the water quality parameters during the sampling campaigns in winter (SC1), summer (SC2) and autumn (SC3)

3.4.1.1 Electrical conductivity (EC)

EC is often used as a measure of solute concentration in rivers. Diurnal changes of EC have been observed in a large number of low-order rivers and streams, for example, by Iwanyshyn et al. (2008) and Nimick et al. (2005). The diurnal changes of EC in some cases have been attributed to the changes in solute composition of rivers due to discharge from waste-water treatment plants (Iwanyshyn et al., 2008; Ort and Siegrist, 2009).

Winter (SC1): The mean EC in the winter campaign varied between 0.5 to 0.57 mS/cm at the different stations, with the lowest mean EC observed at Station A and the highest at Station B (Table 1, Figure 3). The highest EC at Station B is likely a result of the nutrient-rich tributary Murg (which has the large WWTP in its lower part) that joins the Thur River between Stations A and B (Figure 2).

Summer (SC2): The mean EC in the summer campaign varied between 0.38 and 0.43 mS/cm among the stations, with the lowest observed at Station A and the highest at Station E (Table 1, Figure 3). This high value of EC, at the catchment outlet, is attributed to the solute-rich catchment runoff accumulating at the outlet of the catchment during a summer storm event, it is discussed in detail in Section 4.2.2.

Autumn (SC3): The mean EC in the autumn campaign was nearly the same at all stations (0.44 mS/cm at Station C and 0.45 mS/cm at stations B and D) (Table 1, Figure 3).

The EC showed very little (σ<0.1) 24-hour variation in each season (in SC1, SC2 and SC3). Nevertheless, a small diurnal trend was observed at all stations, in all seasons, where the maximum value was noted in the pre-dawn and the lowest was observed in the afternoon. In an earlier study by Hayashi et. al. (2012), a larger (1 mS/cm) increase from day to night was observed during extreme low-flow conditions (average Q=12.1 m^3/s) in summer (September 2010) in the Thur River. This was attributed to the precipitation of calcite by periphytons during the day (reducing the EC). In this study with a seasonal comparison of EC, we can confirm that river discharge has a major effect on the biological processes controlling EC. The influence of runoff during higher flow (for example during a storm event) can override the diurnal effect due to instream calcite precipitation. In both summer (SC2) and autumn (SC3), the EC was found to have a significant positive correlation with nitrate (Table 2).

3.4.1.2 Dissolved oxygen (DO)

Diurnal oscillations of DO were observed at all stations in all seasons (SC1, SC2 and SC3). The temperature-dependent solubility of oxygen indicates that DO should be higher at night when the temperature is lower and vice-versa. Nevertheless, in many rivers, photosynthesis (driven by solar energy) and respiration play a major role in reversing this trend (Loperfido et al., 2009).

Photosynthesis Eq.(1) and respiration Eq.(2) each undergo diurnal cycles in rivers. In the daytime, an increase in sunlight (higher photon energy) contributes to increased photosynthesis, while at night there is increased respiration in the absence of photosynthesis (Forget et al., 2009), according to the following equations:

$$6CO_2 + 6H_2O + h\nu \text{ (photons)} \rightarrow C_6H_{12}O_6 + 6O_2 \quad (1)$$

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \quad (2)$$

Winter (SC1): The mean DO concentration at all five stations in the winter campaign varied between 12.6 and 13.2 mg/l. The lowest mean (winter) concentration of DO was observed at Station E and the highest at Station A (Table 1, Figure 3). The variation of DO over one full day was lowest at Station A (diurnal variation of 1 mg/l, σ=0.28) and highest at Station B (diurnal change of 2.3 mg/l, σ=0.81). The diurnal trend of daytime maximum and nighttime minimum was observed for DO in response to the diurnal solar cycle. The peak arrival time was observed at various times in the afternoon (1 pm-4:20 pm), while the minimum winter DO concentration was observed in the pre-dawn (2:30 am-5:00 am) at the different stations (Table 1, Figure 3).

Summer (SC2): The mean DO in the summer campaign varied between 8.3 and 10 mg/l at all stations, decreasing downstream with increasing temperature (mean temperature upstream (Station A) – downstream (Station E) 17.9-18.8 °C) (Table 1, Figure 3). A diurnal trend of DO was observed in summer, where minimum concentrations were observed in the pre-dawn (3:45-6:00 am) at all five stations, and maximum concentrations were observed during the afternoon (11:35 am-6:00 pm), varying at each station with the peak arrival time shifting gradually downstream. The lowest variation of DO in summer, was observed at Station A, (diurnal variation of 0.7 mg/l, σ=0.23). The highest variation of DO was observed at Station C (diurnal change of 2.7 mg/l, σ=0.82) (Table 1, Figure 3).

Autumn (SC3): In the autumn campaign (SC3), the comparison was made only between stations B and D, both of which were saturated with DO (102 %) with mean concentrations of 10.4 mg/l and 10.3 mg/l, respectively. Comparing these two stations, the highest daily variation was observed at Station D (diurnal change of 2.6 mg/l, σ=0.96) (Table 1, Figure 3).

Thus we find that the seasonal change in mean DO concentration is affected by the mean temperature change, with the highest mean DO concentration observed in winter and the lowest in summer. This is also observed with increasing mean temperature and decreasing mean DO in the downstream direction in summer (Table 1, Figure 3). However, within a single day, photosysnthesis plays a dominant role overriding the temperature dependent-solubility of DO, resulting in higher DO concentrations during the daytime at all stations and over all seasons.

3.4.1.3 pH

Diurnal temperature cycles can also cause small diurnal changes in pH in the river. For instance at neutral pH, the solubilities of calcite and dissolved CO_2 increase with decreasing temperature, thereby producing a higher pH at lower temperature (Bäckström et al., 2002).

The concentration of dissolved CO_2 in the river also controls the pH change in the river. Addition of dissolved CO_2 in the river, which is mainly caused by respiration (Eq.2), will decrease the pH, driven by the following reaction (Eq.3)

$$CO_2\,(g) + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^- \qquad (3)$$

Conversely, the removal of dissolved CO_2 from the river caused by photosynthesis (Eq.1) will increase the pH. Thus, this equilibrium is shifted from day to night depending on which process is more dominant (Eq.3) (Nimick et al., 2011; Wright and Mills, 1967),

The variation of mean pH among the stations was very low (<1 pH unit) varying between 8.3-8.6 among the different stations during winter (SC1) and between 8.3 and 8.5 during the summer campaign (SC2) (Table 1). The diurnal trend of pH was similar to that of DO at all stations in all seasons the minimum was observed in the early mornings and the maximum was observed in the late afternoons. This indicates that the biological processes that control the diurnal DO cycle also affect pH in the river.

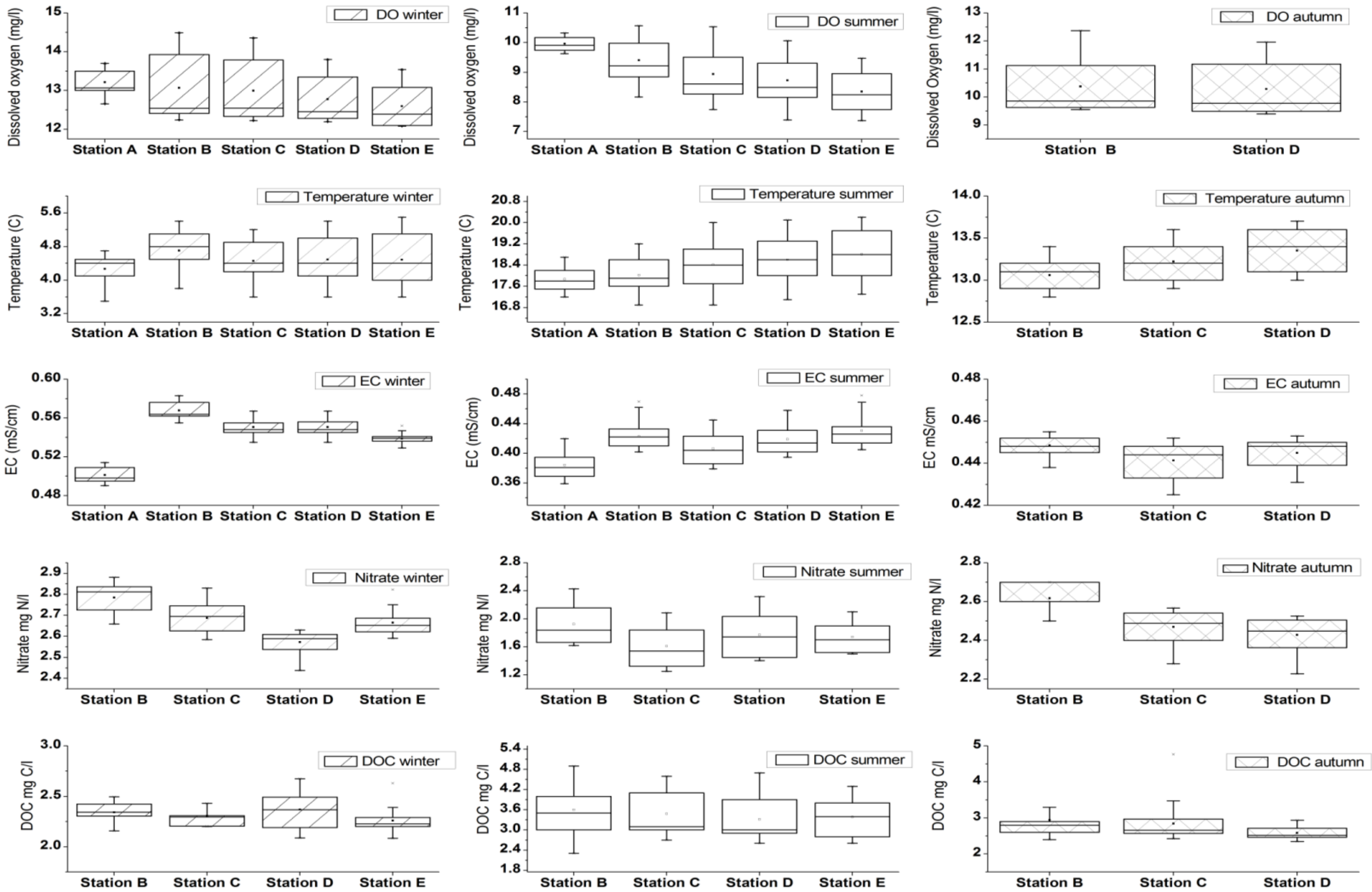

Figure 3 Boxplots of water quality parameters of temperature (°C), dissolved oxygen (DO, mg/l), EC (mS/cm), nitrate (mg N/l) and DOC (mg C/l) at the various sampling stations (A-E) in SC1, SC2 and SC3. The mean is indicated by the shaded square. The tail that extends in both directions indicates the total variation. The range of the box represents the 25^{th} and 75^{th} percentiles.

3.4.1.4 Dissolved organic carbon (DOC)

Dissolved organic matter (DOM) can be measured as the DOC and is found to vary daily and seasonally. The diurnal cycles of DOC noted in several studies indicate a daytime increase (particularly in the afternoons) and a nighttime (and pre-dawn) decrease with some reporting an increase of about 100% (Kaplan and Bott, 1982; Manny and Wetzel, 1973; Nimick et al., 2011). Photosynthesis by autotrophs (Eq.1) results in an increase in photosynthates like carbohydrates (byproducts of photosynthesis) (Parker et al., 2010; Westhorpe and Mitrovic, 2012) and labile DOC by the phototransformation of recalcitrant DOC into more available forms (Bushaw et al., 1996; Lindell et al., 1996; Westhorpe and Mitrovic, 2012). On the contrary, the consumption by heterotrophs like bacteria, is expected to be higher in the nighttime in the absence of photosynthesis, which causes the DOC to decrease overnight (Bertilsson and Jones, 2003; Kuserk et al., 1984; Nimick et al., 2011). Another hypothesis is that when bacteria are exposed to sunlight, their metabolism can decrease during the day (Lindell et al., 1996; Westhorpe and Mitrovic, 2012). Thus the biological processes that control the diurnal cycles of DOC are dependent on various factors including the type of microbial consortia at the site, the lability of organic molecules, and temperature (Nimick et al., 2011; Volk et al., 1997).

Summer (SC2) and Winter (SC1): In the winter campaign (SC1), the mean DOC (2.3 mg C/l) was uniform at all stations, while the mean DOC was higher in summer (SC2), varying between (3.3-3.6 mg C/l) (Figure 3, Table 1). The pattern of diurnal variation of DOC was found to be similar in both seasons with lower values during the day and higher at night, and was found to be significantly inversely correlated to the DO in both seasons (Table 2).

Autumn (SC3): No pronounced diurnal cycle of DOC was observed at Station B or at Station C, although there was a wide variation of DOC at both stations varying between 2.4 and 3.3 mg C/l and between 2.4 and 4.7 mg C/l, respectively (Table 1, Figure 3). Nevertheless, at Station D a small diurnal DOC cycle was observed with an afternoon maximum of 2.94 mg C/l (at 2 pm) with a nighttime decrease reaching a minimum of 2.43 mg C/l during the pre-dawn (at 3 am) (Table 1, Figures 3,4). Further, DOC was also found to be significantly positively correlated to the DO ($r=0.75$, $p<0.05$) at Station D (Table 2). Thus it has been noted that during low-flow in autumn (SC3), the diurnal DOC cycle was found to be influenced by photosynthesis as observed in other studies described above. However, this photosynthetic effect on DOC is only observed at a short distance - downstream of the restored site, at station D.

Table 1 Descriptive statistics (mean ± σ; (min-max); [$Time_{min}$ – $Time_{peak}$], n=number of samples analyzed) of the various water quality parameters from all sampling sites during the winter SC1, summer SC2 and autumn SC3 sampling campaigns.

	Station A		Station B			Station C			Station D			Station E	
Parameters	**Summer (SC2)**	**Winter (SC1)**	**Summer (SC2)**	**Winter (SC1)**	**Autumn (SC3)**	**Summer (SC2)**	**Winter (SC1)**	**Autumn (SC3)**	**Summer (SC2)**	**Winter (SC1)**	**Autumn (SC3)**	**Summer (SC2)**	**Winter (SC1)**
DO (mg/l) n=93	10 ± 0.23 (9.6 - 10.3) [3:45 am- 11:35 am]	13.2 ± 0.28 (12.7 - 13.7) [2:50 am- 1:00 pm]	9.4 ± 0.67 (8.2 - 10.6) [6:00 am – 2:30 pm]	13.2 ± 0.81 (12.2 – 14.5) [2:30 am – 1:30 pm]	10.4 ±0.9 (9.6 -12.4) [11:00 pm- 3:00 pm]	8.9 ± 0.82 (7.8 - 10.5) [6:00 am- 2:45 pm]	13 ± 0.78 (12.2 – 14.4) [3:20 am- 2:00 pm]	----------	8.7 ± 0.74 (7.4 - 10.1) [6:00 am- 4:45 pm]	13 ± 0.58 (12.2 ± 13.8) [5:00 am- 2:20 pm]	10.3 ± 0.96 (9.4 -12.0) [12:00 am- 4:00 pm]	8.3 ± 0.64 (7.4 – 9.5) [6:00 am- 6:00 pm]	12.6 ± 0.54 (12.1-13.5) [4:30 am- 4:20 pm]
DO (%)	108 (103 - 112)	103 (100 - 109)	103 (89 - 118)	104 (97 - 118)	102 (93 - 122)	98 (84 -119)	102 (94 -116)	----------	96 (81 -114)	101 (94 -113)	102 (90 -123)	94 (82 -110)	100 (94 -110)
EC (mS/cm) n =93	0.38 ± 0.02 (0.36 - 0.38)	0.5 ± 0.01 (0.49 - 0.51)	0.42 ± 0.02 (0.4 - 0.47)	0.57 ± 0.01 (0.56 - 0.58)	0.45 ± 0.05 (0.44 - 0.46)	0.4 ± 0.02 (0.38 - 0.45)	0.55 ± 0.01 (0.54 - 0.57)	0.44 ±0.08 (0.42 - 0.45)	0.42 ± 0.02 (0.4 - 0.46)	0.55 ± 0.01 (0.54 - 0.57)	0.45 ± 0.007 (0.43 - 0.45)	0.43 ± 0.02 (0.41 - 0.48)	0.54 ± 0.004 (0.53 - 0.55)
Temp.(^{0}C) n=93	17.9 ± 0.43 (17.2 - 18.7)	4.3 ± 0.36 (3.5 - 4.7)	18 ± 0.7 (17 - 19.2)	4.7 ± 0.5 (3.8 - 5.4)	13 ± 0.2 (12.8 -13.4)	18.4 ± 0.9 (16.9 - 20)	4.5 ± 0.5 (3.6 - 5.2)	13.2 ± 0.24 (12.9 -13.6)	18.6 ± 0.9 (17 – 20)	4.5 ± 0.6 (3.6 - 5.4)	13.4 ± 0.24 (12 - 13.7)	18.8 ± 0.9 (17.3 – 20.2)	4.5 ± 0.64 (3.6 - 5.5)
pH n=93	8.4 ± 0.06 (8.3 - 8.5)	8.5 ± 0.04 (8.5 - 8.6)	8.3 ± 0.06 (8.2 - 8.4)	8.6 ± 0.07 (8.5 - 8.7)	8.3 ± 0.05 (8.1 - 8.3)	8.5 ± 0.1 (8.2 - 8.5)	8.5 ± 0.07 (8.4 - 8.6)	8.3 ± 0.04 (8.2 - 8.4)	8.5 ± 0.1 (8.3 - 8.8)	-----------	8.3 ± 0.04 (8.2 - 8.4)	8.4 ± 0.1 (8.2 - 8.6)	8.3 ± 0.01 (8.2 - 8.4)
NO_3-N (mg N/l) n=24	-----------	-----------	1.9 ± 0.28 (1.6-2.4)	2.8 ± 0.07 (2.7-2.9)	2.6 ± 0.07 (2.5-2.7)	1.6 ± 0.28 (1.3 – 2.1)	2.7 ± 0.07 (2.6- 2.8)	2.5 ± 0.09 (2.3-2.6)	1.8 ± 0.3 (1.4-2.3)	2.7 ± 0.07 (2.4 -2.6)	2.4 ± 0.09 (2.2-2.5)	1.7 ± 0.2 (1.5-2.1)	2.7 ± 0.06 (2.6 – 2.8)
DOC (mg C/l) n=24	-----------	-----------	3.6 ± 0.73 (2.3- 4.9)	2.3 ± 0.1 (2.1-2.5)	2.8 ± 0.21 (2.4 -3.3)	3.5 ± 0.64 (2.7- 4.6)	2.3 ± 0.1 (2.1-2.4)	2.84 ± 0.5 (2.4 - 4.7)	3.3 ± 0.6 (2.6 - 4.7)	2.3 ± 0.2 (2.1-2.7)	2.6±0.16 (2.4 -2.9)	3.4 ± 0.6 (2.6 - 4.3)	2.2 ± 0.1 (2.0 -2.6)
δD ‰ n=12	-----------	-----------	-61.3 ± 1.0 (-63 – -59)	-----------	-----------	-60.9 ± 1.1 (-62 - -58)	-----------	-------------	-60.9 ± 0.9 (-63 - -59)	-----------	-----------	-61.7 ± 0.9 (-63 - -60)	-----------
$\delta^{18}O$ (H_2O) ‰ n=12	-----------	-----------	-8.8 ± 0.08 (-8.9 - -8.6)	-----------	-----------	-8.8 ± 0.1 (-8.9 - -8.6)	-----------	-------------	-8.7 ± 0.1 (-8.8 – -8.5)	-----------	-----------	-8.9 ± 0.1 (-9.1 - -8.8)	-----------
$\delta^{18}O$ (NO_3^-) ‰ n=12	-----------	-----------	-----------	-----------	3.5 ± 2.2 (0 - 7.5)	-----------	-----------	3 ± 2.14 (0.6 - 7.7)	-----------	-----------	2.4 ± 0.4 (1.1 - 4.3)	-----------	-----------
$\delta^{15}N$ (NO_3^-) ‰ n=12	-----------	-----------	-----------	-----------	12.7 ± 1.1 (10.6 - 14.7)	-----------	-----------	12.9 ± 1.2 (11.9 -15.3)	-----------	-----------	12.6 ± 0.4 (11.9 - 13)	-----------	-----------

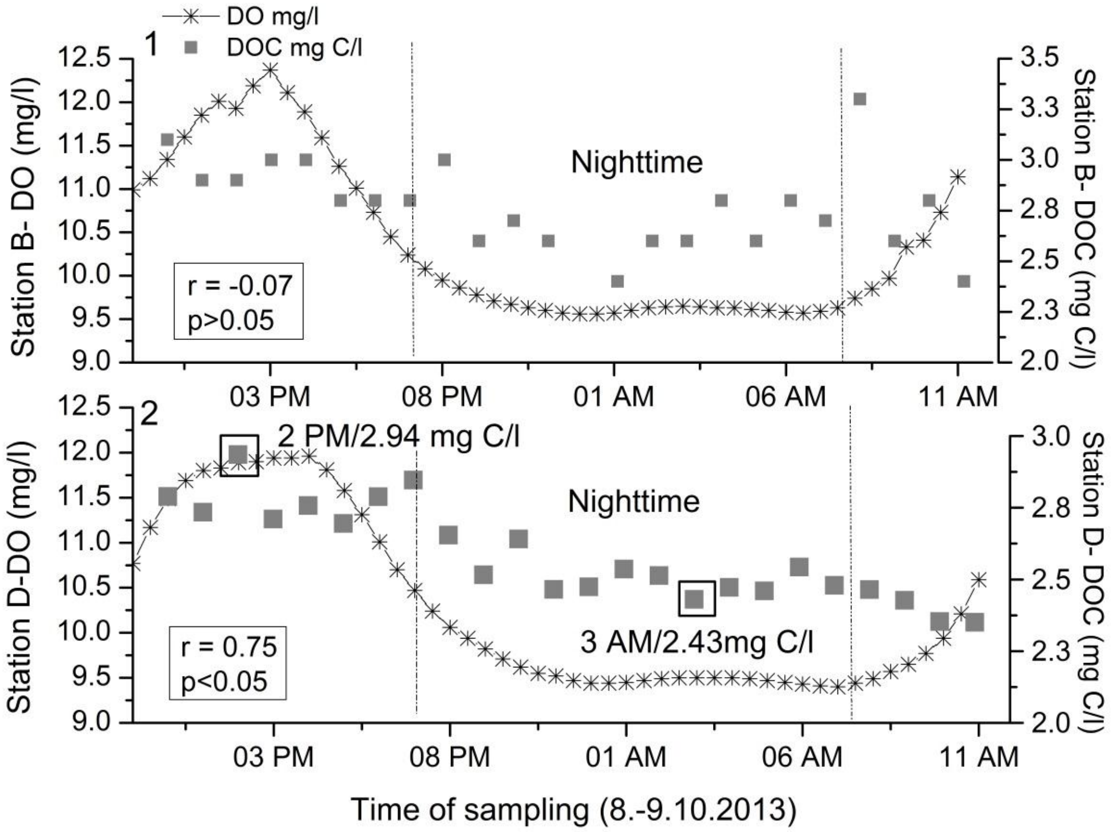

Figure 4 Comparison of the diurnal concentrations of DO (±0.1 mg/l) and DOC (±0.2 mg C/l) at Stations B and D during the autumn sampling campaign (SC3).

Table 2 The inter-relationship between the various parameters, shown using the Pearson correlation coefficient ‘r’ at a 95% confidence interval (reflects a significance level of 0.05, p-value is checked to be < > 0.05 to demostrate the significance) using a two-tail Pearson correlation test. Negative ‘r’ indicates a negative correlation between the two parameters.

Parameters compared	**Station B** r ; p < >0.05			**Station C** r ; p < >0.05			**Station D** r ; p < >0.05			**Station E** r ; p < >0.05	
	Summer (SC2)	**Winter (SC1)**	**Autumn (SC3)**	**Summer (SC2)**	**Winter (SC1)**	**Autumn (SC3)**	**Summer (SC2)**	**Winter (SC1)**	**Autumn (SC3)**	**Summer (SC2)**	**Winter (SC1)**
DOC-DO	-0.62; p<0.05	-0.67; p<0.05	-0.07; p>0.05	-0.54; p<0.05	0.14; p>0.05	-----------	-0.43; p<0.05	-0.56; p<0.05	0.75; p<0.05	-0.84; p<0.05	-0.52; p<0.05
EC - NO_3N	0.94; p<0.05	-0.15; p>0.05	0.91; p<0.05	0.98; p<0.05	0.07; p>0.05	0.95; p<0.05	0.98; p<0.05	0.33; p>0.05	0.96; p<0.05	0.18 p>0.05	0.24 p>0.05
DO – Temp.	0.82; p<0.05	0.61; p<0.05	0.73; p<0.05	0.90; p<0.05	0.56; p<0.05	-----------	0.91; p<0.05	0.38; p<0.05	0.76; p<0.05	0.92; p<0.05	0.54; p<0.05
NO_3N – Q	0.67; p<0.05	-----------	-----------	0.45; p<0.05	-----------	-----------	0.37; p>0.05	-------	---------	0.66; p<0.05	-------
DOC – Q	-0.59; p<0.05	-----------	-----------	-0.57; p<0.05	-----------	-----------	-0.54; p<0.05	-------	--------	-0.5; p<0.05	-------

3.4.1.5 Nitrate

Many documented studies of diurnal nitrate cycles indicate that a minimum concentration is usually observed in the late afternoons, which is attributed to the assimilation of nitrate by the primary producers in the presence of sunlight. In contrast, highest concentrations are observed in the early mornings due to treated waste-water input to the river (Gammons et al., 2011; Heffernan and Cohen, 2010; Nimick et al., 2011). In this study, diurnal variability of nitrate at all stations was very low in the winter (SC1) and autumn (SC3) sampling campaigns ($\sigma<0.1$) (Table 1, Figure 3). The short-term variability of nitrate in summer (SC2) is discussed with respect to the storm event in Section 4.2.5.

Although there was not much variability of nitrate in autumn (SC3), a diurnal cycle was still observed at Stations C and D, varying from a daytime minimum (at about 1:00 pm) to a nighttime maximum (midnight peak at 12:00 am). A 0.3 mg N/l increase at Station C (2.3 to 2.6 mg N/l) and Station D (2.2 to 2.5 mg N/l) (Table 1, Figure S1), was attributed to nitrification during the day, following continuous input of nitrate and ammonia. In the pre-dawn, nitrate concentrations decreased (observed by a small decrease in concentration <0.3 mg N/l) from midnight onwards, reaching a minimum at 5 am at Station C and 7 am at Station D (Figure S1).

To understand the processes that affect this diurnal change, the stable isotopes of nitrate, $\delta^{18}O$- NO_3 and $\delta^{15}N$-NO_3, were measured in autumn (SC3). No distinct diurnal variation in either of the isotopes was observed at Stations B and C (Figure 5a). A diurnal variation of both isotopes of nitrate was observed at Station D, which were enriched during the night, attaining a peak at midnight corresponding to the nitrate concentration peak (12:00 am). The isotopes then decreased progressively from midnight, reaching a minimum at mid-morning (10 am). However, this variation is quite small and is only about 1.1 ‰ for $\delta^{15}N$-NO_3 (varying from 13-11.9 ‰) and 3.2‰ for $\delta^{18}O$-NO_3 (varying from 4.3-1.1 ‰) (Figure 5a). This reduction in the concentration of nitrate and correspnding isotope fractionation from midnight to early morning is attributed to assimilation by the primary producers. Isotopic fractionation during assimilation of nitrate has been reported in many cases (Casciotti et al., 2002; Gammons et al., 2005; Granger et al., 2004).

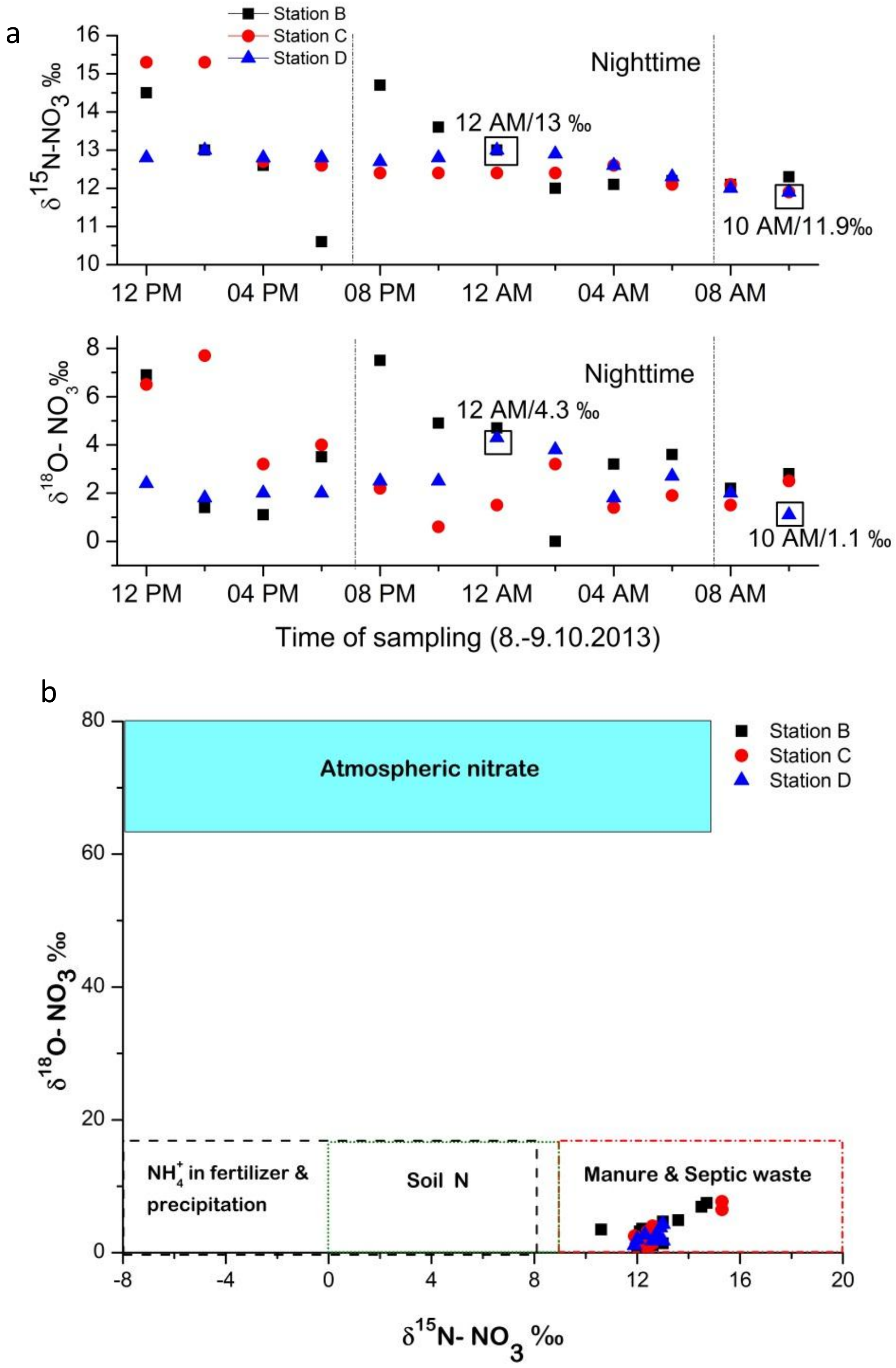

Figure 5 a. The diurnal variation of the nitrate isotopes - δ^{15}N-NO_3‰ (± 0.2 ‰) and δ^{18}O-NO_3‰ (±0.5 ‰) during the autumn campaign (SC3) at Stations B,C,D. Open boxes highlight the diurnal maximum and minimum percentiles at Station D. **b.** The dual-isotope model of these nitrate isotopes (modified after Kendall (2007)).

Determination of sources of nitrate: To understand the sources of nitrate, the dual-isotope model of nitrate was applied in Figure 5b, modified after Kendall (2007). The $\delta^{15}N\text{-}NO_3^-$ of synthetic/inorganic fertilizers (usually ammonia fertilizers) varies between −8 and +7‰ (Kendall, 2007; Hübner 1986; Macko and Ostrom 1994; Vitoria et al., 2004). The range of the $\delta^{15}N\text{-}NO_3^-$ 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; Singleton et al., 2007; Spoelstra et al., 2007; Xue et al., 2009). The nitrate-nitrogen derived from manure or sewage is isotopically distinct and is usually characterized by high $\delta^{15}N\text{-}NO_3^-$ which is +9‰ to more than +20‰ (Choi et al., 2007; Heaton, 1986; Widory et al., 2004; Xue et al., 2009). Nitrate derived from nitrification of ammonium fertilizers and ammonia from precipitation has lower $\delta^{18}O$ values (in the range of −5 to +15‰) when compared to those of direct nitrate input from precipitation (+63‰ to +94‰) and from chemical nitrate fertilizers (+17‰ to 25‰) (Amberger and Schmidt, 1987; Elliott et al., 2007). Thus the major nitrate source is derived from treated waste-water and manure (diffused input) during low flow in autumn in the lower stretch of the Thur River (Figure 5b).

3.4.2 Impact of the summer storm event on the water quality parameters

During the summer sampling campaign (SC2 on 07.- 08.08.2012), the discharge (Q) increased from 16 – 60 m^3/s (average Q=43 m^3/s) within a couple of hours (Figure 6) as recorded at Station E (FOEN, 2012). This event provided an excellent opportunity to study associated changes in water isotopes and in different water quality parameters, as discussed below.

3.4.2.1 Characterization of the summer storm event using water isotopes (δD and $\delta^{18}O\text{-}H_2O$)

The isotopes of water (δD and $\delta^{18}O\text{-}H_2O$) are expected to have a lighter isotopic signature during high flow events which are strongly influenced by precipitation, especially in mountainous catchments (Yurtsever, 1995, Lambs et al., 2003). In this study, the mean $\delta^{18}O\text{-}H_2O$ and δD varied between -8.9 and -8.7‰ and between -61.7 and -60.9‰, respectively, at all the sampling stations in the summer campaign (SC2) (Table 1). The $\delta^{18}O\text{-}H_2O$ signature becomes lighter as the discharge increases, reaching a minimum following the discharge peak. This reflects a delay in the dominance of precipitation in overriding the background (heavier) groundwater signature in the river. This is followed by an enrichment of the isotopic signature after the discharge peak recedes (Figure S2).

3.4.2.2 Impact on electrical conductivity (EC)

The impact of the storm event is evident from dip in the EC signal, which starts with an increase in the discharge, and was attributed to dilution in the river during high flow (Table S2). The maximum EC dilution (EC_{dip}) was observed following the maximum flow peak (Q_{peak}). Observed data from each station showed that the EC_{dip} and the Q_{peak} propagated downstream over time. Furthermore, a delay between the Q_{peak} and the EC_{dip} was found to increase downstream (Table S2). Similar delays between the flood hydrograph and calcium chemograph have been studied in detail by Glover and Johnson (1974) in the South Tyne river in the U.K. They reported that the delay was caused by a flood wave velocity which is faster than the mean water velocity, at which the solutes and sediments in the river travel in the absence of dispersion. The authors also showed that the peak flood velocity plays a vital role in the lag time, and the bigger the flood event, the shorter the lag time. As shown in Table S2, the peak flood velocity calculated by the traveltime of the peak discharge is higher than the mean water velocity at an average discharge (of 28 m^3/s – base flow conditions) calculated using the HEC-RAS 1D hydraulic model. An increase in the EC occurs after the maximum dilution of EC (EC_{dip}), similar to the pattern of the enrichment of the water isotopes following its maximum decrease (Figure S2). This is attributed to the propagation of the storm event water downstream as the system retains its equilibrium.

3.4.2.3 Impact on dissolved oxygen (DO)

Increased loads of suspended solids tend to attenuate the diurnal cycles (Loperfido et al., 2009). The higher turbidity levels in rivers accentuated by storm events are likely to reduce the concentrations of DO by shading the water column and inhibiting photosynthesis, and can also increase the oxygen demand through disturbance of benthic mud and detritus (Colangelo and Jones, 2005; Furse et.al, 1996; Toth et.al., 1990; Toth, 1993).

During the storm event of the summer campaign SC2, only limited variability of DO was observed within 24 hours at Stations B (σ=0.67) and E (σ=0.64) (Table 1, Figure 3). Stations C (σ=0.82) and D (σ=0.74) have higher daily variability (higher DO concentrations in the daytime and lower at night) as clearly demonstrated in Figure 3. Additionally, when the paired t-test was applied to compare the average hourly oxygen concentration change, the stretch CD (that includes the 2 km restored corridor) (n=15, mean=0.29, σ=0.096) had a statistically significant (t-test, $t(14)= -4.9$, $p<0.05$) higher hourly oxygen change, when compared to the upstream reference stretch AB (n=15, mean=0.15, σ=0.11) at a 95% confidence interval. This higher diurnal variability of DO in the restored stretch is indicative of clear streams with lower turbidity that allows ample light penetration which then sustains photosynthesis and production of DO during the day and active consumption by heterotrophic organisms in both daytime and nighttime periods. This indicates that the storm event's effect in nullifying the biological processes and overriding the dirunal oxygen variability was not strong in the restored stretch of the Thur River.

3.4.2.4 Impact on dissolved organic carbon (DOC)

During the storm event in summer (SC2), the DOC was found to be significantly inversely correlated to the discharge (Q) ($r= -0.5$ to $r= -0.6$ and $p<0.05$) at all stations (Table 2, Figure 6). This decrease in DOC corresponding to the increase in Q is attributed to the dilution effect of the event. At Stations C and D, the DOC concentrations were lower (<3.5 mg C/l) at 6 am before the start of the storm event, decreased further following the rise of the discharge reaching minimum concentrations and increased again after the discharge recedes (Figure 6). At Stations B and E, however, a higher DOC concentration (>3.5 mg C/l) was observed at 6 am, which then reaches a minimum concentration in the late afternoon and increases again after the discharge recedes (Figure 6), thus indicating a higher pre-event DOC at these stations, indicative of waste-water releases or through diffuse inputs.

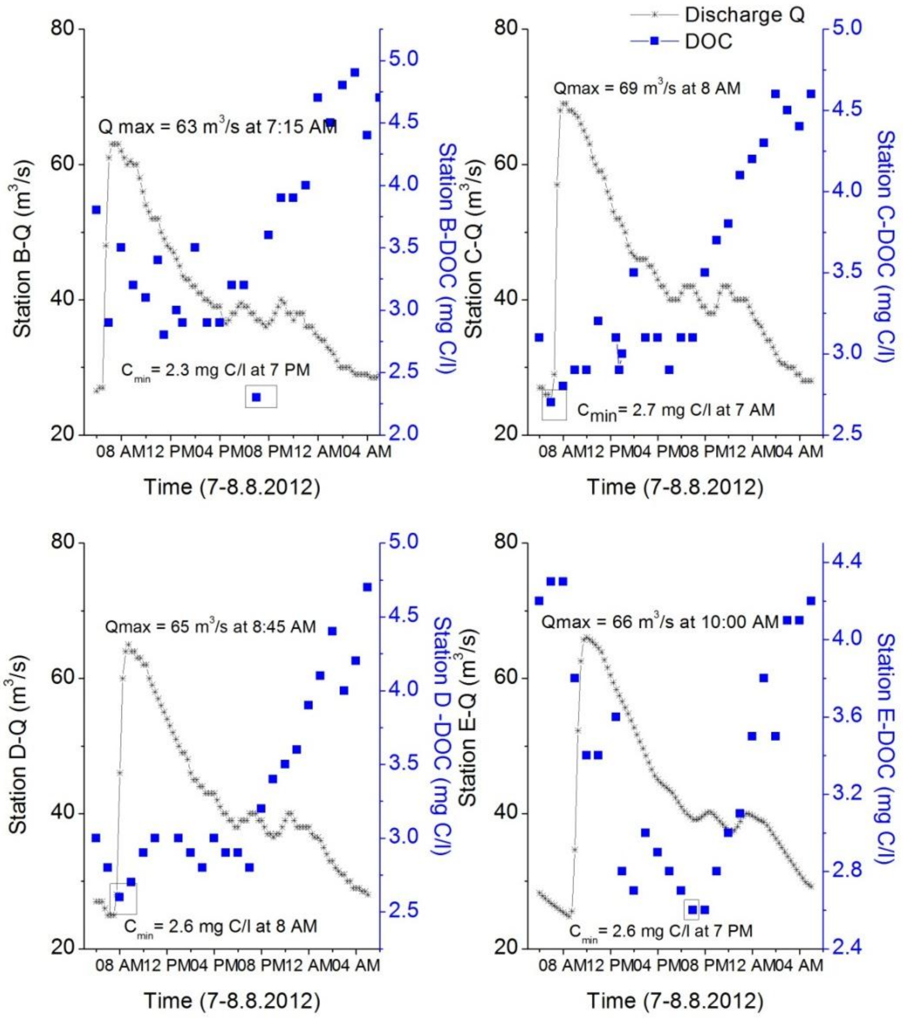

Figure 6 Relationship between discharge (Q) and DOC (mg C/l) at stations B, C, D, E during the summer sampling campaign (SC2) on 7.-8.08.2012. The minimum (C_{min}) concentrations of DOC are indicated in the boxes.

3.4.2.5 Impact on nitrate

The effect of the storm event in summer SC2 was instantaneously accompanied by the dilution of nitrate at Stations B, C and D (Figure 7). The variation of nitrate within 24 hours was highest at Station C (σ= 0.28) and D (σ=0.3) in summer (SC2) (Table 1, Figure 3). The high variation of nitrate during the storm event (as observed at stations C and D), is due to the reduction in the concentrations by dilution. However, at Station E, nitrate is significantly positively correlated to the discharge (r =0.66, $p<0.05$) (Table 2) indicating nitrate input by the flood waters here, causing a peak of 2.1 mg N/l during the afternoon (2-3 pm) (Figure 7). Filoso and Palmer (2011) attributed this trend to storage of nitrogen in lowland reaches during pre-event periods, followed by flushing from groundwater and bank seepage during high flows. This post-event accumulation is also observed with a conservative tracer like chloride, a concentration peak is observed following the discharge peak at the outlet of the catchment (Figure S3).

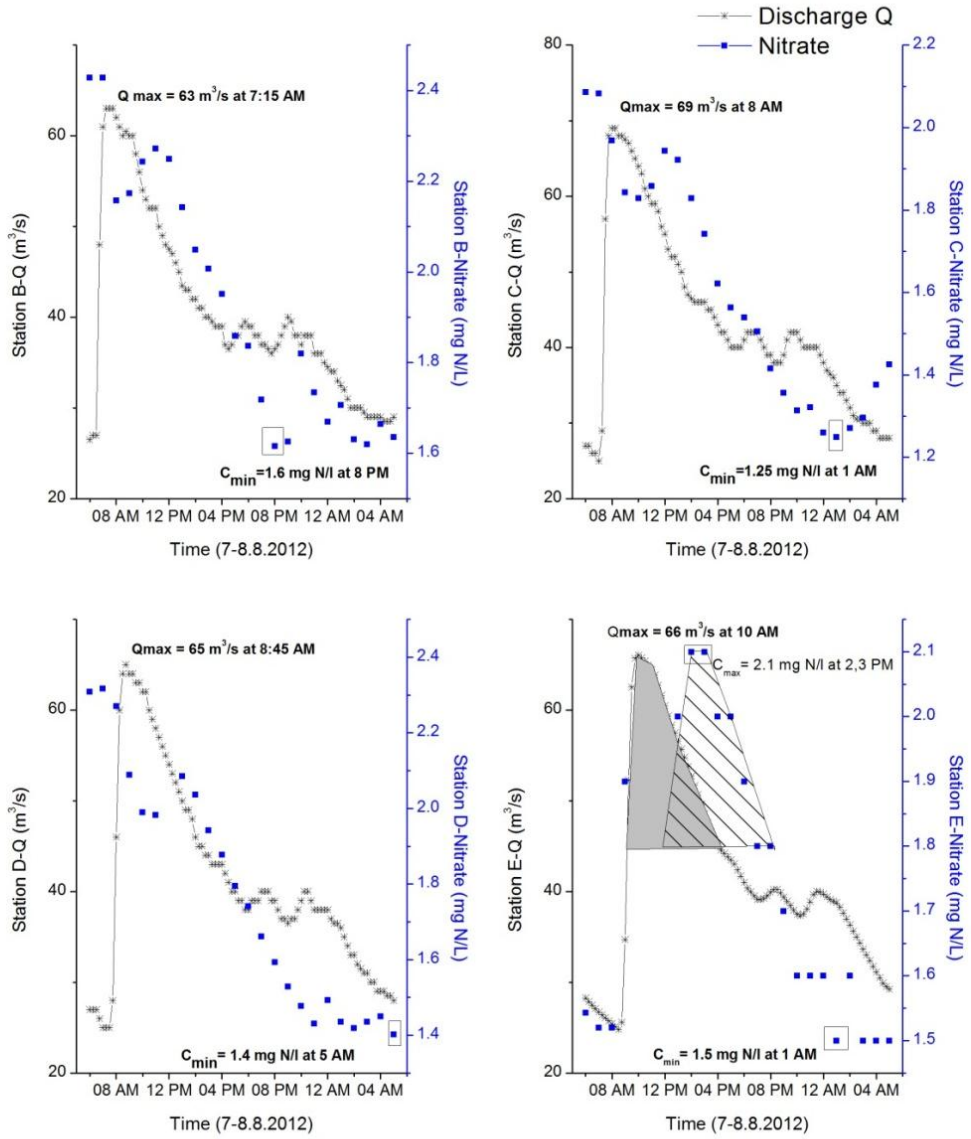

Figure 7 Relationship between discharge (Q) and and nitrate concentration during the summer sampling campaign (SC2) at stations B, C, D, E. The shaded portion shows the accumulation of nitrate at station E following the discharge peak. The minimum (C_{min}) concentrations are indicated in the boxes.

3.4.3 Effect of river restoration on stream ecosystem functioning

The stream ecosystem functioning model modified after Mulholland et al. (2009) and Sudduth et al. (2011) is illustrated here, to highlight the main expectations from river restoration on water quality amelioration at a river reach and catchment scale (Figure 8 a,b).

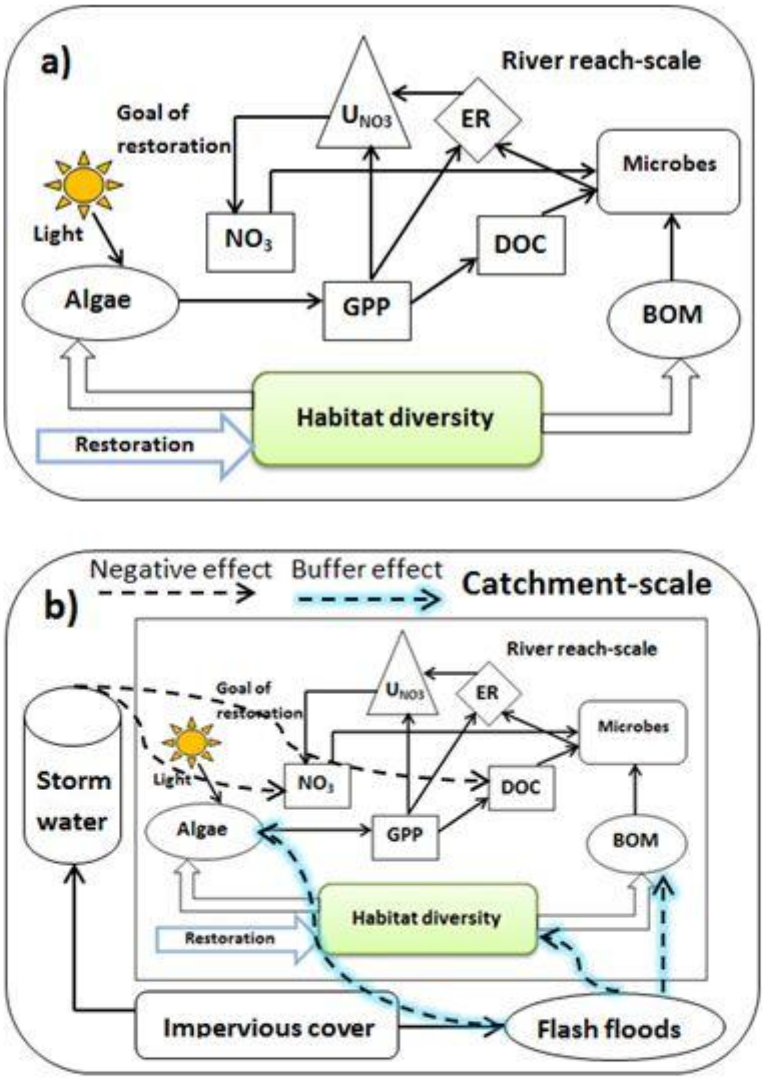

Figure 8 Hypothetical model of stream ecosystem functioning (modified after Mulholland et al., (2009) and Sudduth et al. (2011)), showing a) Desired river-reach-scale effect of river restoration on water quality, and b) Desired effect of river restoration on a catchment scale - to act as a buffer during flash floods. GPP - gross primary productivity, BOM - benthic organic matter, ER - ecosystem respiration, U_{NO3} – areal uptake of nitrate

River restoration is expected to improve habitat diversity leading to increases in algae, BOM and microbes. This in turn is expected to result in enhanced gross primary productivity (GPP), which causes an increase in DOC in the presence of sunlight. Ecosystem respiration (ER) by microbes is a parallel process that can cause areal uptake of nitrate, which along with GPP, results in assimilation of nitrate. Thus these processes reduce nitrate concentrations in the river, which is the end goal of many restoration projects (Figure 8a).

On a catchment scale, impervious urban covers can result in increased storm-water flow and flash floods. This can result in scouring of BOM and removal of algae, which can reduce habitat diversity.

River restoration projects aim to buffer some of these negative effects by nullifying the catchment flash flood-driven scour effects by creating more moderated flow regimes (Figure 8b).

In this study, it was found that the hydrological condition in the river plays a significant role in the alteration of the instream biological processes. It was found that at the downstream part of the restored site there was an indication of nitrate uptake in the pre-dawn period (by a small reduction of nitrate concentrations) attributed to nutrient uptake for GPP. There was also DOC production during the day and its reduction at night during respiration. These effects were observed only during low-flow periods (in autumn SC3) at a short distance downstream of the restored site.

However, following the storm event (in summer SC2), a dilution of solutes (chloride and nitrate) and DOC was observed along the entire monitored river stretch, that overrides the diurnal variation (observed in low flow condition in autumn S3). Nevertheless, the increased DO variability in the restored stretch during the flood event indicates lower turbidity and scour effects in this stretch. Thus, it can be concluded that although the catchment flashiness was not completely nullified, there was an indication of buffering effects of river restoration against scour of bottom algal biomass (for eg. periphytons on rocks).

3.5 Conclusions

Diurnal and seasonal changes in DO, pH, DOC, nitrate isotopes and water isotopes were observed and inter-relationships analyzed along a river reach, part of which was restored. The diurnal cycles of pH and DO were driven by instream biological processes, mainly photosynthesis and respiration. During low flow in the autumn sampling campaign (SC3), a reduction of DOC (in nighttime) and nitrate (in pre-dawn period) was observed downstream of the restored section, which is attributed to biological processes that are expected to be accentuated by increased habitat diversity post-restoration.

The summer storm event in SC2, resulted in increased nitrate and chloride accumulation at the outlet of the catchment followed by a delayed dilution, in comparison to the immediate dilution effect observed along the rest of the river stretch. This storm event also caused a reduction of DOC by dilution along the entire observed river stretch. The observed reduction in the diurnal variability of DO in the channelized parts of the river during the storm event is an indication of higher turbidity turnover affecting the production-respiration pattern - but this does not affect the diurnal variability in the restored section.

Thus, this study has laid the foundation for further work that would focus on post-restoration effects on water quality in large catchments by identifying a subset of critical water quality parameters affected by bio-geochemical processes in a river. Although there are signs of a post-restoration increase of habitat diversity, the desired restoration effect is restricted to a short stretch and during certain seasonal/hydrological conditions. This is attributed to the relatively short (2 km) length of the restored section, which is not sufficiently effective to achieve the desired water quality improvements.

In the absence of pre-restoration temporal data, monitoring post-restoration success is only possible by spatial comparison of the restored stretch with a reference stretch. Such a spatial comparison study needs to consider local effects like diffuse inflow/outflow and major point sources of pollution. The everchanging physical meandering of the river at the restored stretch can also result in temporarily altered biota and thus the system might take a long time to reach equilibrium, up to several years or decades.

The main take-home message from this study for future restoration projects is a recommendation for restoration of longer river stretches and conducting a detailed pre-restoration water quality survey using a pre-defined set of water quality parameters (like those selected in this study) before performing physical alterations to the river. This should be followed by monitoring of these selected parameters at regular time intervals post-restoration. In particular, the performance of the restoration outcomes under various discharge conditions in different seasons needs to be evaluated.

Acknowledgements

The authors would like to thank the Swiss Federal Office for the Environment (FOEN) for providing archived data and forecasts of hydrological and chemical data (NADUF), Dr. Andreas Scholtis, Ulrich Göttelmann (Agency for the Environment, Canton Thurgau) and Dr. Michael Berg (Eawag) for their insightful comments and discussions while planning the field campaigns and for maintaining close cooperation, and the members of the hydrogeology group at Eawag 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 analyses. Additionally, the authors are indebted to the members of the Catchment Hydrology Department at UFZ, Halle-Saale, Germany for their support in the measurement of the nitrate isotopes and Dr. Kay Knoeller and his colleagues in the lab for their close collaboration.

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3.6 Supplementary Information

Table S1 Flashiness index (Q5/Q95) calculated after Robertson and Roerish (1999), from the long term (1970-2011) discharge data from the outlet of the catchment at Andelfingen (Fig. 1).

Seasons	Q95 – Low flow quantile	Q5 – High flow quantile	Flashiness Index, Q5/Q95
Spring	16.4	137.2	8.4
Summer	10.9	143	13.1
Autumn	7.9	114	14.4
Winter	10.7	128	12
Entire year	10.2	134	13

3.6.1 Methods

3.6.1.1 Continuous field monitoring of electrical conductivity (EC), temperature, absolute pressure, pH and dissolved oxygen (DO).

The parameters EC, temperature and absolute pressure were measured (at 15 minute intervals) using continuous measurement probes installed in the river. The sensors were coupled to an integrated data logger that recorded values at 25°C after temperature compensation – (DL/N 70, STS AG, Switzerland; single measurement precision is ±0.1% for absolute pressure head and is ±2% for EC). The pH and DO were measured using HACH probes (HACH Lange GmBH, Germany; single measurement precision is ±0.1 mg/l for DO and is ±0.1 pH unit for pH), which are installed temporarily (like the EC probes) in the river, immersed at approximately 0.5 m below the water surface. The pH and DO probes were calibrated in the lab and validated.

3.6.1.2 Collection of hourly samples over 24 hours using auto samplers and laboratory analysis of samples

ISCO 6700 auto samplers (Teledyne ISCO Inc., U.S.A) were installed at each station which collected 24 hourly samples from the river, which were then stored at 4°C and taken for lab analysis. The samples were filtered immediately using 0.45 µm cellulose nitrate filters (Sartorius AG, Göttingen, Germany). The samples were then analyzed within a week for the major water quality parameters, namely NO_3-N, alkalinity (as HCO_3) and DOC. Concentrations of NO_3-N (± 0.1 mg N/l) were measured using ion chromatography using a Metrohm 761 compact IC (Metrohm, Schweiz AG, Zofinger, Switzerland). Alkalinity (± 0.1 mmol/l) was measured by titration. DOC (± 0.2 mg C/l) was measured using a total organic carbon analyzer Shimadzu, TOC-VCPH (Shimadzu Corporation, Kyoto, Japan). In addition, some of the samples collected (bihourly) in summer, were analyzed for the water isotopes namely δD and $\delta^{18}O$ to characterize the summer storm event (explained in Section 4.2.1). 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) against calibrations performed with water isotope standards of the International Atomic Energy Agency. The corresponding isotope signatures of $\delta^{18}O$ and δD 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 $\delta^{18}O$ and δD, respectively. Analyses of nitrogen and oxygen isotopes of nitrate were carried out using the denitrifier method (Casciotti et al., 2002; Sigman et al., 2001) which is based on the isotopic analysis of nitrous oxide (N_2O) produced by denitrifying *Pseudomonas chlororaphis* (ATCC#13985) strains. The produced N_2O 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 N_2 gas against air nitrogen. Nitrogen and oxygen isotope ratios are expressed in the delta notation ($\delta^{15}N$ and $\delta^{18}O$) relative to atmospheric nitrogen and Vienna Standard Mean Ocean Water (VSMOW) in the conventional isotope terminology:

$$\delta(‰) = [(R_{sample}/R_{standard}) - 1] \times 1000 \qquad \text{(i)}$$

where R is the $^{15}N/^{14}N$ or $^{18}O/^{16}O$ ratio of the sample and standard, respectively. Results are given in per mil (‰). Analyses of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ were standardized using the internationally distributed KNO_3 reference material IAEA-N3 with an assigned $\delta^{15}N$ value of 4.7‰ versus air N_2 (Böhlke and Coplen, 1995) and a reported $\delta^{18}O$ value of 22.7‰ versus VSMOW (Révész et al., 1997). Analytical precision (one standard deviation) is ± 0.2 ‰ for $\delta^{15}N$ and ±0.5 ‰ for $\delta^{18}O$, respectively. The stable isotopes of nitrate were measured at the Helmholtz Centre for Environmental Research UFZ, Halle, Germany, which were measured for bihourly samples in autumn in addition to the other parameters to better characterize the consumption pattern of nitrate in this season.

3.6.1.3 1D hydraulic model in HEC-RAS

The major difficulty in monitoring a dynamic river such as the Thur is to tackle the highly variable discharge conditions due to the absence of a natural reservoir. This also makes it necessary to measure these rapid changes in discharge conditions, both temporally and spatially.

The estimation of the travel time of the water between the stations and the discharge at each of the stations is done by using a one-dimensional (1D) hydraulic model of the Thur River, developed using HEC-RAS (US Army Corps of Engineers, Washington DC, U.S.A.) obtained from Hunziker, Zahn & Partner (Aarau, Switzerland). This model extends for a 32 km stretch from the upstream water level measurement gauge maintained by FOEN at Halden to the restored site at Niederneunforn. The normal depth is used as the boundary condition at both the upstream and downstream ends. This model was extended 7 km further to the outlet of the catchment in order to calibrate the discharge obtained from the model with that of the discharge measured at the outlet of the catchment at Andelfingen. With several steady-state runs of different discharge conditions defined at the boundaries, a time series of water levels was obtained at each of the stations. These were then compared with the water levels measured in the field (calculated from the absolute pressure values, corrected for air pressure) to back-calculate the discharge values in each of the cross-sections. The model computes the discharge as a product of flow area and velocity in the channel, and is particularly useful as it is difficult to measure the discharge at each cross-section owing to the wide cross-sections with varying velocities. It is also used to determine the sampling duration based on the discharge forecast at the outlet of the catchment, particulary during storm events in order to capture the discharge peaks at each station.

Table S2 The travel time of Q_{peak} – (discharge at peak flow) and EC_{dip} – (the EC at maximum dilution) during the propogation of the flood wave together with the wave velocity (V_w), the mean water velocity (V) and time lag between Q_{peak} and EC_{dip}.

Stations	Distance between stations (km)	Time of Q_{peak}	Time of electrical conductivity EC_{dip}	Time of the start of Q increase	Time of start of EC decrease	Flood peak - travel time (min)	Wave velocity V_w (m/s)	Mean velocity V (at Q= 28 m^3/s) (m/s)	EC_{dip} Travel time (min)	Time lag between Q_{peak} - EC_{dip} (min)
A		6:00 am	6:30 am							30
B	A-B 8.7	7:15 am	8:30 am	6:45 am	7:00 am	A-B - 75	1.9	1	A-B- 120	75
C	B-C 4.0	8:00 am	9:30 am	7:30 am	8:00 am	B-C - 45	1.5	0.7	B-C- 60	90
D	C-D 3.9	8:45 am	10:30am	8:00 am	8:30 am	C-D - 45	1.5	1	C-D- 60	105
E	D-E 7.1	10:00 am	12:00am	9:00 am	9:00 am	D-E - 75	1.7	1.1	D-E- 90	120

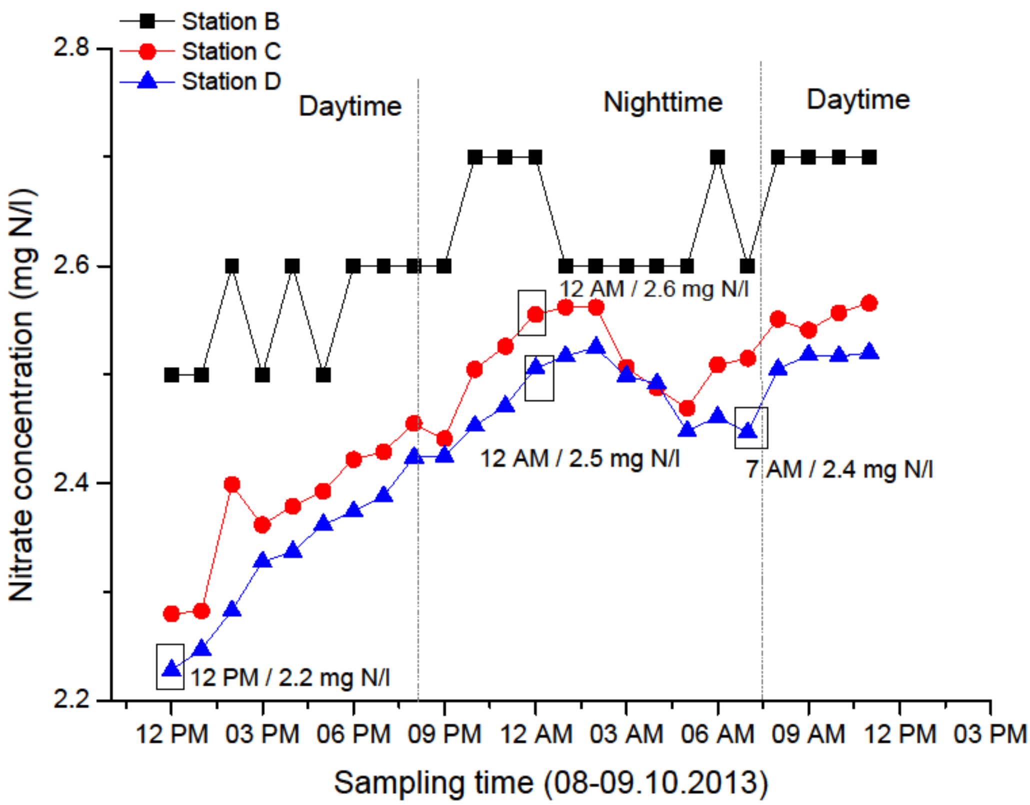

Figure S1: Nitrate concentration (mg N/l) during the autumn sampling campaign (SC3) at stations B, C and D.

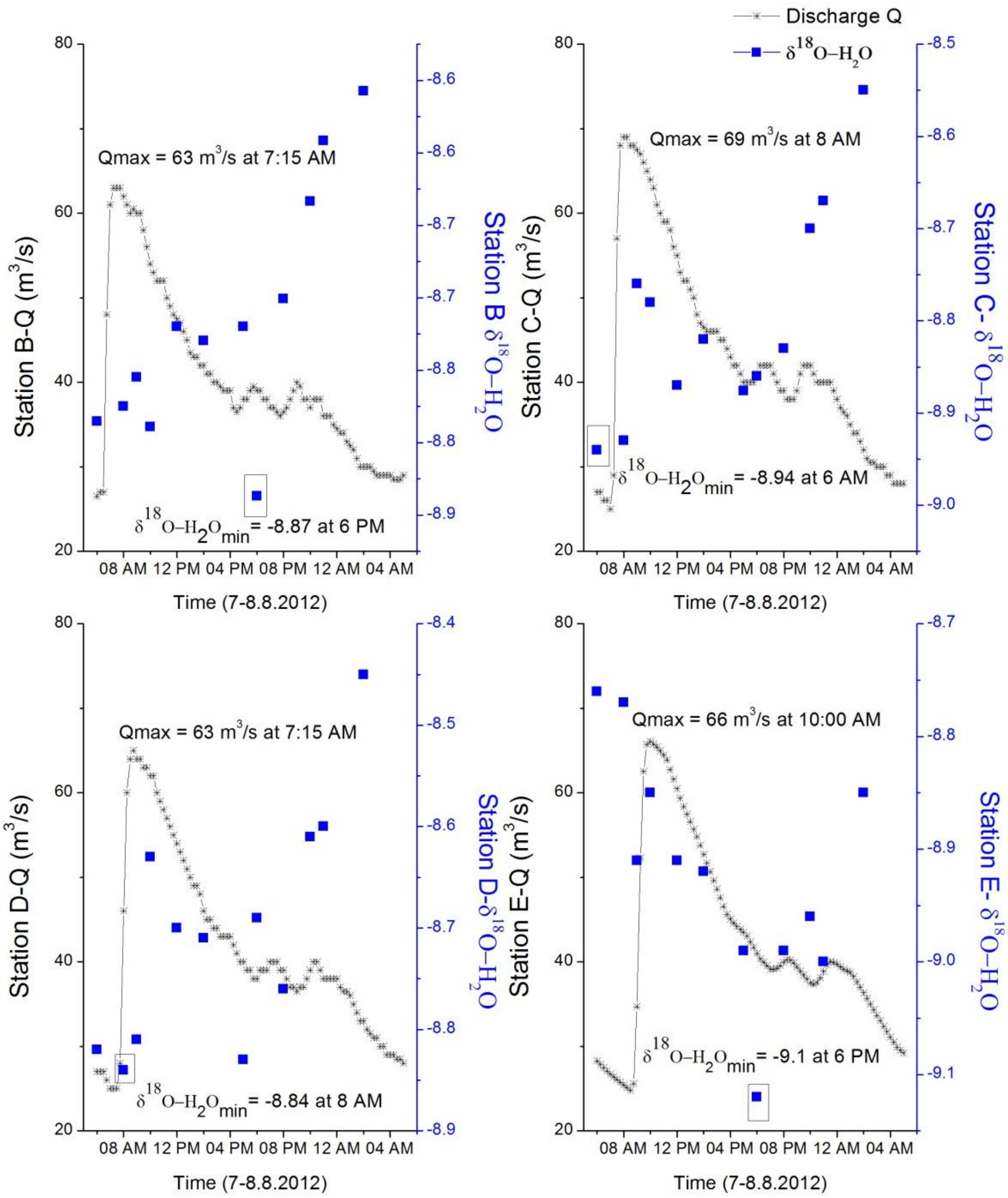

Figure S2 The relationship between discharge - Q (m^3/s) and water isotope - $\delta^{18}O$-H_2O ‰ at stations B, C, D, E during summer SC2 (on 7-8.08.2012). The minimum (C_{min}) concentrations of $\delta^{18}O$-H_2O ‰ are indicated in the boxes. The maximum discharge (Q_{max}) is also indicated.

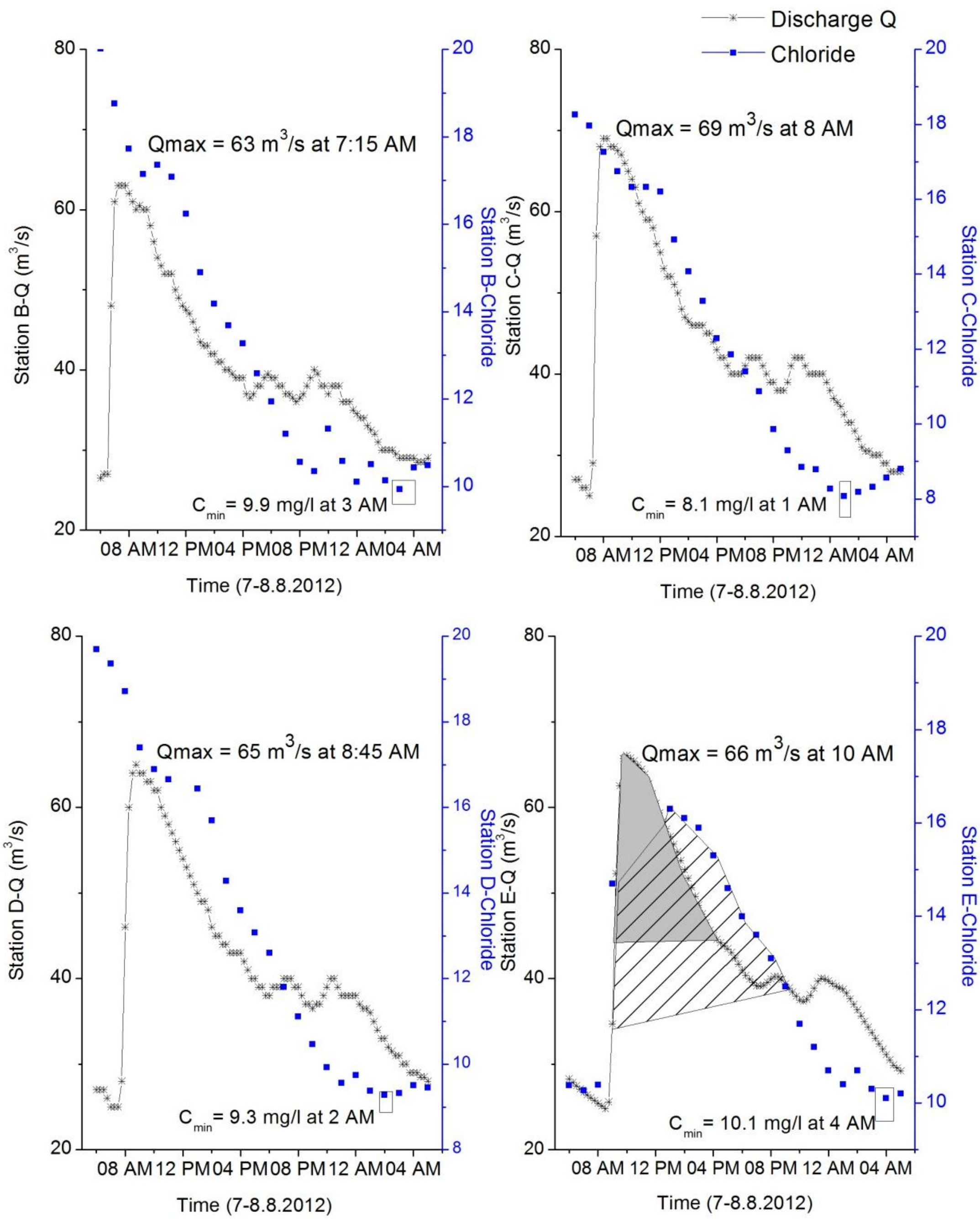

Figure S3 The relationship between discharge - Q (m^3/s) and chloride (mg/l) concentration during the summer sampling campaign (SC2) at stations B, C, D, E. The minimum (C_{min}) concentrations of chloride are indicated in the boxes. The shaded portion shows the accumulation of chloride at station E following the discharge peak (Q_{max}).

Chapter 4 An integrated spatial snap-shot monitoring method for identifying seasonal changes in surface water quality

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Abstract

Integrated catchment-scale approaches for managing large river basins are often hindered due to the lack of understanding of the spatially and seasonally-variable pathways of pollutants. Monitoring large catchments is therefore resource intensive and challenging. In particular, large elevation differences in mountainous catchments can result in a dramatic change in the source of water from highlands to lowlands that can then influence solute loads. Nitrate and total phosphorus, for example, are critical nutrients in agricultural catchments and it is important to understand their pathways as they are also potential contaminants for ecosystems. Thus, an understanding of the source of water and nitrate together with solute loads can provide insight for identifying the hotspots of water quality and their seasonal changes within a large catchment. This is achieved in this study with a new simplified approach - Integrated spatial snap-shot monitoring (ISSM). This multi-parameter approach is applied using the isotopes of water ($\delta^{18}O$-H_2O and δD) and nitrate ($\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^-) together with the fluxes of nitrate, total phosphorus and other solutes, which are used as chemical markers. The study is 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). This method involved selection of sampling stations at the junctions where the major tributaries join the Thur River, which are identified as the hotspots of water quality change in the catchment. There is a significant seasonal change in the sources of water between the two seasons, indicated by the lighter water isotopic signature (indicative of more melt water) in spring in the Thur River and its tributaries. Major differences are observed in the nitrate loads among the two seasons, with higher spring contributions of nitrate from the head water of the Thur River and from a tributary located at higher elevation. The sources of nitrate also demonstrate a seasonal shift, which change from a strong treated waste water signature during the low flow season to a mixture of other sources (soil nitrogen and nitrified ammonia from precipitation), when there is a higher flow in the Thur River and its tributaries. Upon analyzing the contribution of the treated waste water to the total flow of the river it is concluded that during the low flow in summer its contribution is twice as high as during high flow. This demonstrates the influence of other sources that override WWTP influence during high flow as observed in the spring sampling campaign. Thus the developed integrated method involving a multi-parameter approach, using a combination of solute fluxes and isotopes measured at two representative campaigns (in low flow and high flow seasons) with few sampling stations at select locations. This method is expected to be a cost-effective alternative to identify the source pathways of solutes and their seasonal and spatial changes in catchments.

Keywords: *Catchment monitoring, Nitrate isotopes, Water isotopes, Nutrient loads, Seasonal* changes

4.1 Introduction

The European Union (EU) Water Framework Directive (European Union, 2000) calls for sustainable management of water resources on a catchment scale (Gilvear, 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, 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).

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 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 $\delta18O$ 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 along the river as well as to identify the seasonal variations in surface water quality within a catchment.

4.2 Study Area

The study was conducted in the Thur catchment in northeastern 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 (Figure 1).

The Thur River is a peri-alpine river (127 km long) originating from Mount Santis and drains into the Rhine River (Figure 1). The catchment area measured to the catchment outlet is 1,696 km^2. 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 8.5-550 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 (Figure 1). The Necker (ca. 125 km^2) and the Sitter (ca. 354 km^2) arise from the highlands with the mean catchment elevation of 902 m and 939 m, respectively. The Murg (ca. 197 km^2), arises from the lowlands with an average catchment elevation of 590 m. The mean yearly discharge 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 (19.1%), and urban areas (9%), while the rest is unoccupied land (1.7%). Waste water discharges to the Thur and its tributaries through 45 waste water treatment plants (WWTPs) (Figure 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%) and the least urban influence (4%) as shown in Figure 1 (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.) (Figure1). The main urban areas in the catchment are the three towns of St. Gallen (Sitter Sub-Cat.), Frauenfeld (Murg sub-cat.) and Weinfelden (Lower Thur Sub-Cat.) with 72000, 23000 and 10000 inhabitants, respectively. In the Murg Sub-Cat. there are two important WWTP's at Frauenfeld (located before M3) and at Matzingen, located up-gradient from station M2 (avg. yearly Q (2013) = 17,260 and 9,740 m^3/day, respectively).

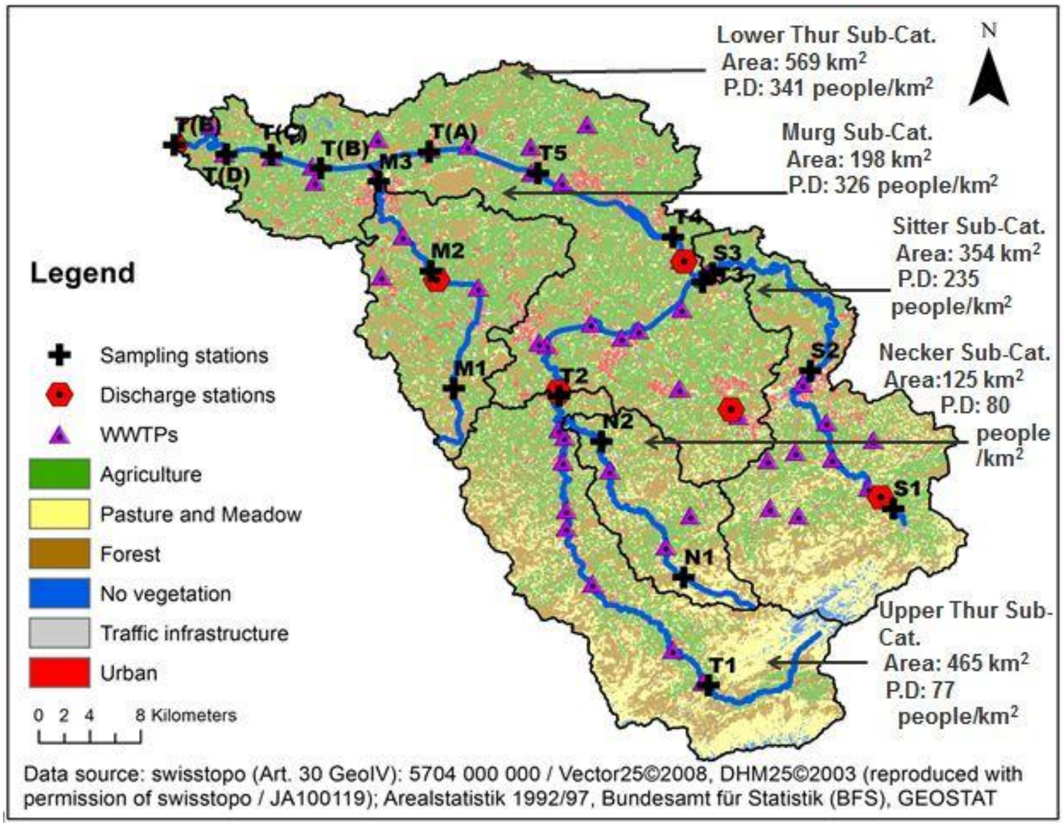

Figure 1 Location of the sampling sites, sub-catchments (Sub-Cat.), major discharge stations, waste water treatment plants (WWTPs) and the land use classification in the Thur catchment. The area and the population density (P.D.) of the various sub-catchments are also indicated. Data source: Swisstopo,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

4.3 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 are located from the headwater of the Thur River to its lower reach (T1) – T(E) and its tributaries (S1-S3 along Sitter, N1-N3 along Neckar, M1-M3 along Murg) (Figure 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 (Figure 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) 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 Figure 2.

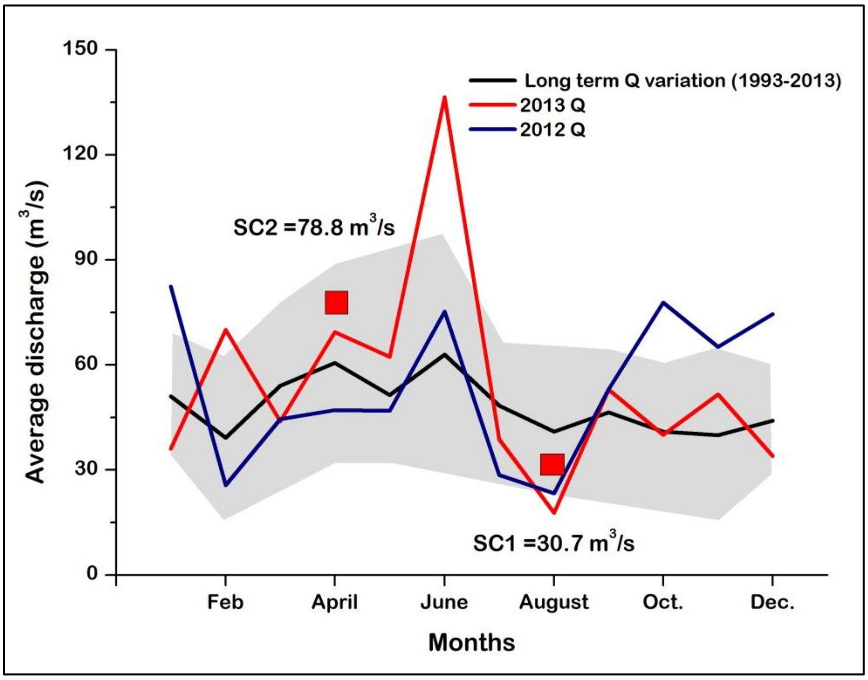

Figure 2 Averaged daily discharge (Q) during the sampling periods (SC1 and SC2) marked with shaded squares along with average monthly Q variation in 2012 and 2013. This is compared together with the long-term seasonal Q variation (1993-2013). The monthly average standard deviation in the two decades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

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 ($\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$) and water isotopes ($\delta^{18}O\text{-}H_2O$ and δD). Isotopic analyses of nitrogen and oxygen of nitrate ($\delta^{15}N\text{-}NO_3$- and $\delta^{18}O^-$ NO_3^-) were carried out using the denitrifier method (Sigman et al., 2001; Casciotti et al., 2002). Isotope ratios $^{18}O/^{16}O$ and $^2H/^1H$ of the water samples were determined by cavity ring-down spectroscopy (Picarro L1102-i, Santa Clara, CA) and corresponding isotope signatures δ18O-H2O 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 analysed. 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-Cat. (Figure 1). A detailed method description of the measurement of the various parameters can be found in the supplementary information.

4.4 Results and Discussion

4.4.1 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. Significant 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 which is consistent with the comparatively lower population density and less intensive agriculture landuse (Figure 1,3, 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 (Figure 3, Table S1). The maximum change in TP concentration was observed at M3 (with 100 µg P/l increase from SC1-SC2). Station M3, located in the lower part of the Murg (before it joins the Thur), is critical because of the presence of WWTP's 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 Figure 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, Figure 3). This dilution effect is more apparent in the conservative solutes like Na^+, Cl^-, Ca^{2+} and K^+.

Hotspots of water quality change: As shown in Figure 3, the water quality in the Thur River changes mainly at junctions with its primary tributaries as shown by an increase/decrease in the 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 (Figure 1,3, Table S1). Due to higher discharge in SC2, dilution of Cl^-, Ca^{2+}, Na^+, and K^+ is reflected by dips in the concentrations at T2 and T4, particularly at the junctions of the head water tributaries of the Necker and Sitter flowing from higher elevations. These tributaries are expected to carry comparatively more melt water and are not solute-rich like the lower tributary Murg.

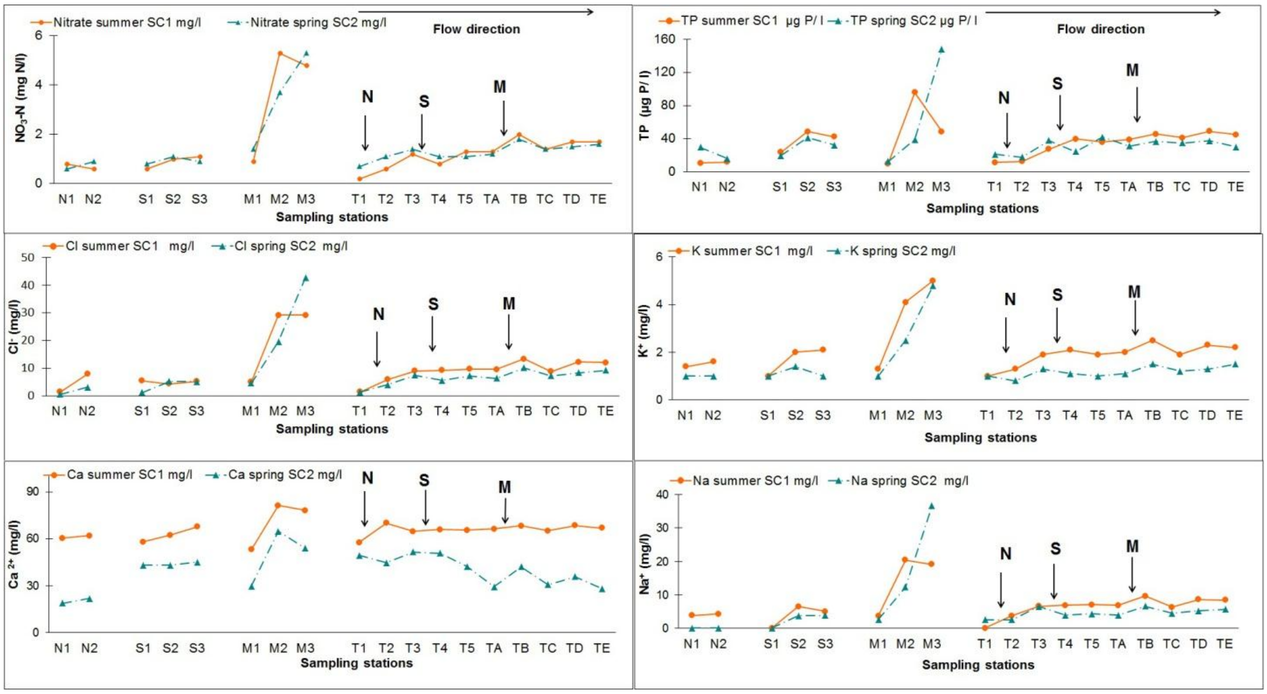

Figure 3 Hydrochemistry variations in the Thur River and its tributaries measured at the sampling stations in summer SC1 and spring SC2. Concentrations of NO_3-N (± 0.1 mg N/l), Cl^- (± 0.2 mg/l), Ca^{2+} (± 1.7 mg/l), K^+ (± 0.3 mg/l), Na^{2+} (± 0.8 mg/l), TP (± 3 µg P/l) are illustrated. The hotspots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

4.4.2 Water isotopes - δD and δ^{18}O-H_2O – Capturing the seasonal and catchment elevation effect on the sources of water in the rivers

The δ^{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 to SC2, with 2.7‰ and 23 ‰ decreases in the mean over all stations for δ^{18}O-H_2O and δD, respectively (Table 1, Figure 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 δ^{18}O-H_2O, which matches with the SC1 (low flow) isotopic composition in the Thur River and its tributaries (Figure 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, Figure 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 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 (Figure S2).

The changes in catchment elevation and its effect on the water isotopes, was clearly noticeable along the Thur River, with decreasing elevation from T1 to TE. 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-TE (Table 1, Figure 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 the isotopic compositions 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 (Figure S2).

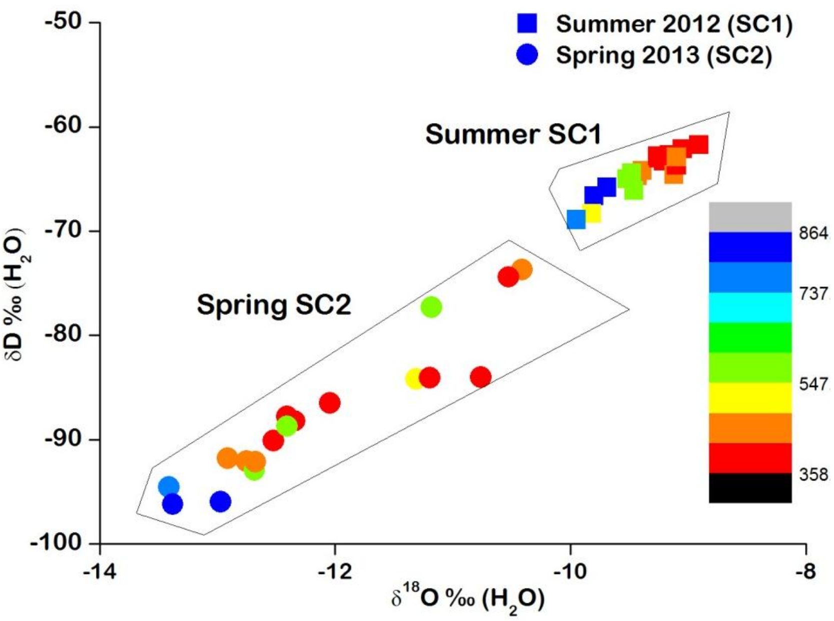

Figure 4 The isotopic composition of water (δD and δ^{18}O-H_2O) and its varyiability with elevation in summer 2012(SC1) and spring 2013(SC2) in the Thur catchment. Legend shows the colour map of the catchment elevation (m).

4.4.3 Nitrate isotopes - Tracking nitrate sources using a dual isotope approach

In each season, the $\delta^{15}N$ and $\delta^{18}O$ of nitrate ($\delta^{18}O-NO_3^-$ and $\delta^{18}O-NO_3^-$) had an increasing trend from upstream to downstream in the Thur River and its tributaries (Figure 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 $\delta^{15}N-NO_3^-$ ranging between −15 and +15‰ (Kendall et al., 1995, 2007; Kendall, 1998; Elliott et al., 2007). The $\delta^{15}N-NO_3^-$ of synthetic/inorganic fertilizers (usually ammonia fertilizers) varies between −8 and +7‰ (Kendall, 2007; Hübner, 1986; Macko and Ostrom, 1994; Vitoria et al., 2004). Nitrate fertilizers that are organic and derived from plant composts, liquid and solid animal waste have a higher $\delta^{15}N-NO_3^-$ range between +2 to +30‰ when compared to inorganic fertilizers (Kendall, 2007). Since the range of atmospheric deposition of nitrate has overlapping signature of $\delta^{15}N-NO_3^-$ with synthetic fertilizer the $\delta^{18}O-NO_3^-$ is used additionally. Nitrate derived from nitrification of ammonium fertilizers and ammonia from precipitation has lower $\delta^{18}O$ 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 nitrate fertilizers (+17‰ to 25‰) (Amberger and Schmidt, 1987; Elliott et al., 2007).

The range of the $\delta^{15}N-NO_3^-$ 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 $\delta^{15}N-NO_3^-$ 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 $\delta^{15}N-NO_3^-$ was lower varying between 3‰ and 7‰, during SC1 and varying between -3.3 and 2.8‰ in SC2. The $\delta^{18}O-NO_3^-$ values, in all the samples are in the range of 0.1 to 3.5‰ in SC1 and between -4.6 to 5.7‰ in SC2 (Table 1, Figure 5). Thus, the combination of the ranges of the signatures of both the isotopes indicate the sources of nitrate can be from nitrified ammonia in synthetic fertilizers and precipitation/soil organic nitrogen in SC1 and from nitrified ammonia in synthetic fertilizers and precipitation in 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 sub-section 4.1. Thus indicating that this lower concentration is likely derived from nitrified ammonia from precipitation and not from synthetic fertilizer from these higher regions in both SC1 and SC2.

However, in the lower Thur (from T3 to TE), Sitter (S2, S3) and Murg (M2, M3) there was an enrichment of $\delta^{15}N-NO_3^-$, 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, Figure 5). In SC2, in the lower Thur (from T3 to TE) and Sitter (S2, S3), the $\delta^{15}N-NO_3^-$ 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, Figure 5).

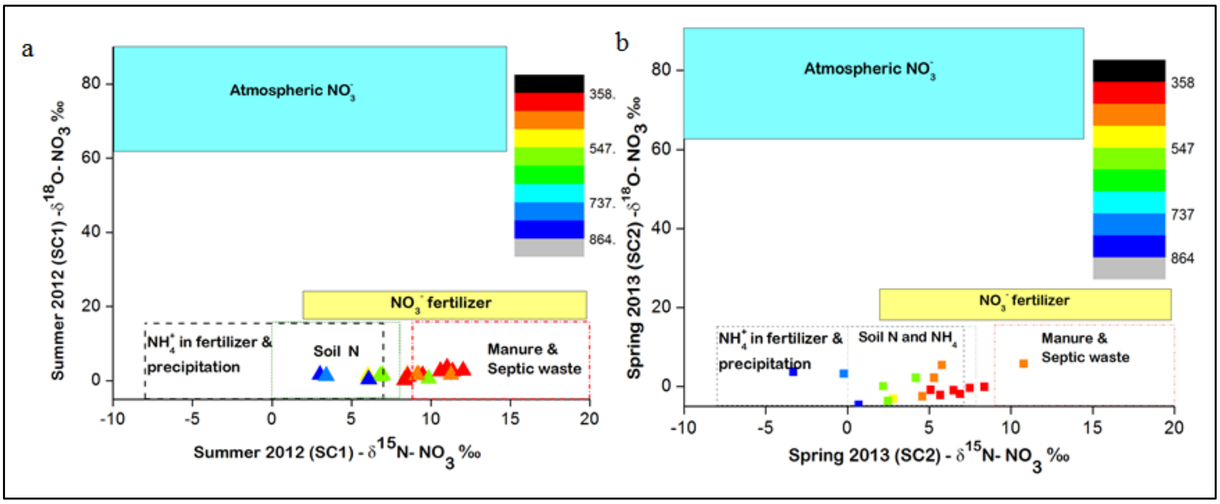

Figure 5 Relationships between δ^{15}N and δ^{18}O of nitrate in the Thur River and its tributaries in summer SC1 (a) and spring SC2 (b). The isotopic composition of various sources is also provided in the diagram (modified after Kendall et al., 2007).

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 expected δ^{18}O-NO_3^- in the Thur River from nitrification is calculated with a mean value of 1.58‰ across all stations in SC1 and 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 ammonia 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 good linear correlation was observed between chloride (a conservative tracer) and nitrate concentrations (r^2=0.95) in both seasons, indicating that both are derived from the same sources and that nitrate accumulates from upstream to downstream, with little loss of nitrate in the river which is well oxygenated (Figure S1).

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. Additionally, when monthly average ammonia concentrations in rain samples collected in 2012 and 2013 from an industrial area in Switzerland were compared, the concentrations were highest (nearly 1 mg/l) during the spring season (March and April) (Figure S4). Such seasonal increases of ammonium in the precipitation samples in spring have also been observed in $\delta^{15}N\text{-}NH_4$, 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 ammonia from precipitation has a greater influence in SC2 (in spring during high flow) than during SC1 (during low flow in summer).

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

Sampling stations	**$\delta^{15}N_{NO3}$ (‰)**		**$\delta^{18}O_{NO3}$ (‰)**		**$\delta^{18}O\text{-}H_2O$ (‰)**		**$\delta D\text{-}H_2O$(‰)**		**$\delta^{18}O\text{-}NO_3$(‰)**	**$\delta^{18}O\text{-}NO_3$(‰)**
	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	1.53	0.37
M2	11.3	10.8	1.6	5.7	-9.1	-10.4	-64.6	-73.7	1.75	0.90
M3	12.0	21.6	2.7	4.5	-9.1	-10.5	-63.7	-74.4	1.77	0.83
N1	6.1	-3.3	0.3	3.7	-9.7	-13.4	-65.8	-96.2	1.37	-1.10
N2	7.0	2.2	1.5	0.1	-9.5	-12.4	-65.0	-88.7	1.49	-0.43
S1	3.4	-0.2	1.3	3.2	-10.0	-13.4	-68.9	-94.6	1.20	-1.10
S2	9.9	4.2	0.5	2.2	-9.5	-12.7	-64.4	-92.9	1.51	-0.63
S3	9.1	5.3	1.45	2.2	-9.1	-12.7	-62.9	-92.1	1.77	-0.63
T1	3.0	0.7	1.5	-4.6	-9.8	-13.0	-66.6	-95.9	1.30	-0.83
T2	6.0	2.8	1.4	-3.1	-9.8	-11.3	-68.3	-84.2	1.29	0.30
T3	8.5	5.8	1.5	-2.7	-9.4	-12.9	-64.2	-91.8	1.57	-0.77
T4	9.2	4.6	1.5	-2.5	-9.4	-12.8	-64.7	-92.1	1.55	-0.70
T5	8.4	5.7	0.1	-2.2	-9.2	-12.5	-62.7	-90.1	1.73	-0.50
TA	9.5	5.1	1.5	-0.9	-9.3	-12.3	-63.0	-88.2	1.67	-0.37
TB	10.6	8.4	2.5	-0.1	-9.2	-11.2	-63.3	-84.1	1.69	0.37
TC	8.6	6.5	1.0	-1.0	-8.9	-10.8	-61.7	-84.0	1.89	0.63
TD	11.4	6.9	2.4	-1.9	-9.1	-12.4	-62.1	-87.8	1.80	-0.43
TE	11.0	7.5	3.5	-0.4	-9.3	-12.0	-62.8	-86.5	1.66	-0.17
Mean	8.43	5.4	1.5	-0.08	-9.4	-12.1	-64.5	-87.5	1.59	-0.24

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.

Station	**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	17400	176
T4	23.2	71.7	209	1600	6860	328	79	152	92	18400	34400	88
T(E)	30.7	78.8	157	4510	11000	144	119	204	71	31800	63000	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	15000	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

4.4.4 Tracking the seasonal contribution from the various tributaries and WWTPs using solute loads

The total load (kg/day) was calculated for the different solutes (Table 2, Figure 6) showing that discharge increased from SC1 to SC2 in all stations. The increase was between 150 and 200% in most stations, while the Necker (at N2) recorded a nearly 400% higher discharge, which is reflected in the upper Thur at T2. The nitrate load increase from SC1 to SC2 is comparable to the increase in discharge at the outlet of the catchment (at TE). However, the nitrate load varies significantly from SC1 to SC2 in the lower part of the Necker (600% increase at N2), which is also reflected in the upper Thur Sub-Cat. (677% increase 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, Figure 6).

The contribution of the various tributaries to the total discharge of the Thur River was also calculated. Accordingly, the contribution of the Necker was calculated at station T2, the Sitter's contribution at T4 and the Murg's contribution was calculated at TE. We find that the contribution from the Murg to the Thur River's discharge in both the seasons remained the same at 5%. However, the Necker and Sitter contributed 3% more discharge to the Thur in SC2 compared to SC1. There was a higher contribution (10% higher) of the nitrate load from the Sitter in SC1 compared to SC2. This was 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) was 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 were consistent with the average monthly variation observed over the past two decades as shown in Figure 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 loads from the Matzingen WWTP (L_{wwtp}) with the loads from a surface water quality monitoring station (L_{wwtp}) 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 (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 4-24% in 2012 and from 5-30% in 2013 for nitrate and from 4-94% 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 discharge (3.6 % and 4.3%, respectively) from the WWTP to the river Q. Therefore, in the months when there is very high Q in the river, there is a lower contribution of 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=14625 m3/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 (1,210,055). Thus the estimated loads from the WWTP are 3,400 kg/day and 3,860 kg/day, respectively, in SC1 and SC2. The WWTP contribution to the total nitrate load calculated at the catchment outlet (at TE) is 76% in SC1 and 35% in SC2.

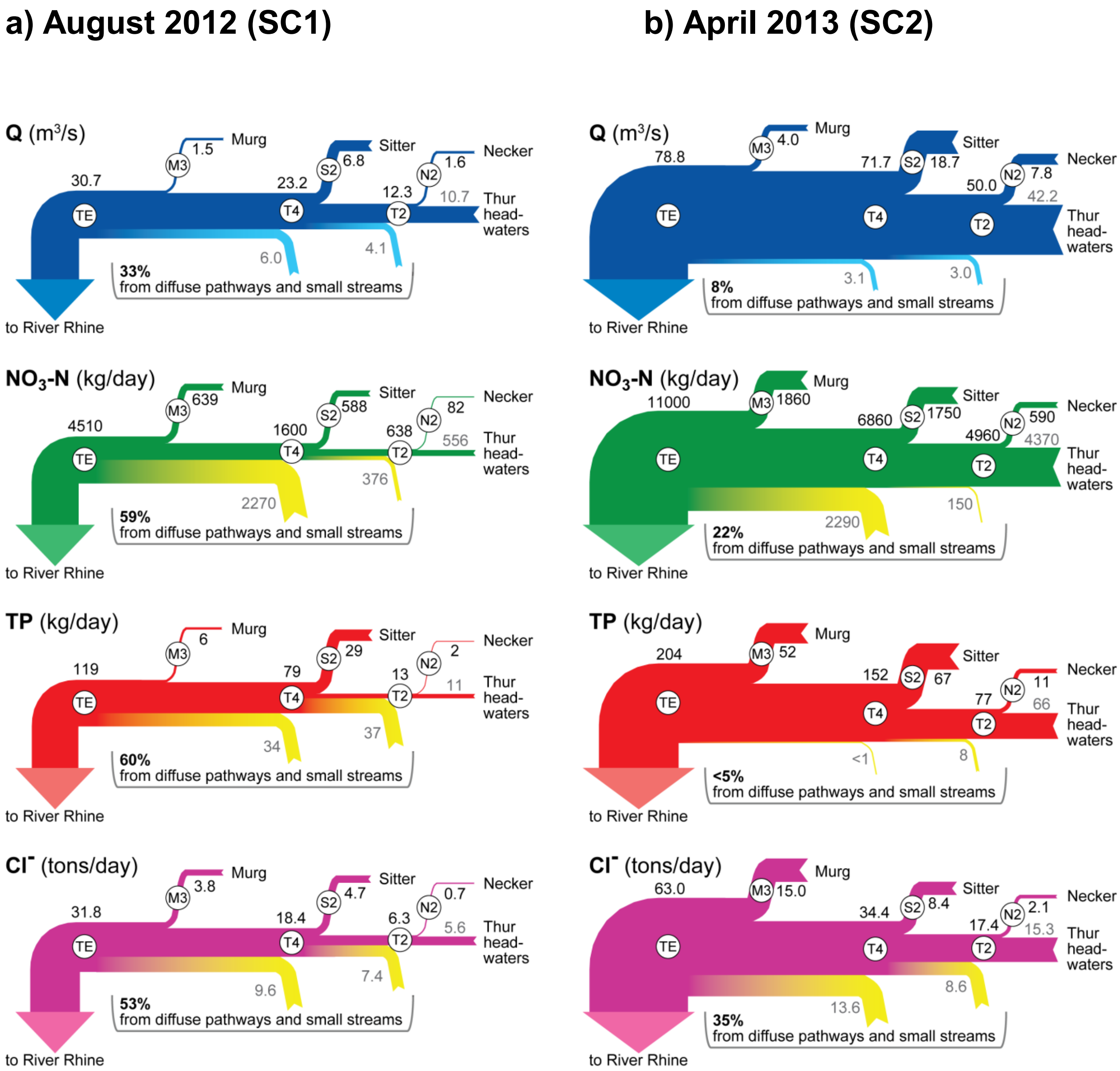

Figure 6 Flow diagrams of water discharge (Q), NO_3-N, TP, and chloride along the course of the River Thur in a) summer 2012, and b) spring 2013. Encircled numbers refer to the monitoring stations labeled in Figure 1. The grey shaded (or: yellow colored) inputs were calculated to match the observed mass flows at sites T4 and TE. They 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.

This is consistent with the earlier conclusion that during low flow periods, there is a higher contribution of nitrate from the WWTP compared to the high flow season. This is also consistent with the conclusion obtained from section 4.4.3 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.

4.5 Conclusion

The seasonal and spatial changes in surface water quality in a large peri-alpine catchment were studied by developing a new method of integrated catchment monitoring with only two snap-shot campaigns during low and high flow seasons. 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 changes were identified. The hotspots of water quality changes were identified at the junctions of the tributaries. The Murg River in the lower part of the catchment, which has the highest population density and subsequently numerous waste-water treatment plants (WWTPs), alters the Thur River chemistry during both seasons. Furthermore, the dilution of conservative tracers like Na^{+}, Ca^{2+}, K^{+} and Cl^{-} is evident during high flow, particularly at the junctions of the higher tributaries, which are expected to carry more melt water in spring. This is validated with a lighter isotopic composition of water isotopes in spring, particularly in the headwaters of the Thur River and in the higher tributaries like the Sitter and Necker that are more influenced by precipitation. During low flow, the heavier isotopic composition of the water isotopes in the rivers was comparable to that of the isotopic composition of groundwater indicating it was mainly groundwater fed in base flow conditions.

The nitrate isotopes reveal a significant seasonal differentiation in the sources of nitrate in the lower parts of the catchment. It changes from predominantly a manure/WWTP signature during low flow to a mixture of signatures from soil nitrogen and nitrified ammonia from rain during the high flow season in spring. This interpretation is supported by comparing the WWTP loads and the river loads in the lower part of the Murg, which show lower WWTP contributions during high flow. Additionally, when the total load from the largest WWTP in the catchment is extrapolated to the total population in the catchment (to calculate the total contribution of WWTP loads), its contribution during SC1 is double that of SC2. Therefore, there is clear evidence suggesting additional nitrate contribution from the catchment other than WWTP in SC2, while WWTP loads play a significant role during low flow as observed in the summer sampling (SC1). In addition to this, when the river loads are compared in both seasons, there is a significant contribution of nitrate from the headwaters of the Thur and Neckar in spring. Here there seems to be a significant effect of manure application and soil flushing in spring, that contribute additional nitrate to the river apart from nitrification of ammonia from wet deposition as indicated by the nitrate isotopes.

Thus, in this study it is shown that a good understanding of nutrient pathways and hotspots of water quality change can be obtained with the help of the ISSM method with only two snap-shot campaigns in two extreme variable flow seasons. This method is particularly effective when the snap-shot campaigns are representative of the major hydrological changes in the catchment. It is useful in remote areas and developing countries where routine sampling is restricted by lack of adequate resources. This method can be further enhanced using additional isotopes like boron and with bacterial source tracking to differentiate sewage and manure. The limitations of this method over high-frequency sampling is the lack of data to verify pollutant peaks especially during events. Thus, this is recommended as a preliminary method to identify the critical areas in a large catchment, which can then be frequently monitored to obtain further insights.

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4.6 Supplementary Information

4.6.1 Analytical Methods

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^+ (± 0.8 mg/l) were measured using ion chromatography using Metrohm 761 compact IC (Metrohm, Schwiez AG, Zofinger, Switzerland). Total phosphorus (±3 µg P/l) was measured by chemical digestion with Potassium peroxodisulfate in an autoclave at 121°C in the first step followed by ortho-phosphate measured colorimetrically using the molybdenum blue method (Vogler, 1965).

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) against calibrations performed with water isotope standards of the International Atomic Energy Agency. The corresponding isotope signatures $\delta^{18}O$-H_2O and δD 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 $\delta^{18}O$-H_2O and δD, respectively.

The cooled samples (at 4°C) were measured for the isotopes of nitrate at the Colorado Plateau Analytical Laboratory, Northern Arizona University, U.S.A and at Helmholtz Centre for Environmental Research – UFZ Department Catchment Hydrology, Halle, Germany for SC1 and SC2 samples. Isotopic analyses of nitrogen and oxygen of 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 (N_2O) produced by denitrifying *Pseudomonas aureofaciens* (ATCC#13985) and *Pseudomonas chlororaphis* (ATCC #13985) strains respectively for the SC1 and SC2 measurements. The N_2O 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 N_2 gas against air nitrogen. Nitrogen and oxygen isotope ratios are expressed in the delta notation ($\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3^-$) relative to atmospheric nitrogen and Vienna Standard Mean Ocean Water (VSMOW) in the conventional isotope terminology:

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

where R is $^{15}N/^{14}N$ or $^{18}O/^{16}O$ ratio of sample and standard, respectively. Results are given in per mil (‰). Analyses of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ were standardized using the internationally distributed KNO_3 reference material IAEA-N3 with an assigned $\delta^{15}N$ value of 4.7‰ versus air N_2 (Böhlke and Coplen, 1995) and a reported $\delta^{18}O$ value of 22.7‰ versus SMOW (Revesz et al., 1997). Analytical precision (one standard deviation) was better than 0.2‰ for $\delta^{15}N\text{-}NO_3^-$ and better than 0.4‰ for $\delta^{18}O\text{-}NO_3^-$, respectively.

Table S1 Location and elevation of the sampling stations and concentration of the various anions and cations measured in summer 2012 (SC1) and spring 2013 (SC2) in the Thur river and its tributaries measured at the sampling stations indicated in Figure 1. 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 tabulated.

Stations	**River, location, elevation (m)**	**NO_3-N mg N/l**		**TP µg P/l**		**Cl^- mg/l**		**Ca^{2+} mg/l**		**Na^+ mg/l**		**K^+ mg/l**	
		SC1	**SC2**	**SC1**	**SC2**	**SC1**	**SC2**	**SC1**	**SC2**	**SC1**	**SC2**	**SC1**	**SC2**
M1	Murg, Fischingen 605	0.9	1.4	10.1	12.6	5.0	4.6	53.2	29.8	3.7	2.6	1.3	<1
M2	Murg, Wängi 460	5.3	3.7	96.0	38.9	29.2	19.6	81.3	64.8	20.4	12.3	4.1	2.5
M3	Murg,Frauenfeld 391	4.8	5.3	48.8	148	29	42.7	78.2	54.1	19.1	36.7	5.0	4.8
N1	Necker, Hemberg 863	0.8	0.6	10.9	29.8	4.3	0.5	60.6	19.0	3.8	<2.5	1.4	<1
N2	Necker, Gantershwil 584	0.6	0.9	11.7	15.8	5.2	3.1	62.0	22.0	4.3	<2.5	1.6	1.0
S1	Sitter, Schwende 789	0.6	0.8	23.7	19.6	1.5	1.2	58.2	43.1	<2.5	<2.5	<1	<1
S2	Sitter, St.Gallen 564	1.0	1.1	48.8	41.1	7.9	5.2	62.4	43.1	6.5	3.7	2.0	1.4
S3	Sitter, Bischofszell 466	1.1	0.9	42.5	32.2	5.5	5.1	67.7	45.2	5.0	3.8	2.1	1.0
T1	Thur, Stein 836	0.2	0.7	11.6	21.3	1.5	1.3	57.8	49.4	<2.5	2.5	<1	<1
T2	Thur, Jonschwil 538	0.6	1.1	12.4	17.9	5.9	4.0	70.2	44.7	3.7	2.5	1.3	0.8
T3	Thur, Bischofszell 464	1.2	1.4	27.3	37.7	9.0	7.5	64.9	51.7	6.6	6.5	1.9	1.3
T4	Thur, Kradolf-Schönenberg 453	0.8	1.1	39.6	24.5	9.2	5.6	66.0	50.9	6.9	3.9	2.1	1.1
T5	Thur, Amlikon-Bisegg 415	1.3	1.1	36.1	41.8	9.7	7.2	65.6	42.4	7.0	4.3	1.9	1.0
TA	Thur, Pfyn 395	1.3	1.2	38.8	31.3	9.6	6.3	66.4	29.4	6.9	3.9	2.0	1.1
TB	Thur, Uesslingen 380	2	1.8	45.7	36.6	13.3	10.1	68.3	42.2	9.6	6.6	2.5	1.5
TC	Thur, Niederneunforn 372	1.4	1.4	41.3	35.0	8.8	7.2	65.2	30.8	6.3	4.5	1.9	1.2
TD	Thur, Gütigheusen 368	1.7	1.5	49.2	37.6	12.2	8.3	68.5	35.9	8.6	5.2	2.3	1.3
TE	Thur, Kleinandelfingen 358	1.7	1.6	44.9	30.0	12.0	9.2	67.1	28.2	8.4	5.7	2.2	1.5
Mean		**1.5**	**1.5**	**35.5**	**36.2**	**9.9**	**8.3**	**65.8**	**40.4**	**7.9**	**7.0**	**2.2**	**1.5**

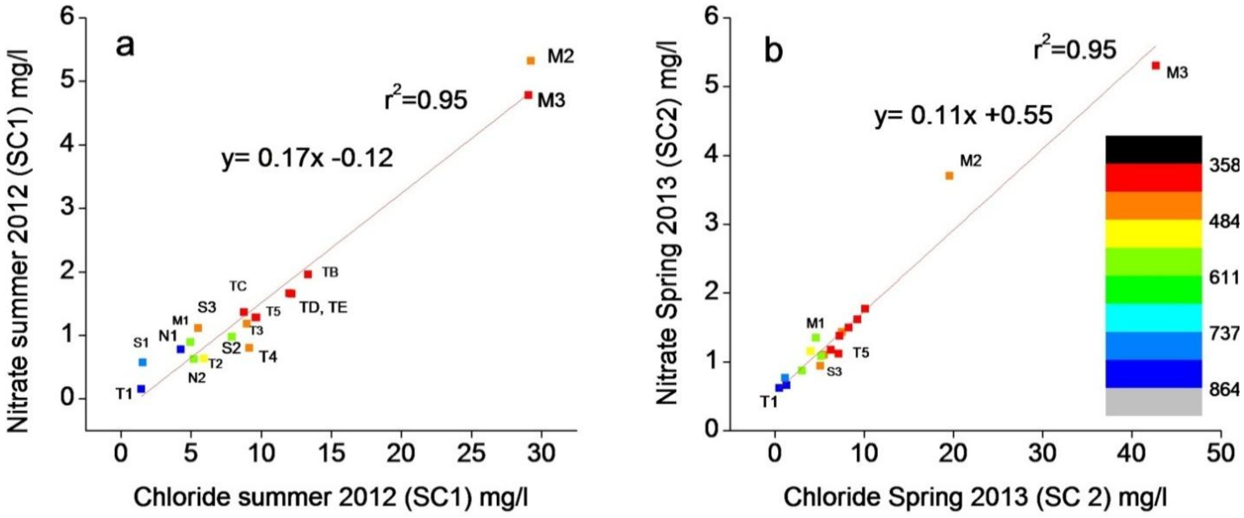

Figure S1 Relationship between nitrate (± 0.1 mg N/l) and chloride (± 0.2 mg/l) concentration in summer SC1 (a) and spring SC2 (b) Legend indicates the color map of elevation.

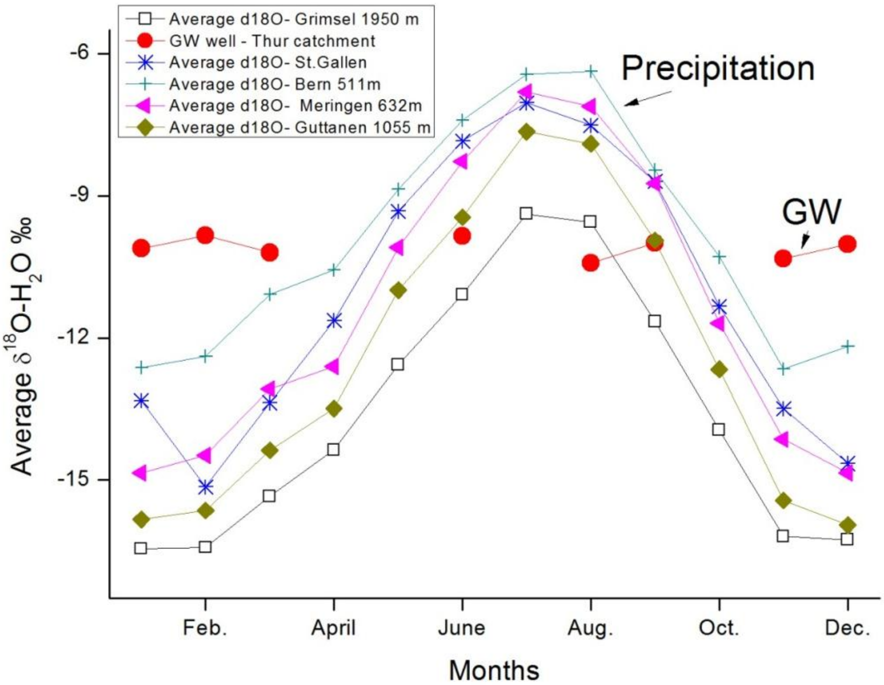

Figure S2 Average $\delta^{18}O$ (H_2O) ‰ over a decade in precipitation samples from the NAQUA ISOT monitoring stations maintained by FOEN in Switzerland (1970-2008) with varying elevations namely Bern at 511 m, Meringen at 632 m, Guttanen at 1055 m, Grimsel at 1950 m and from St. Gallen at 779 m station (between 2004-2013). The average $\delta^{18}O$ (H_2O) in the period 2010-2013 in groundwater from the Thur catchment is also represented at the Marstätten station 417 m. **Source:** FOEN-NAQUA monitoring program.

Table S2 A comparison of average monthly nitrate, total phosphorus (TP) and ammonium loads in the Murg river and at the Matzingen WWTP located in the lower Murg SC in 2012 and 2013. The ratio of the loads released from the WWTP to the river load are calculated to show the contribution of the WWTP load to the river load.

Sampling period	Discharge Q (m^3/day)				Nitrate Load (kg/day)						Total Phosphorus Load (kg/day)						Ammonium Load (kg/day)					
	Murg 2012	Murg 2013	WWTP 2012	WWTP 2013	Murg 2012	WWTP 2012	Ratio 2012	Murg 2013	WWTP 2013	Ratio 2013	Murg 2012	WWTP 2012	Ratio 2012	Murg 2013	WWTP 2013	Ratio 2013	Murg 2012	WWTP 2012	Ratio 2012	Murg 2013	WWTP 2013	Ratio 2013
January	470020	641950	12630	17290	1760	126	0.07	3875	190	0.05	30	4.9	0.17	96	4	0.04	15.04	0.88	0.06	40.44	0.52	0.01
February	271300	274750	9680	8100	1280	310	0.24	536	162	0.30	14	13.0	0.94	3	2	0.70	15.74	0.68	0.04	3.30	0.24	0.07
March	200450	351650	5430	8330	930	85	0.09	2244	175	0.08	7.0	1.8	0.26	63	3.5	0.06	3.01	0.33	0.11	81.93	0.58	0.01
April	217730	268700	5160	12900	1120	130	0.11	1061	219	0.21	13	2.6	0.20	8	3.7	0.45	3.70	0.46	0.13	3.76	0.77	0.21
May	159840	273890	5680	9820	700	33	0.05	1189	167	0.14	13	1.9	0.15	25	6.6	0.26	5.75	0.28	0.05	0.82	0.98	1.20
June	521860	292030	6390	9280	1980	84	0.04	1212	102	0.08	22	2.0	0.09	30	6.6	0.22	8.87	0.38	0.04	8.76	0.56	0.06
July	174530	127000	5050	5520	970	83	0.09	880	72	0.08	7	2.0	0.28	15	3.2	0.21	8.20	0.20	0.02	-------	0.33	----
August	162430	133060	5900	5640	750	127	0.17	955	214	0.22	9	1.8	0.21	6	3	0.52	3.57	0.18	0.05	4.39	0.45	0.10
September	307580	247970	9290	16820	1050	207	0.2	1123	118	0.10	17	3.5	0.21	25	5.4	0.21	3.69	0.37	0.10	3.97	0.67	0.17
October	505440	241060	14130	6160	2080	156	0.08	1396	123	0.09	36	5.4	0.15	20	2.3	0.12	4.55	0.28	0.06	7.95	0.25	0.03
November	535680	274750	22730	9070	2030	273	0.13	1289	127	0.10	55	16.0	0.29	15	5.3	0.35	5.36	1.14	0.21	6.04	0.64	0.11
December	941760	237600	23850	6280	2800	262	0.09	1171	107	0.09	107	4.1	0.04	10	2.1	0.21	36.73	1.19	0.03	4.75	0.38	0.08

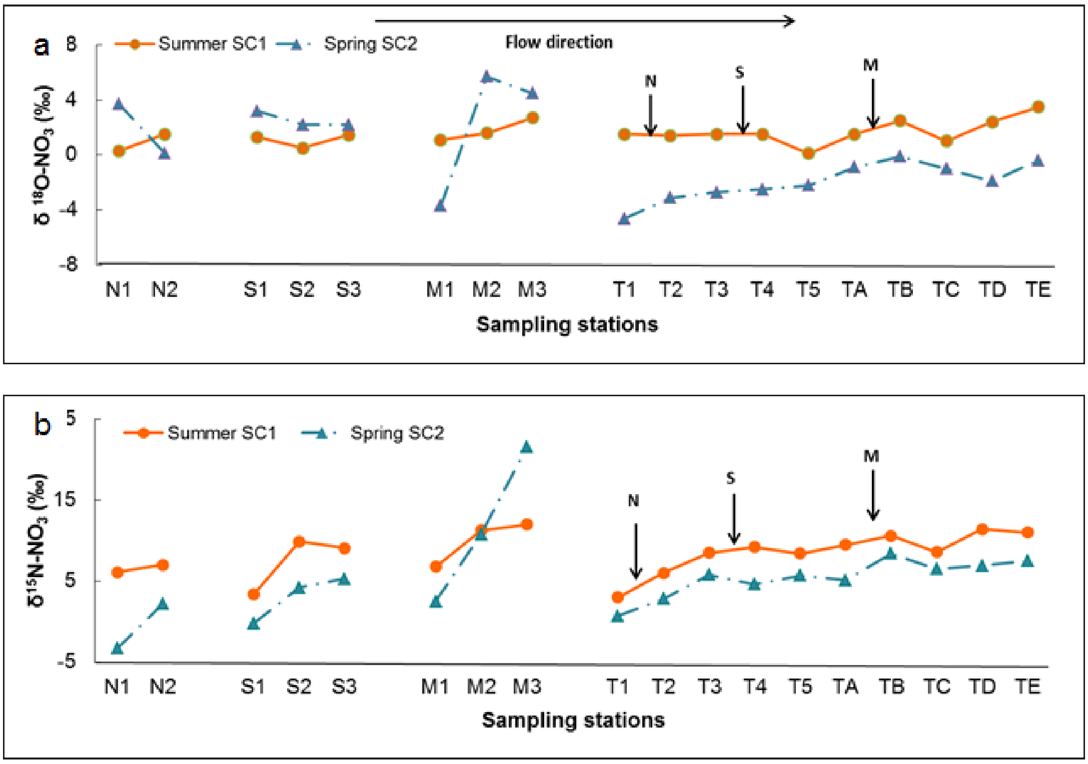

Figure S3 The variation of the isotopes of nitrate (a. $\delta^{18}O\text{-}NO_3$ ‰ and b. $\delta^{15}N\text{-}NO_3$ ‰) in the Thur River and its tributaries. The junctions of the tributaries Murg (M), Necker (N) and Sitter (S) are also indicated.

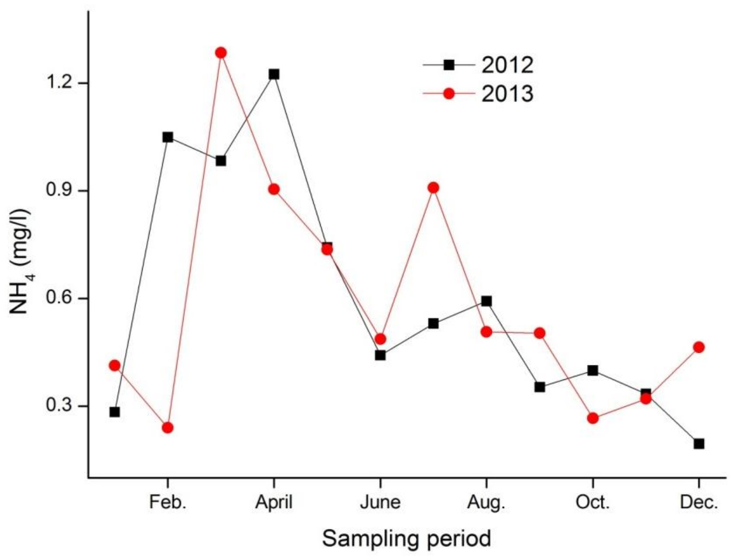

Figure S4 The average monthly concentration of ammonium in precipitation samples from Duebendorf from the FOEN-NAQUA-ISOT isotope monitoring program from FOEN in 2012 and 2013.

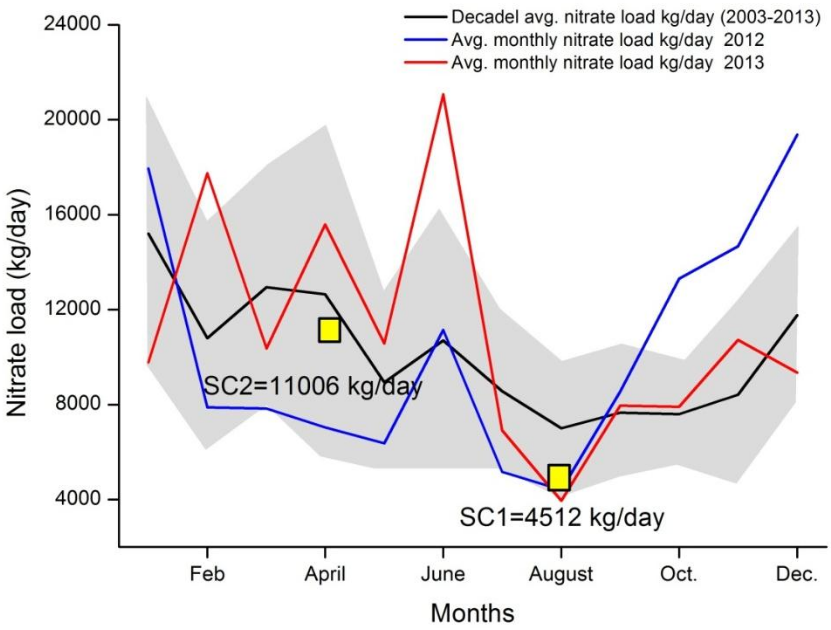

Figure S5 The SC1 and SC2 nitrate loads (kg/day) illustrated in shaded squares, average monthly nitrate load variation in 2012 and 2013 compared together with the long-term monthly load variation (1993-2013). The standard deviation representing monthly variation over the two decades is represented in the grey shaded area.

Chapter 5 Conclusions

The large investment in river restoration projects around the world, together with regulatory changes in countries promoting restoration along several thousand kilometres of rivers pose several challenges to practitioners. There is an urgent need to increase the mechanistic understanding of coupled hydrological and ecological processes with respect to ecosystem functioning, biodiversity and water quality in rivers along restored corridors. Understanding the feedback mechanisms between hydrological, ecological and morphological processes is vital and should then be followed by process-based prognostic modeling of key coupled processes at several scales. However, often many restoration projects around the world are large-scale trial-and-error field experiments, potentially lacking effective strategies for achieving desired goals.

Riparian vegetation typically occurs in patches (i.e., areas that differ from their surroundings in structure or function) that are controlled by the hydrological regime of the river (frequency and magnitude of flooding events). The dynamic and interactive mosaic characteristic for floodplains not only allows many species to co-exist but facilitates the cycling of organic matter and nutrients at the floodplain scale. Because the various habitat patches of a floodplain are connected, there may be extensive fluxes of nutrients and energy across boundaries and many organisms may derive resources from more than one type of habitat. Many studies in the past have investigated the morphological changes occurring due to river restoration and its impact on flood levels. Studies of restoration effects on travel time distribution between river and groundwater, together with localized groundwater – reactive transport models to better understand the hyporheic connectivity have been done. Although, there exists a general consensus among the restoration practitioners about the increase in the natural attenuation capacity of rivers, by accentuating in-stream ecosystem functioning along restored corridors, it has been seldom investigated. The changes to bio-geochemical processes on a temporal scale taking into account the seasonal and hydrological changes have been seldom investigated along river reach-scales. A catchment-scale perspective to understand the solute pathways and seasonal changes to solute fluxes at critical points in the catchment is also recognized to be important in planning future restoration projects, but it has not be investigated much, especially in large catchments.

The overall goal of this Ph.D. thesis was to deepen the understanding of the effect of river restoration and hydrological changes on the biogeochemical processes affecting water quality in a river and comparing the effects on different spatial and temporal scales. Extensive field investigations and lab measurements were thus conducted to assess several water quality indicators and the processes that affect them on a river reach and catchment scale.

The first step towards understanding the needs and shortcomings of restoration projects was to make a systematic evaluation of the completed restoration projects in various geographical regions around the world. A detailed targeted technical review of case studies of those projects that aimed for water quality amelioration through river restoration was done as described in Chapter 2. The projects were selected from four industrialized countries spread across three continents - South Korea, Japan (from Asia), Scotland (from Europe) and U.S.A. (from North America); to compare and contrast the significant climatic, socio-political differences and their influence on the choice of restoration measures and outcomes. Although geographically different, the countries selected have faced similar problems (increased agriculture and urban development) that have caused water quality deterioration and in turn habitat destruction in their surface water bodies. To address this, changes to water management policies have evolved with time. They have periodically changed from primarily addressing pollution-related problems to a more holistic approach, by adopting integrated river basin management. In the case-studies considered, the restored corridors varied in size and the adopted measures were different, reflecting the localized problems and objectives. However, a common thread was identified among these successful projects, in that there was a strong emphasis on clearly defining the objectives of the restoration projects with systematic pre-restoration monitoring of pre-defined indicators. In addition to this, there was an emphasis on restricting the source of the pollutants through engineering alterations to the public infrastructure in the catchment like creating new or up-grading storm water controls, sewage treatment plants and decommissioning of highways/culverts that covered the river. Thus, the main points learned from the case studies, for water quality amelioration through river restoration are:

a. Selection of appropriate site-specific restoration measures (often in combination) by pre-restoration identification of the critical parameters that are to be rectified.

b. Involvement of the public is encouraged at various phases of the restoration project, in the planning phase as well as in the pre - and post-restoration monitoring phases.

c. Having a designated post-restoration monitoring period with specific budget allocation to test success.

d. Reducing the pollutant source by the creation of buffer strips in agricultural areas and up-grading/installation of necessary public infrastructure.

The changes to the water management policies in the industrialized nations discussed in this review are also an important factor in the realization of successful restoration projects in these countries. They have achieved this by adopting a holistic approach to river basin management. Additional changes to these policies are desired that lay more emphasis on public participation and promoting catchment - wide pollution prevention in tandem with the river reach-scale measures.

The next step was to make a detailed investigation of the bio-geochemical processes affecting water quality on a river reach-scale by conducting high-frequency monitoring of selected water quality parameters. This was done to estimate the natural attenuation capacity of the rivers particularly for understanding the function of a restored river corridor. The lack of pre-restoration temporal data poses a major challenge for success evaluation of several completed restoration projects. In this thesis, a spatial method of post-restoration water quality monitoring is implemented upstream and downstream of the restored section as described in Chapter 3. A sub-set of critical water quality parameters was indentified from a large dataset of more than 20 measured parameters. The bio-geochemical processes that affect their daily changes and alter their seasonal inter-relationships was studied by conducting the sampling campaigns in three different seasons (under different hydrological conditions). The high-frequency monitoring has been proven essential to capture the significant daily changes, which are related to the daytime – nighttime biological changes that occur in relation to the solar photo cycle.

A summer storm event, resulted in increased nitrate and chloride accumulation at the outlet of the catchment followed by a delayed dilution, in comparison to the immediate dilution effect observed along the rest of the river stretch. This storm event also caused a reduction of dissolved organic carbon (DOC) by dilution along the entire observed river stretch. The observed reduction in the diurnal variability of dissolved oxygen (DO) in the channelized parts of the river during the storm event is an indication of higher turbidity turnover affecting the production-respiration pattern - but this does not affect the diurnal variability in the restored section. The stream ecosystem functioning, which is expected to be altered by river restoration, was tested under different flow conditions. The diurnal cycles of pH and DO were driven by in-stream biological processes, mainly photosynthesis and respiration. During low flow in autumn a reduction of DOC (in nighttime) and nitrate (in the pre-dawn period) was observed downstream of the restored section, which is attributed to biological processes that are expected to be accentuated by increased habitat diversity post-restoration.

Therefore, the main conclusions are that, during the spatial comparison of the restored stretch with a reference stretch, local effects like diffuse inflow/outflow and major point sources of pollution need to be considered and incorporated in the post restoration assessment. The ever-changing physical meandering of the river at the restored stretch can also result in temporarily altered biota and thus the system might take a long time to reach equilibrium, up to several years or decades. Therefore, a post-restoration success assessment needs to be made at regular intervals (5 years, 10 years and so on) until a system equilibrium is reached. The main take-home message from this study for future restoration projects is a recommendation for restoration of longer river stretches and conducting a detailed pre-restoration water quality survey using a pre-defined set of water quality parameters (like those selected in this study namely pH, DO, EC, temperature, nitrate and DOC) before performing physical alterations to the river. This should be followed by monitoring of these selected parameters at regular time intervals post-restoration. In particular, the performance of the restoration outcomes under various discharge conditions in different seasons needs to be evaluated. The methods and outcomes derived from this part of the thesis is considered to be vital for the planning of future restoration projects and for comparison of these outcomes with other such completed projects.

The final step was a scale-up to incorporate a catchment-scale perspective to identify the pathways of various solutes in the catchment. The simplified method - Integrated Spatial Snap-shot method (ISSM), involves the identification of a select group of monitoring stations at critical points in the catchment and the analysis of fluxes at two contrasting discharge patterns in two extreme seasons.

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 changes were identified. The seasonal changes to catchment fluxes were studied to determine the seasonal patterns affecting the variation of the pathways. The major sources of nitrate in the catchment were identified using nitrate isotopes. The hotspots of water quality changes were identified at the junctions of the tributaries. A nutrient rich tributary – the Murg River in the lower part of the catchment, which has the highest population density and subsequently numerous waste water treatment plants (WWTPs), alters the Thur River chemistry during both seasons. Furthermore, the dilution of conservative tracers like Na^+, Ca^{2+}, K^+ and Cl^- is evident during high flow particularly at the junctions of the higher tributaries, which are expected to carry more melt water in spring. This is validated with a lighter isotopic composition of water isotopes in spring, particularly in the headwaters of the Thur River and in the higher tributaries like the Sitter and Necker that are more influenced by precipitation. During low flow, the heavier isotopic composition of the water isotopes in the rivers was comparable to that of the isotopic composition of groundwater, indicating it was mainly groundwater fed in base flow conditions.

The nitrate isotopes reveal a significant seasonal differentiation in the sources of nitrate in the lower parts of the catchment. Nitrate changes from predominantly a manure/WWTP signature during low flow to a mixture of signatures from soil nitrogen and nitrified ammonia from rain during the high flow season in spring. This interpretation is supported by comparing the WWTP loads and the river loads in the lower part of the Murg, which show lower WWTP contributions during high flow. Additionally, when the total load from the largest WWTP in the catchment is extrapolated to the total population in the catchment (to calculate the total contribution of WWTP loads), its contribution during the low flow season (in summer) is double that of the high flow season (in spring). Therefore, there is clear evidence suggesting additional nitrate contribution from the catchment other than WWTP in the high flow season.

While WWTP loads play a significant role during low flow, as observed in the summer sampling. In addition to this, when the river loads are compared in both seasons, there is a significant contribution of nitrate from the headwaters of the Thur and Necker in spring. Here there seems to be a significant effect of manure application and soil flushing in spring, that contribute additional nitrate to the river apart from nitrification of ammonia from wet deposition as indicated by the nitrate isotopes.

This method is particularly effective when the snap-shot campaigns are representative of the major hydrological changes in the catchment. It would be useful in remote areas and developing countries where routine sampling is restricted by lack of adequate resources. This method can be further enhanced using additional isotopes like boron and with bacterial source tracking to differentiate sewage and manure. The limitations of this method over high-frequency sampling is the lack of continuous data to verify pollutant peaks especially during events. Thus, the ISSM is recommended as a preliminary method to identify the critical areas in a large catchment, which can then be frequently monitored to obtain further insights.
In this thesis, two contrasting methods with two different objectives were developed and implemented. While on one hand the ISSM method requires less data and is a simplified catchment-wide monitoring method, on the other hand the river reach-scale study involved a high-frequency monitoring method, which is data intensive. Both these methods are suitable for different types of studies, the ISSM method is suitable as a preliminary study to understand the catchment fluxes and nutrient dynamics. The river reach-scale high frequency monitoring method, is mainly recommended to study river reach-scale processes and bio-geochemical reactions at a localized river section and the dynamic hydrologic regimes that can influence these processes.

In summary, the following main objectives of the thesis have been achieved:

- The important lessons learned from past restoration projects have been summarized, to make and inventory of do’s and do-not’s for future projects.

- The key water quality parameters and the bio-geochemical processes affecting them on a river reach scale have been identified, which are useful for the post-restoration monitoring of future restoration projects.

- The effect of hydrological changes on bio-geochemical processes was also studied by adopting monitoring in different seasons under different hydrological conditions.

- A catchment-scale simplified monitoring method is developed to identify the solute pathways and to classify the major sources of nitrate and their seasonal variation is assessed through solute fluxes. This method is applicable to different catchments in different geographical conditions.

In the following chapter an outlook is given. Some ideas for future research projects and preliminary analysis of some data obtained during the course of this thesis of some sub-projects are presented that would be interesting to pursue.

Chapter 6 Outlook – Recommendations for further studies

This is a summary of some additional studies conducted during the course of the thesis. These studies are presented together with a rudimentary analysis of the data collected. This chapter is intended to summarize the initial promising findings to make recommendations for further studies on these topics.

6.1 River restoration's influence on hyporheic exchange

6.1.1 Introduction

Restoration projects that involve physical alterations in the river bed include measures like removal of overbanks, and bank armouring etc. An increase in hyporheic exchange as a result of such river restoration measures is common (Vogt et al., 2010). This improved connectivity between river and groundwater is expected to be positive for the self-cleaning capacity of the river by making it a hotspot for biogeochemical processing and as thermal refugia for biota (e.g., Johnston 1991; Tockner and Stanford 2002; McClain et al., 2003; Lautz and Fanelli 2008; Cha et al., 2009; Vogt et al., 2010). Fluctuations of electrical conductivity (EC) in rivers may be caused by several factors. Impacts due to waste water input, road salting and precipitation events are common factors affecting the EC concentration in the river.

In this sub-chapter, we investigate travel times of the infiltered river water during passage through groundwater. The EC time series are used to calculate travel time between the river and young hyporheic groundwater. This is done to compare the hyporheic connectivity of a restored section at the lower reach of the losing Thur River with that of a channelized section (6 km upstream of the restored section). This is done using long-term time series of EC in the river and in the adjacent piezometers. By analysing the diurnal oscillations of EC observed in the river and nearby piezometers, we obtain the full distribution of travel times by applying cross-correlation and non-parametric deconvolution methods. This method has been developed by Cirpka et al. (2007) and previously applied in the Thur River by Vogt et al. (2010).

6.1.2 Methods

Continous monitoring (at 30 minute temporal frequency) of EC and absolute pressure (m) was carried out at three surface water monitoring stations (DL/N 70, STS AG, Switzerland). The sensors were coupled to an integrated data logger that recorded values at 25°C after temperature compensation; single measurement precision is ±0.1% for absolute pressure head and is ±2% for EC. In the corresponding piezometers the high frequency monitoring (also at 30 minute temporal frequency) was carried out using in-situ loggers (from Terra Transfer GmbH, Germany), which were employed after correcting for depth, to measure water level (m) and EC. The single measurement precision was ±0.1% for water level and ±1% for EC.

The surface water monitoring stations were set up at three locations in the lower part of the Thur River at Uesslingen (upstream of the restored section) – Station B (704980 E; 270675 N), Niederneunforn (location of the restored section) – Station C (700192 E; 271978 N), Gütighausen (downstream of the restored section) - Station D (698019 E; 271 877 N) (Figure 1). The piezometers were chosen adjacent to the surface water stations, at <100 m distance to capture the hyporheic exchange between the river and young groundwater. The selected piezometers were G2805 (704 565 E; 270 545 N) near Station B; R006 (700878 E; 271853 N) – located adjacent to the the channelized part and R059 (700447 E; 272001 N) – located adjacent to the restored section, near Station C and T13 (697 969 E; 271 677 N) near Station D (Figure 1). The time series of EC in the surface water monitoring station – Station B and its corresponding piezometer-G2805 and for the surface water monitoring station - Station D and its corresponding piezometer piezometer-T13 were analysed between 9.9.2013 and 31.12.2013 (Table 1). However, it was found that the connectivity between the river and the groundwater was not strong between the surface water monitoring station – Station D and the piezometer T13, therefore, this data has not been used for this study.

To compare the connectivity between the river and the aquifer, cross correlation and parametric deconvolution methods were applied to calculate travel time between river and aquifer at two locations. Station B – Uesslingen and G2805, located 5 km upstream of the restored site and at the downstream site, Station C - Niederneunforn and the two adjacent piezometers R059 and R006. Before the application of cross-correlation and parametric deconvolution methods, the data was corrected to remove outliers and adjusted for missing data by interpolation with adjacent data points to obtain a continuous data set. Further, the seasonal differences in the data was removed to make the data homogeneous. A large seasonal bias in the data was observed at the Thur River in late spring when EC in the river was significantly lower when compared to the groundwater, which has been attributed to influence of spring melt water in the river (Cirpka et al., 2007; Vogt et al., 2010). The seasonal trends were removed by fitting sine and cosine functions with various frequencies to the data by standard least square fitting and the trend signals were subtracted from the data as described in Vogt et al. (2010). The cross correlation method applied to calculate the travel time between the river and groundwater has been described by Vogt et al. (2010). Details on the deconvolution method have been described by Cirpka et al. (2007).

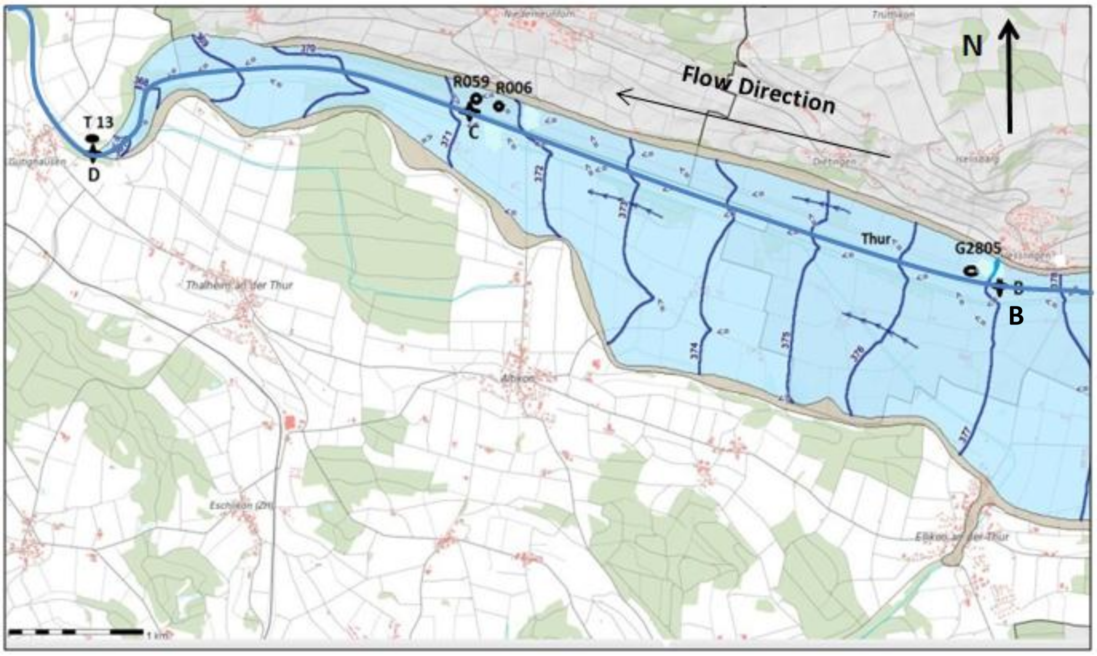

Figure 1 The location of the surface water monitoring stations (B,C and D) and corresponding piezometer (T13) located close to the river, from upstream-downstream located in the lower Thur River, Station B (upstream channelized part) - Uesslingen and piezometer G2805; Station C - Niederneunforn and piezometers R006 (in channelized part) and R059 (in the restored part); Station D (downstream channelized part) – Gütighausen and piezometer T13. The shaded portion represents the extent of the aquifer.

6.1.3 Preliminary Results

6.1.3.1 Travel time between the river and groundwater in the channelized and restored parts

For the piezometer G2805, the mean travel times (τ_{opt} respectively $t_c(g)$) determined by the two methods (cross-correlation and parametric deconvolution) were found to agree well. However, for wells R006 and R059 they do not agree very well (Table 1). This difference can be attributed to the inability of the cross-correlation method with a rectangular filter function to represent a transport process that in reality is a long tailed or multimodal transfer function.

In addition to this, the first breakthrough (initial breakthrough time – $t_0(g)$) to the piezometer G2805 is just 2 hours, which hints at an instantaneous infiltration of the river water. Comparatively, both the piezometers (R006 and R059) located at Niederneunforn have an initial breakthrough time – $t_0(g)$ of >1 day. Among the wells located in Niederneunforn, the well located in the restored part (R059) has shorter mean travel times- $t_{mod}(g)$ and shorter initial breakthrough times (Table 1, Figure 2 b, c).

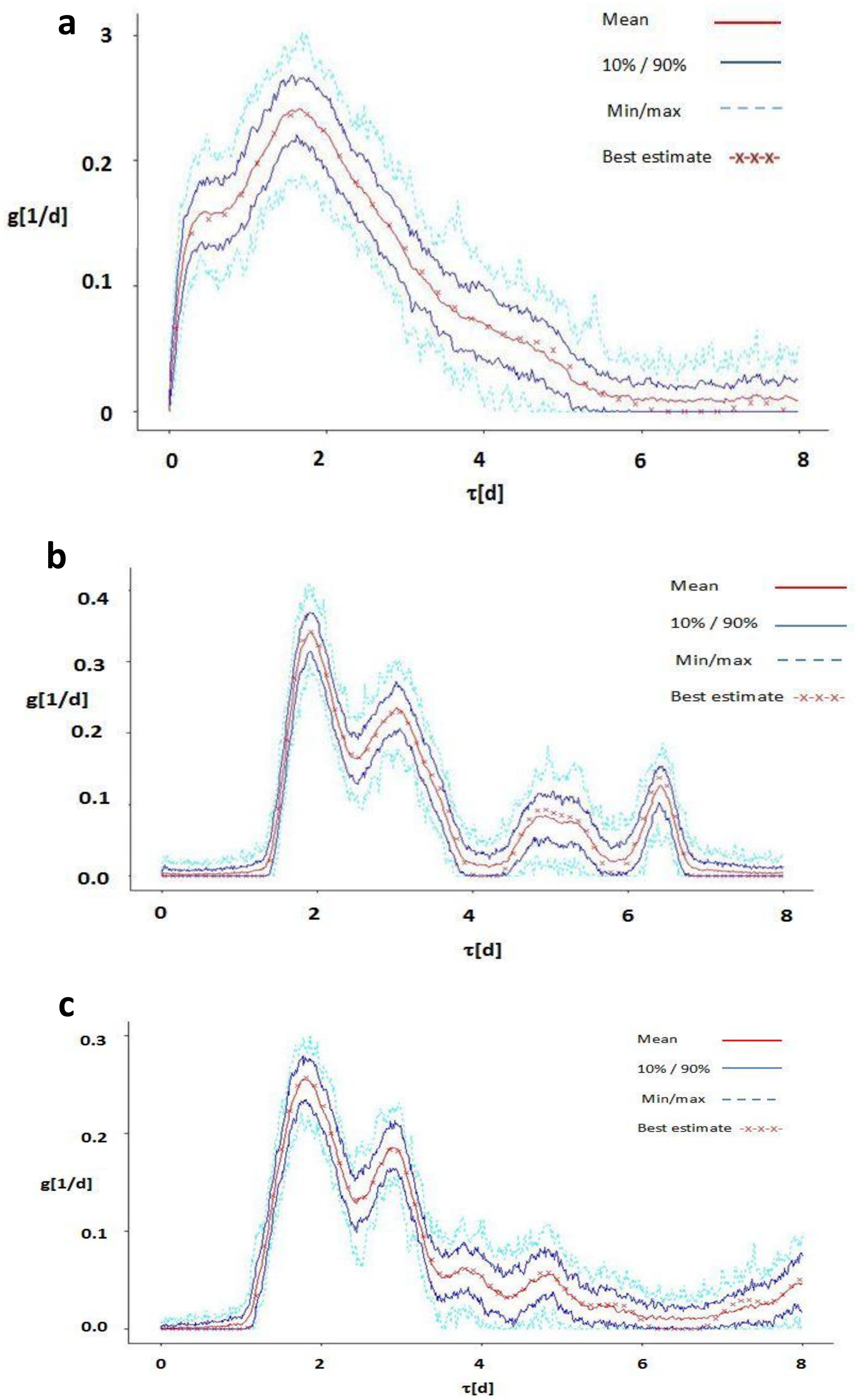

Figure 2 Transfer functions of EC from the river to groundwater as determined by non-parametric deconvolution. a.) between Station B and G2805, b.) between Station C and R006, c.) between Station C and R059

A particular strength of non-parametric deconvolution is that the shape of the travel time distribution is not predefined, facilitating the detection of multiple peaks, which is evident from Figure 2 b, c. Here, several secondary maxima of the transfer functions have been identified, the positions of which differ by integer multiples of one day. We conjecture that this is because we have used partially periodic data where the diurnal signals were not removed from the EC time series from river and groundwater.

Table 1 Summary of the parameters obtained from cross-correlation and deconvolution methods applied to calculate travel times between the river and piezometer at Uesslingen – Station B and corresponding piezometer G2805; at Niederneunforn – Station C and R006 (adjacent to the channelized part) and R059 (adjacent to the restored part). The parameters obtained from the correlation are: maximum correlation coefficient $\mathbf{r_{max}}$; optimal time shift $\boldsymbol{\tau_{opt}}$; optimal filter width $\mathbf{w_{opt}}$. The parameters obtained from deconvolution are: Recovery rate for deconvolution (zeroth moment) $\mathbf{m_0(g)}$; time of first breakthrough $\mathbf{t_0(g)}$; peak time $\mathbf{t_{mod}(g)}$; standard deviation $\boldsymbol{\sigma_g}$; center of gravity, mean travel time $\mathbf{t_c(g)}$

			Cross-Correlation			**Deconvolution**				
Surface water station-Piezometer	**Distance to river**	**Time period**	r_{max}	τ_{opt}	w_{opt}	$m_0(g)$	$t_0(g)$	$t_c(g)$	$t_{mod}(g)$	σ_g
Station B-G2805	52 m	9.9.2013 – 31.12.2013	0.97	2 d 12 h	2 d 10 h	0.72	2 h	2 d 06 h	1 d 16 h	1 d 18 h
Station C-R006	20 m	20.4.2010 – 5.1.2011	0.82	2 d 16 h	2 d 10 h	0.64	1 d 09 h	3 d 06 h	1 d 23 h	1 d 23 h
Station C-R059	25 m	4.5.2010 – 5.1.2011	0.84	2 d 15 h	3 d 10 h	0.61	1 d 02 h	3 d 01 h	1 d 19 h	2 d 07 h

6.1.3.2 Mixing between young infiltrated water and old alluvial groundwater

The zeroth moment $m_0(g)$ of the transfer function $g(\tau)$ indicates the mixing ratio of freshly infiltrated river water with older infiltrate or alluvial groundwater. Our results show that almost all water flowing through piezometers close to the river is freshly infiltrated river water. With increasing flow distance, the mixing ratio is supposed to decrease. It is interesting to note here that in the case of the piezometer in the upstream channelized part of the Thur River (G2805), the zeroth moment - $m_0(g)$ is high (72%) indicating more infiltration of freshly infiltered river water.

6.1.4 Outlook – Recommendation for further studies

A preliminary assessment of the connectivity between the river and groundwater was done by travel time estimation using EC time series, in the restored section and a upstream channelized part (5 km upstream of the restored section) along the lower Thur River. The connectivity between the river and groundwater was strong in the upstream channelized part of the Thur River indicated by a very short initial breakthrough time, as well as the shorter mean travel time of the infiltered river water. The limitation in this study, was the lack of EC time series for longer time period at the upstream channelized part. In addition to this, the diurnal periodicity in the data was not removed during the calculation, as this would have shortened the available data further; removing the diurnal periodicity would reduce the multiple peaks in the deconvolution transfer function. From this preliminary study it is clear that shorter travel times between the river and groundwater are also possible in channelized parts with embankments in losing rivers like the Thur River. In future studies, detailed local site investigations together with the calculation of the travel times with a tracer like radon-222 is recommended, to have an independent approach to determine the groundwater age.

6.2 Algal presence in the Thur River and its relationship with water quality

6.2.1 Introduction

Water quality assessment in rivers is insufficient to understand the trophic status of a river reach. Dissolved nutrients are directly available for plant uptake and both inorganic nitrogen (N) and phosphorus (P) may be low during active growth periods when there is high demand for nutrients. Therefore a cumulative understanding of the nutrient presence along with plant biomass is essential to understand the trophic status in a river (EPA, 2000).

Algae, as either free floating (as phytoplankton) or attached to the substratum (as periphyton), cause most problems associated with excessive nutrient enrichment in the river. The direct effects of excess algal presence in a river are indicated by the presence of unsightly periphyton mats or surface plankton scums (EPA, 2000).

6.2.1.1 Phytoplankton Chlorophyll a as an indicator of algal abundance

Chlorophyll is a color pigment found in primary producers like plants, algae and phytoplankton. This molecule is used in photosynthesis, as a photoreceptor. Photoreceptors absorb light energy, and chlorophyll specifically absorbs energy from sunlight (Speer, 1997). Among the different types of chlorophyll identified (a, b, c, d, e and f), each reflecting slightly different range of green light, chlorophyll a is the primary molecule responsible for photosynthesis (Speer, 1997; Fitch et. al., 2014). Therefore, for the preliminary comparison of chlorophyll presence in a river, phytoplankton chlorophyll a measurements from water samples are done in this study. Depending on the mean annual phytoplankton chlorophyll a concentrations, the trophic status of the river can be described as shown in Table 1.

Table 1 The default benchmark category boundaries for phytoplankton chlorophyll a as an indicator of algal abundance. Values are derived from DWAF (2002), Walmsley & Butty (1980) and Walmsley (1984).

Boundary	*Mean annual Phytoplankton Chlorophyll a (µg/l)*
Natural (Oligotrophic)	<10
Good (Mesotrophic)	10 – 20
Fair (Eutrophic)	20 – 30
Poor (Hypertrophic)	>30

6.2.1.2 Background theory of measurement of chlorophyll a by spectrophotometry

Spectrophotometry is a technique used for measuring the quantity of light that is absorbed or transmitted by a sample solution or mixture. The data provided by the spectrophotometer takes on two general forms: percent transmission and absorbance. **Percent transmission** is the number of photons present after passage through a sample divided by the number of photons that entered the sample multiplied by 100 (*i.e* % transmission = (photons out/ photons in) x 100) (Vernier, 2006). It relates to the quantity of absorbing component in a solution in an inverse logarithmic proportionality. **Absorbance** (A) is a function of percent transmission (T), namely $A = -\log T$. Because absorbance is plotted on a logarithmic scale, there is a direct linear relationship between the concentration of the absorbing substance and absorbance. Each substance within a given sample will absorb light at characteristic wavelengths. The color displayed by a substance represents the wavelengths reflected. An **absorption spectrum** can be generated by measuring the absorbance (after zeroing on a blank) over a range of wavelengths (Vernier, 2006).

By measuring the absorption spectrum of a substance (*i.e.* all the wavelengths at which it absorbs) it is possible to identify it or at least place it in a particular class of compounds. The wavelength at which peak absorption occurs, the **absorption maximum** (λ max), is very useful when trying to identify an unknown substance. By creating and measuring a series of standards (*e.g.* serial dilutions), it is possible to quantify the amount or concentration of a substance in a sample.

Chlorophyll a absorbs light within the violet, blue and red wavelengths while mainly reflecting green (Vernier, 2006). The most prominent absorption caused by chlorophyll a is at about 670 nm in red light (Figure 1) (Murphy et. al., 2005). The absorption of chlorophyll b is between 450 – 500 nm in blue light (Figure 1) (Vernier, 2006).

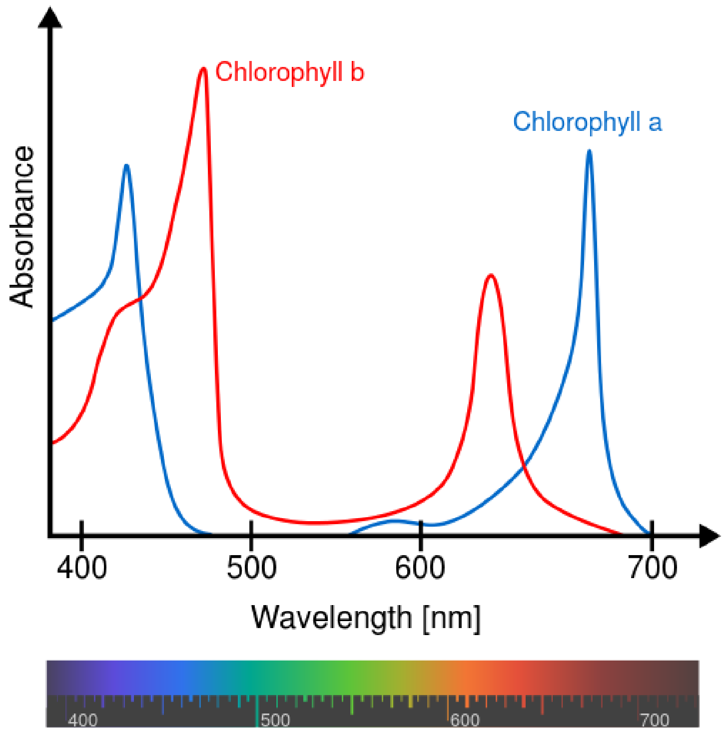

Figure 1 The comparison of absorption spectra in relation to the wavelength of light and the corresponding ranges of chlorophyll a, b. (**Source**: Licensed under CC BY-SA 3.0 via Wikimedia Commons
http://commons.wikimedia.org/wiki/File:Chlorophyll_ab_spectra-en.svg#/media/File:Chlorophyll_ab_spectra-en.svg)

6.2.2 Methods

River water samples were collected in summer, during low flow (average discharge = 16 m^3/s) on 12.06.2014 at 3 sampling locations at 0.3 m depth - Station B (6km upstream of the restored section) – Uesslingen (704980 E; 270675 N), in the restored section at Station C- Niederneunforn (700192 E; 271978 N) and at Station D – Gütigheusen (698019 E; 271 877 N) (4km downstream of the restored section) (Figure 2). The samples were collected at the sides of the cross section as well as in the middle of the river. The water quality parameters like major nitrogen species (nitrate, ammonium, nitrite), ortho-phosphate and dissolved organic carbon (DOC) were also measured. The chlorophyll a in the water samples were measured by spectrophotometry method as described in section 1.2. The laboratory method developed by Navarro et. al. (2007) was used for the measurement of chlorophyll a by spectrophotometry. The chlorophyll a standard used for calibration is from *Anacystis nidulans* algae obtained from Sigma-Aldrich Co. LLC.

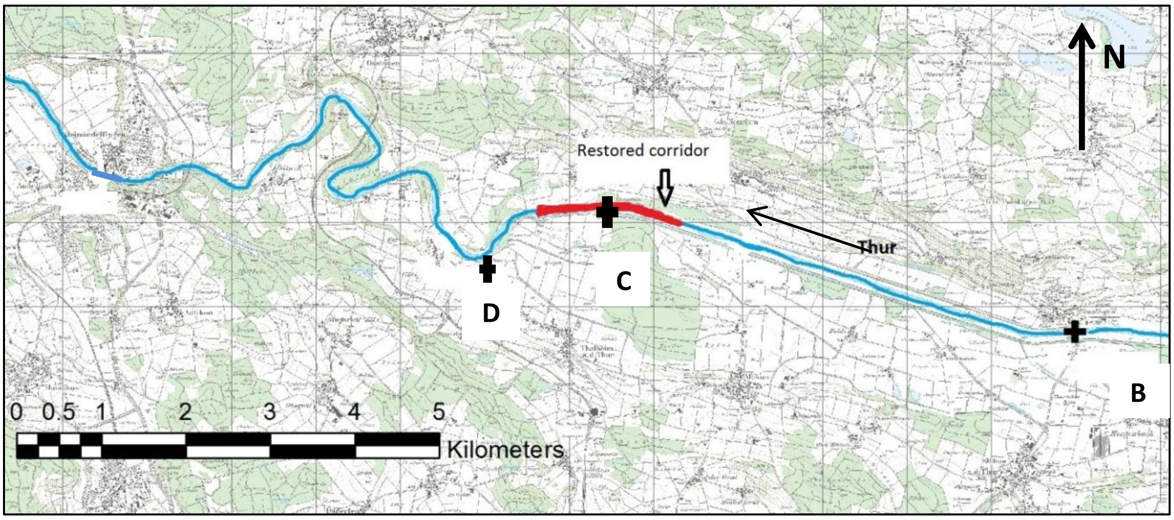

Figure 2 Location of the sampling points upstream of the restored section - Station B, at the restored section – Station C, downstream of the restored section – at Station D, located in the lower reach of the Thur River. The arrow indicates the flow direction.

6.2.3 Preliminary Results

6.2.3.1 Water quality

All samples analyzed had uniform water quality status < 30 µg /l of ortho phosphate, <45 µg /l of nitrite, <3.5 mg/l of nitrate and DOC. The only noticeable difference in water quality among the samples was in the concentration of ammonium, the sample from the middle of the cross section at station B with > 75 µg N /l of ammonium, while the rest of the samples had a concentration of < 35 µg N /l of ammonium (Figure 3).

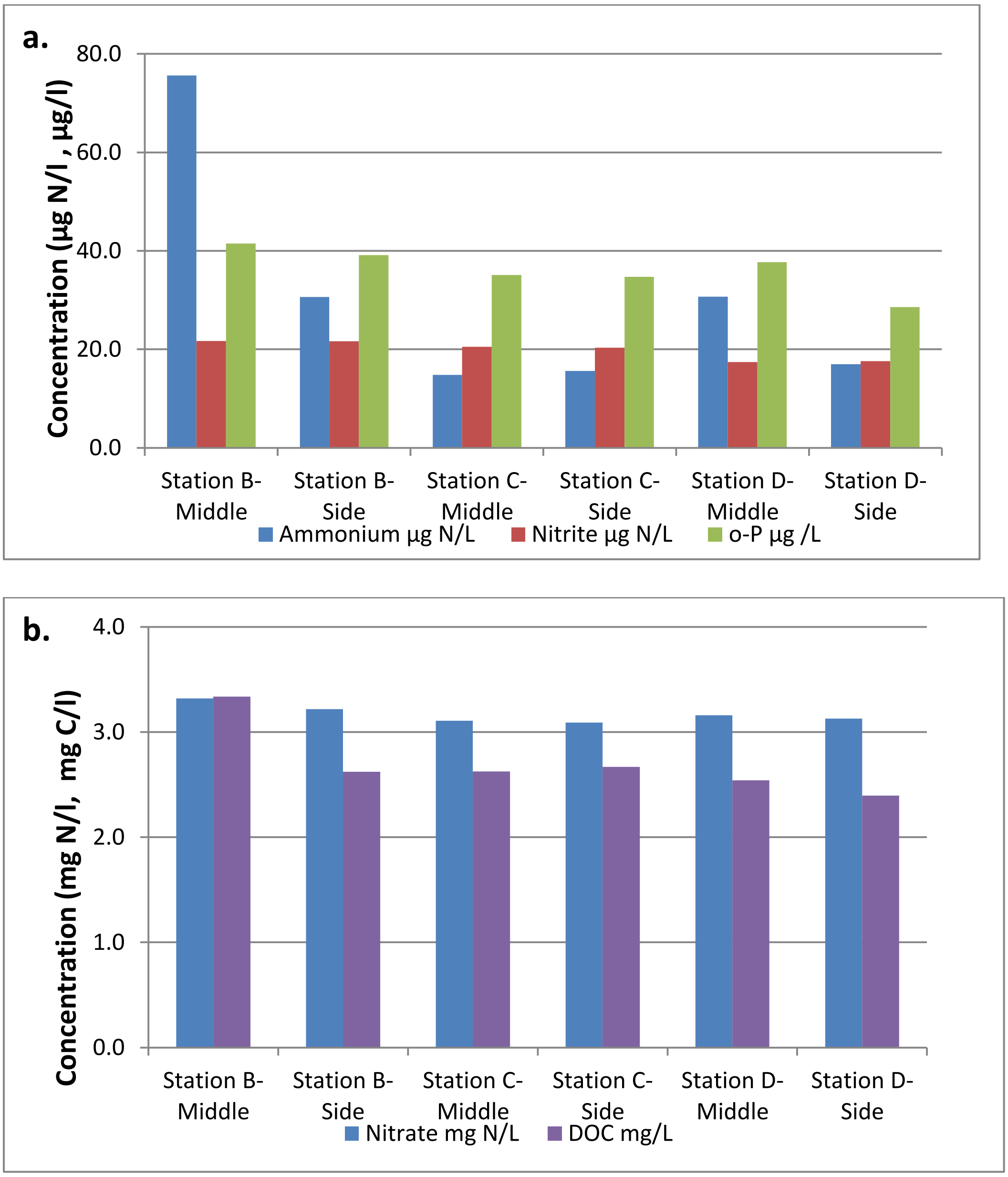

Figure 3 a. Concentrations of nitrogen species – Ammonium, nitrite (µg N/l) and concentration of ortho phosphate (µg/l) **b.** Concentration of nitrate (mg N/l) and DOC (mg C/l) at all the sampling points on 12.06.2014.

6.2.3.2 Chlorophyll a concentration determined by spectrophotometry

The chlorophyll a absorption maximum in the red light (around 670 nm) is observed for all the samples (Figure 4). The absorbance (A) values are obtained after correction for turbidity by subtracting the values obtained between wavelengths at 665 nm and 750 nm (Table 2). The absorbance values thus obtained for the various stations are then fitted in a linear regression of the calibration range of the standard in various dilutions in order to calculate the concentration of chlorophyll a as shown in Table 2.

The concentrations of chlorophyll a from all the samples is <10 µg/l, which is representative of an oligotrophic stream (Table 1). Higher chlorophyll a concentrations (>5 µg/l), are observed in the restored reach compared to the upstream and downstream samples. When the water quality was compared with the chlorophyll a concentration, a higher concentration of ammonium was found in the upstream Station B (Figure 3a), which had lower chlorophyll a concentrations (Table 2). Thus the abundance of chlorophyll a is not dictated by nutrient enrichment in the observed lower stretch of the Thur River, but rather an enhanced nutrient assimilation by phytoplankton seems to be more plausible, particularly at the restored stretch.

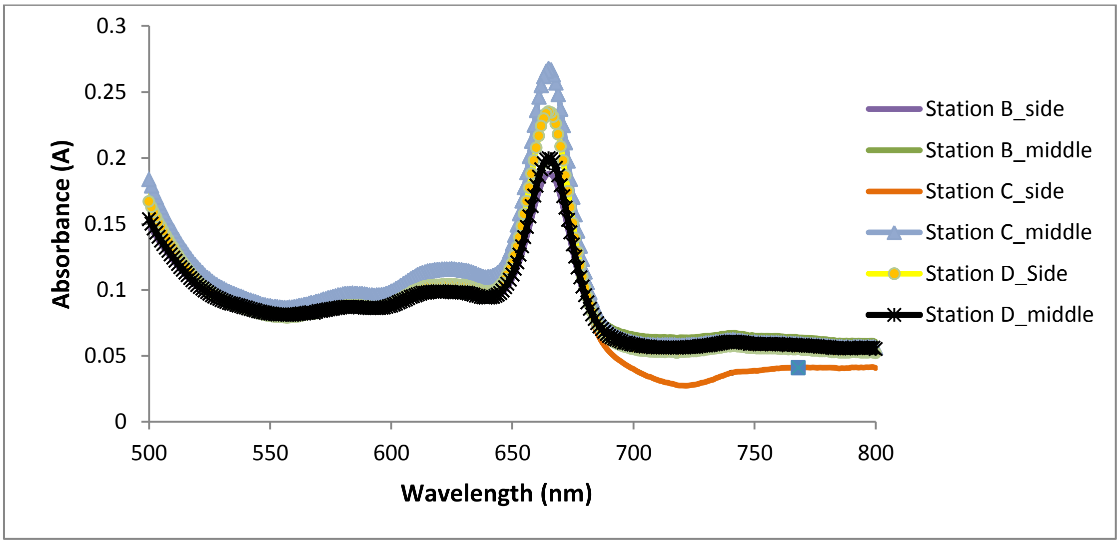

Figure 4 The chlorophyll a absorption maximum in the red light (around 670 nm) for all samples.

Table 2 The location of the sampling stations, the absorbance values of chlorophyll a observed in the wavelength of red light (around 670 nm). The calculated phytoplankton chlorophyll a values are also shown.

Stations	**Absorbance (A)**	**Phytoplankton Chlorophyll a (µg/l)**
Station B_side	0.13	3.61
Station B_middle	0.13	3.72
Station C_side	0.20	5.44
Station C_middle	0.21	5.67
Station D_side	0.18	4.93
Station D_middle	0.14	3.93

6.2.4 Outlook – Recommendation for further studies

A preliminary assessment of the algal presence in the lower reach of the Thur River is done in this study by using phytoplankton chlorophyll a as an indicator. A higher phytoplankton presence in the restored reach at Niederneunforn is indicated by the higher phytoplankton chlorophyll a (>5 µg/l**)** concentrations obtained from samples from this stretch of the river. Further studies with routine sampling during summer during various discharge conditions in the river is recommended. The determination of ash-free dry mass, algal cell bio-volume, algal species composition or production/respiration ratios in addition to phytoplankton and periphyton chlorophyll a determination is recommended to better understand the activity of algae in relation to the nutrient assimilation in the river, particularly at the restored stretch of the river.

6.3 The effect of storm events on water quality and the impact of the restored river reach

6.3.1 Introduction

The effect of various discharge regimes on different water quality parameters are seldom studied in large catchments. It has been observed by Cirpka et. al. (2007), that storm events lead to a rapid decrease in electrical conductivity (EC) by 20-50% within hours, indicating dilution of groundwater–borne water by meteoric water with considerably lower EC in the Thur River. Smith (1975) showed that peak flows caused by precipitation can play a major role in the water temperature variability in rivers. Increased streamflow by storm events can also result in increased turbidity in the rivers due to resuspension of settled sediments and erosion of riverbanks (EPA, 2012). The effect of storm events on temperature and turbidity in the river can in turn affect the dissolved oxygen (DO) in the river, by affecting the temperature-dependent solubility of DO and the biological processes causing the diel DO variability in the river as discussed in the earlier part of the thesis.

In this chapter, two sample storm events are considered from summer 2014, to assess the effect of high discharge in the river on water quality parameters like DO, EC, turbidity, and temperature

6.3.2 Methods

The sampling points were chosen in the lower part of the Thur River, one station 6 km upstream (Station 1-at Uesslingen (704980, 270675)) of the restored section and one station at the restored section (Station 2 – at Niederneunforn (700192, 271979)).

The multi-parameter probes - Aquaprobe 2000 from Aquaread Ltd., England, were used to measure DO (± 1% of reading), EC (+/- 1 uS/cm), turbidity (+/- 0.1 NTU), TDS (± 1mg/l), pH (± 0.1 pH) and temperature (± 0.5˚C) at 30 minute intervals in all the sampling locations. Further, at the outlet of the catchment – at Andelfingen (693510, 272500), the continuous monitoring of Q, EC and temperature and DO is done at 15 minute intervals from the Federal Office for the Environment, Switzerland (FOEN). This data is also used for comparison with the water quality data from the other monitoring stations. The multi-parameter probes were used to monitor various high discharge events between June and August 2014, in the Thur River. Two storm events from June-July 2014 were selected and their effects on water quality parameters are discussed in this chapter. Event 1, is defined within the following time period - (24.06.2014 (7:00) – 28.06.2014 (10:00)) and Event 2 is defined with the time period – (28.06.2014 (16:00) – 02.07.2014 (13:45)) based on the rise and fall of discharge from base-flow. The minimum - maximum range of values in the event period for the various parameters are shown in Table 1.

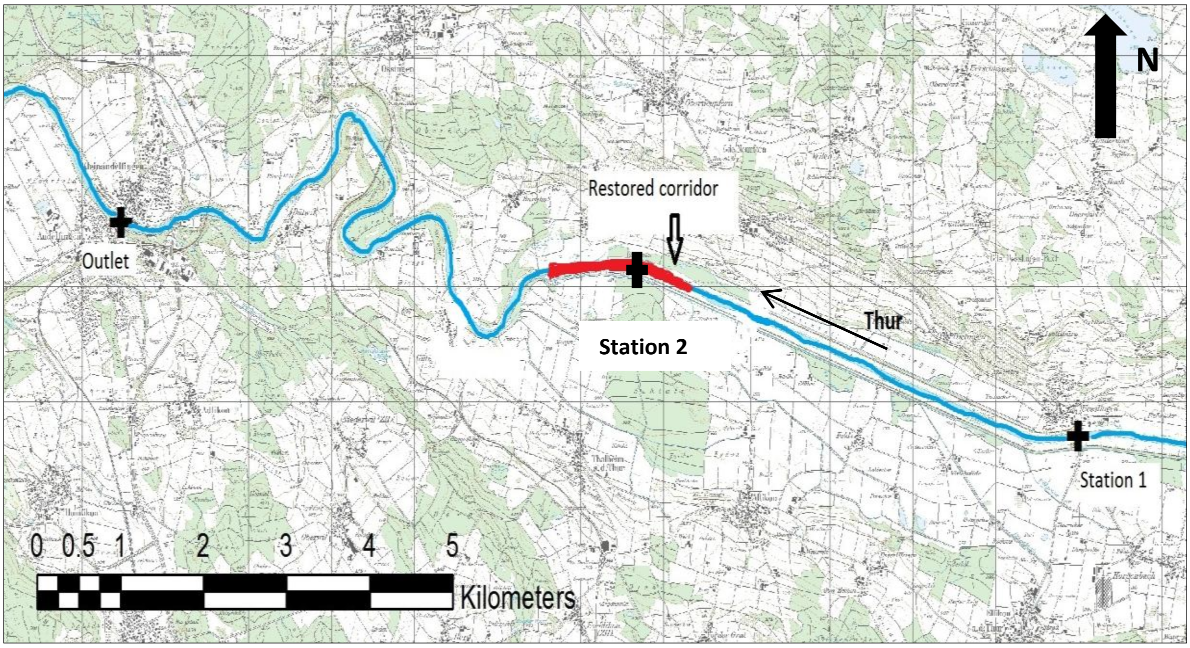

Figure 1 Location of the sampling stations – Station 1, Station 2 and the location of the FOEN monitoring station at the outlet of the catchment is also indicated. The restored river section (2 km) is shown along the Thur River. The arrow indicates the flow direction.

6.3.3 Preliminary Results

6.3.3.1 Relationship between discharge (Q) and EC

The increase of Q resulted in a decrease of EC by dilution thereby overriding the pre-event diurnal cycle of EC (Figure 2). In the monitoring period, following the peak discharge (Q_{peak}) during both Event 1 and 2, the EC continued to decrease and attained a minimum after a few hours. The delay between the flood peak and the maximum dilution of EC was observed owing to the higher velocity of the flood wave than that of the solutes. A significant negative correlation between Q and EC has been observed at the outlet of the catchment where the discharge has been measured (Table 2).

At the catchment outlet

During Event 1, the EC concentration decreased from 0.56 mS/cm at the start of the event ($Q_{initial}$ = 12.1 m^3/s) at 24.06.2014 (7:00), reaching a minimum of 0.34 mS/cm at 25.06.2014 (6:00); a 35% decrease was observed within 47 hours (Figure 2). Following the discharge peak (Q_{peak} = 81 m^3/s), there was a 10 hour delay until maximum dilution of EC_{min} was obtained (Figure 2).

During Event 2, EC decreased from 0.51 mS/cm at the start of the event ($Q_{initial}$ = 12.4 m^3/s) at 28.06.2014 (16:00), reaching a minimum of 0.30 mS/cm at 30.06.2014 (9:30); a 33% decrease was observed within 41 hours and 30 minutes. Following the discharge peak (Q_{peak} = 150 m^3/s), a 7 hour 45 minute delay was observed before the minimum EC (EC_{min}) was attained (Figure 2).

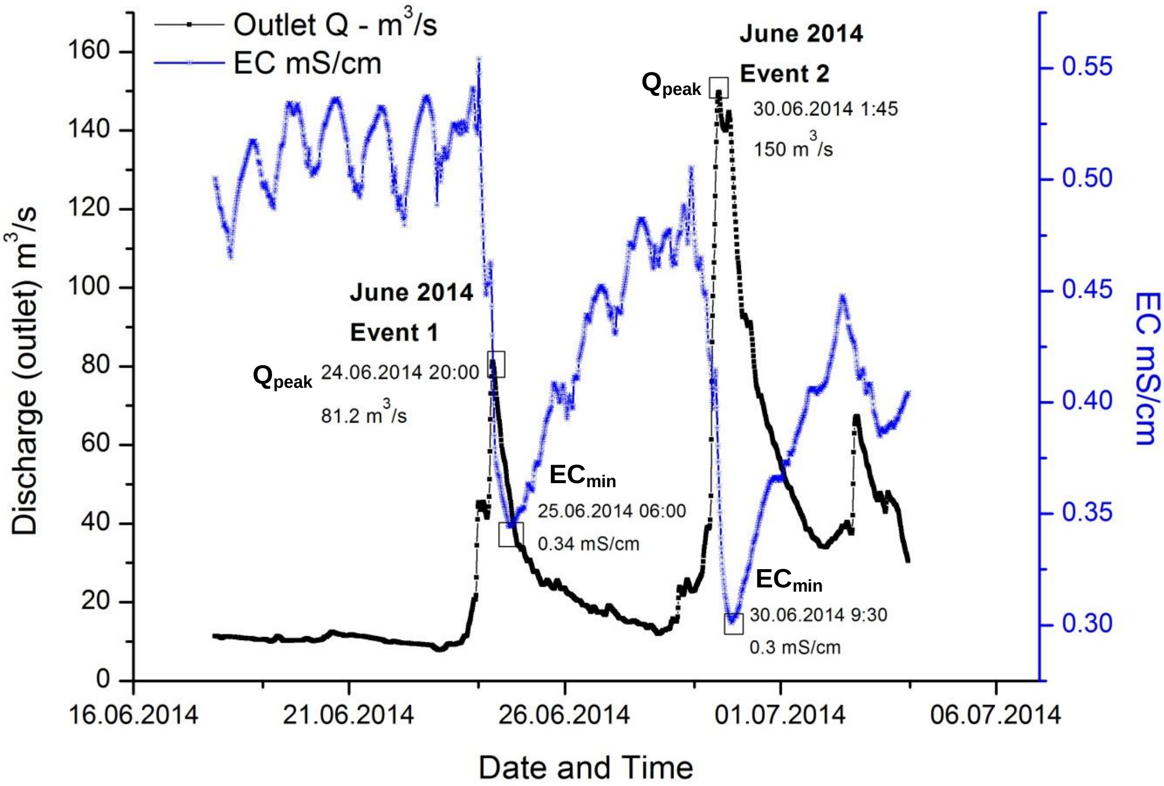

Figure 2 Relationship between discharge - Q (m^3/s) and electrical conductivity - EC (mS/cm) at the catchment outlet. The boxes indicate peak discharge (Q_{peak}) and lowest EC (EC_{min}).

At Station 1 - upstream of the restored site

During Event 1, the EC decreased from 0.556 mS/cm at the start of the event ($Q_{initial}$ = 12.1 m^3/s) at 24.06.2014 (7:00), reaching a minimum of 0.287 mS/cm at 25.06.2014 (5:10); a 48% decrease was observed within 22 hours 10 minutes (Figure 3). Following the discharge peak (Q_{peak} = 81.2 m^3/s), the maximum dilution of EC (EC_{min}) is attained after a delay of 8 hours 10 minutes.

During Event 2, the EC decreased from 0.446 mS/cm at the start of the event ($Q_{initial}$ = 12.4 m^3/s) at 28.06.2014 (16:00), reaching a minimum of 0.248 mS/cm at 30.06.2014 (7:10); a 44% decrease was observed within 39 hours 10 minutes (Figure 3). Following the discharge peak (Q_{peak} = 150 m^3/s at 30.06.2014 1:45), there was a 5 hour 25 minute delay before maximum dilution - EC_{min} is attained (Figure 3).

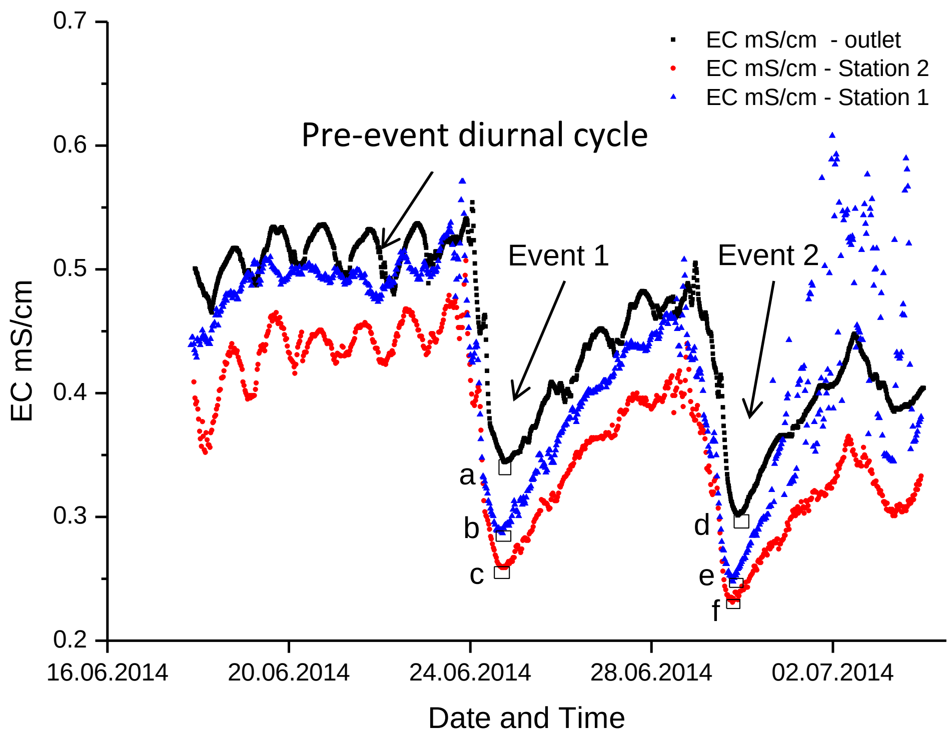

Figure 3 The EC time series in the sampling stations, the pre-event diurnal cycle is shown, dilution of EC during Event 1 and Event 2, the minimum EC - EC_{min} is indicated in boxes: **Event 1**: **a. at Outlet** - 25.06.2014 (6:00) - 0.344 mS/cm **b. at Station 1** - 25.06.2014 (5:10) - 0.287 mS/cm **c. at Station 2** - 25.06.2014 (4:50) - 0.259 mS/cm

Event 2: d. at Outlet - 30.06.2014 (9:30) - 0.301 mS/cm **e. at Station 1** - 30.06.2014 (7:10) - 0.248 mS/cm **f. at Station 2 -** 30.06.2014 (06:50) - 0.231 mS/cm

At Station 2 – at the restored section

During Event 1, the EC decreased from 0.462 mS/cm at the start of the event ($Q_{initial}$ = 12.1 m^3/s) at 24.06.2014 (7:00), reaching a minimum of 0.259 mS/cm at 25.06.2014 (4:50); a 44% decrease was observed within 21 hours 50 minutes (Figure 3). Following the discharge peak (Q_{peak} = 81.2 m^3/s), the maximum dilution of EC (EC_{min}) is attained after a delay of 7 hours 50 minutes.

During Event 2, the EC decreased from 0.446 mS/cm at the start of the event ($Q_{initial}$ = 12.4 m^3/s) at 28.06.2014 (16:10), reaching a minimum of 0.231 mS/cm at 30.06.2014 (6:50); a 48% decrease was observed within 38 hours 40 minutes (Figure 3). Following the discharge peak (Q_{peak} = 150 m^3/s) at 30.06.2014 (1:45), there was a 5 hour delay before maximum dilution - EC_{min} was attained (Figure 3).

6.3.3.2 Temperature

The temperature was observed to decrease with increasing Q. In the monitoring period, following the peak discharge (Q_{peak}) during both event 1 and 2, the temperature continued to decrease and attained a minimum after several hours in all the monitored stations (Figure 4).

At the catchment outlet

During Event 1, the temperature decreased from 18.8°C at the start of the event ($Q_{initial}$ = 12.1 m^3/s) at 24.06.2014 (7:00), reaching a minimum of 15.5°C at 26.06.2014 (6:45); a 18% decrease was observed within 47 hours 45 minutes (Figure 4). During Event 2, the temperature decreased from 20.6°C ($Q_{initial}$ = 12.4 m^3/s) at 28.06.2014 (16:00), reaching a minimum of 13.1°C at 1.07.2014 (5:15), 36% decrease was observed in 61 hours 15 minutes.

At Station 1 - upstream of the restored site

During Event 1, the temperature decreased from 18.8°C at the start of the event ($Q_{initial}$ = 12.1 m^3/s) at 24.06.2014 (7:00), to a minimum temperature of 15.9°C at 26.06.2014 (5:00), 15.4% increase was observed in 46 hours (Figure 4). During Event 2, the temperature decreased from 21.4°C ($Q_{initial}$ = 12.4 m^3/s) at 28.06.2014 (16:00), reaching a minimum of 13.2°C at 1.07.2014 (5:30), 38% decrease was observed in 61 hours 30 minutes.

At Station 2 – at the restored site

During Event 1, the temperature decreased from 18.8°C at the start of the event ($Q_{initial}$ = 12.1 m^3/s) at 24.06.2014 (7:00), to a minimum temperature of 16°C at 26.06.2014 (6:00), 14.8% decrease was observed in 47 hours (Figure 4). During Event 2, the temperature decreased from 22.5°C ($Q_{initial}$ = 12.4 m^3/s) at 28.06.2014 (16:00), reaching a minimum of 13.6°C at 1.07.2014 (6:00), 40% decrease was observed in 62 hours.

Table 1 Descriptive statistics of the various water quality parameters DO (mg/l), EC (mS/cm), turbidity (NTU) and temperature (°C) measured at all sampling stations (Station 1, Station 2 and at the outlet of the catchment) during both Event 1 (Ev. 1) and Event 2 (Ev. 2). The range: minimum – maximum values during the event are shown, n=number of values considered in the event period.

Stations	**Temperature °C**		**DO (mg/l)**		**pH**		**EC (mS/cm)**		**Turbidity (NTU)**	
Ev.1, Ev. 2	**Ev.1**	**Ev. 2**	**Ev.1**	**Ev. 2**	**Ev.1**	**Ev. 2**	**Ev.1**	**Ev. 2**	**Ev.1**	**Ev. 2**
Station 1 n = 199, 193	16-22.5	13.2-21.5	8.1–11	7.6-11.3	8-8.4	7.9-8.7	0.287 - 0.571	0.248 - 0.608	49-161	49-483
Station 2 n = 199, 189	16-23.4	13.6-22.7	7.2–10.5	6.8–10.1	8.2-8.6	8.1-8.6	0.259 - 0.507	0.231 - 0.440	0-85	0-200
Outlet n = 397, 376	15.5-22	13 - 21	7-10.8	7-10	n/a	n/a	0.344 - 0.554	0.301 - 0.505	n/a	n/a

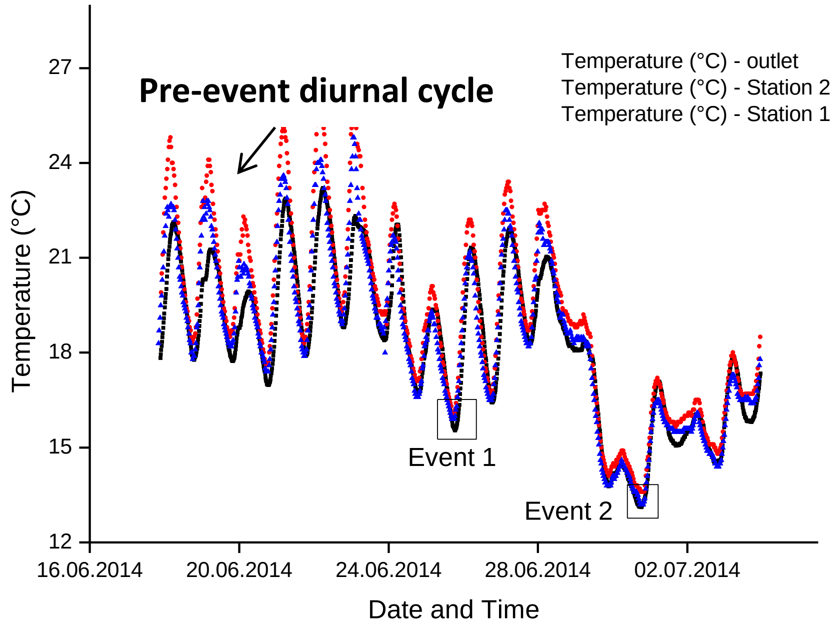

Figure 4 The temperature time series in the sampling stations, the pre-event diurnal cycle is shown, there is a decrease in the temperature during Event 1 and Event 2, the minimum temperature is indicated in boxes:

Event 1 – 26.06.2014 (6:45) – 15.5°C (Outlet); 26.06.2014 (5:00) – 15.9°C (Station 1); 26.06.2014 (6:00) – 16°C (Station 2);. **Event 2** – 1.07.2014 (5:15) – 13.1°C (Outlet); 1.07.2014 5:30 – 13.2 °C (Station 1); 1.07.2014 (6:00) – 13.6 °C (Station 2)

7.3.3.3 Dissolved oxygen (DO) and turbidity

Turbidity is the measurement of scattered light that results from the interaction of incident light with particulate material in a liquid sample. It is an expression of the optical properties of a sample that causes light rays to be scattered and absorbed rather than being transmitted as straight lines through a sample (Clesceri et. al., 1998). The turbidity is often caused by the presence of particulate or dissolved matter in the river. Higher turbidity reduces the amount of light penetrating the water, which reduces photosynthesis and the production of DO (Washington State Department of Ecology, 1991).

The high turbidity in the river due to high discharge was observed during Event 1 and 2 (Figure 5). During Event 1, following the peak discharge at the outlet ($Q_{peak\ =}$ 81 m^3/s), at 24.06.2014 (20:00) the highest turbidity value was observed at 24.06.2014 (22:40) at station 1; within 2 hours 40 minutes (Figure 5). At station 1, the peak turbidity was observed at 24.06.2014 (19:20) (the Q_{peak} is expected to have arrived earlier at station 1 compared to the catchment outlet) an instantaneous turbidity increase was observed.

Table 2 Correlation between the various water quality parameters considered. A negative sign indicates negative correlation among the parameters considered. The Pearson correlation coefficient 'r' is shown in the table, it was applied at 5% significance level.

Stations	**Q – EC**		**DO - T**		**DO - Turbidity**	
	Event 1	**Event 2**	**Event 1**	**Event 2**	**Event 1**	**Event 2**
Station 1	--------	--------	0.42	-0.78	-0.24	0.15
Station 2	---------	--------	0.46	-0.63	-0.35	0.42
Outlet	-0.4	-0.82	0.25	-0.59	-------	--------

During Event 2, following the peak discharge at the outlet ($Q_{peak\ =}$ 150 m^3/s) at 30.06.2014 (1:45), at station 1, the turbidity peak was observed at 30.06.2014 (2:40), in 55 minutes. At Station 2, it was observed at 30.06.2014 (00:50) (as the Q_{peak} would have arrived earlier at the upstream station) and an instantaneous turbidity increase was observed here. The turbidity peaks observed at the upstream station was double of the peak turbidity values observed at the restored corridor (Figure 5). The DO diurnal variation was reduced during the event period (Figure 6). The variability within a day was higher (σ>2, n=97) during the pre-event days between 18.06.2014 and 23.06.2014. During Event 1, the diurnal variability was lower (σ=0.6, n=97) on 24. - 25.06.2014. During Event 2, the diurnal variability was lower (σ=0.67, n=97) on 29. - 30.06.2014 (Figure 6). The turbidity is negatively correlated with DO during event 1 (Table 2), indicating lower oxygen productivity in high turbid water. During event 2, there is a significant positive correlation between DO and turbidity, this is hypothesized to be due to increased reaeration due to higher water velocity during a bigger event (Q_{peak}=150 m^3/s) and rapid flushing of suspended particles in the river. Further, significant negative correlation between temperature and DO was observed in all the stations during Event 2 (Table 2). This is contrary to the pre-event pattern of positive correlation between DO and temperature as explained in the earlier part of the thesis. This is attributed to the increased reaeration due to increased water velocity during high flow leading to subsequent increase in DO. Further the event water is expected to have low temperatures, which in turn affects the solubility of oxygen. Thus, when the temperature is reduced due to meteoric water in the river there was higher concentration of DO.

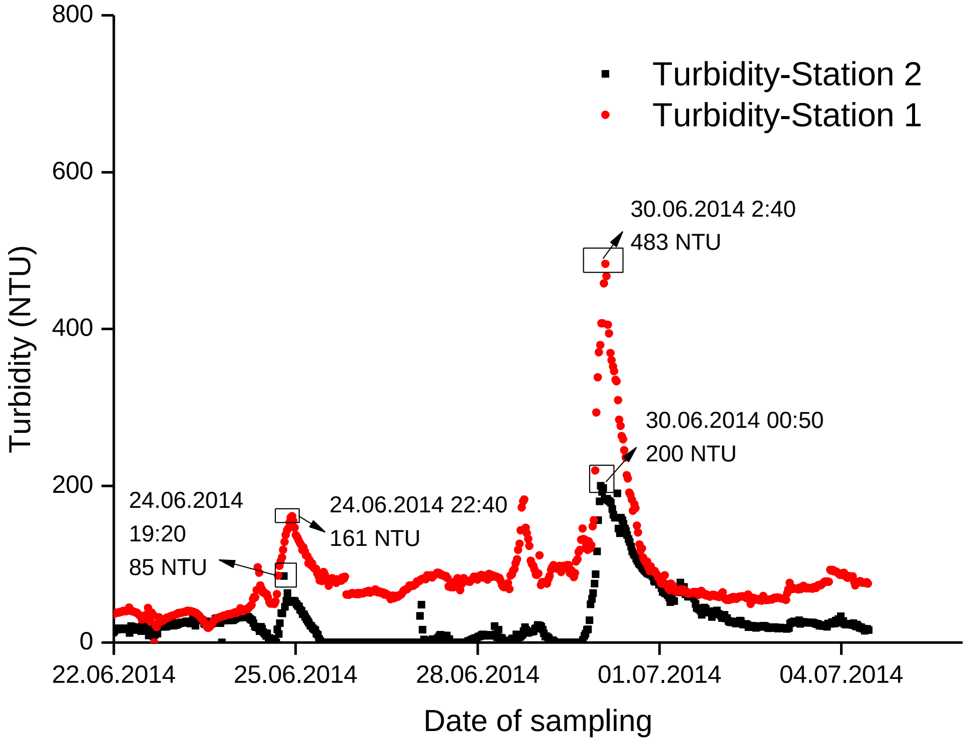

Figure 5 Turbidity measured during Event 1 and 2 at Stations 1 and 2. The peak turbidity concentrations are shown in squares for both the events.

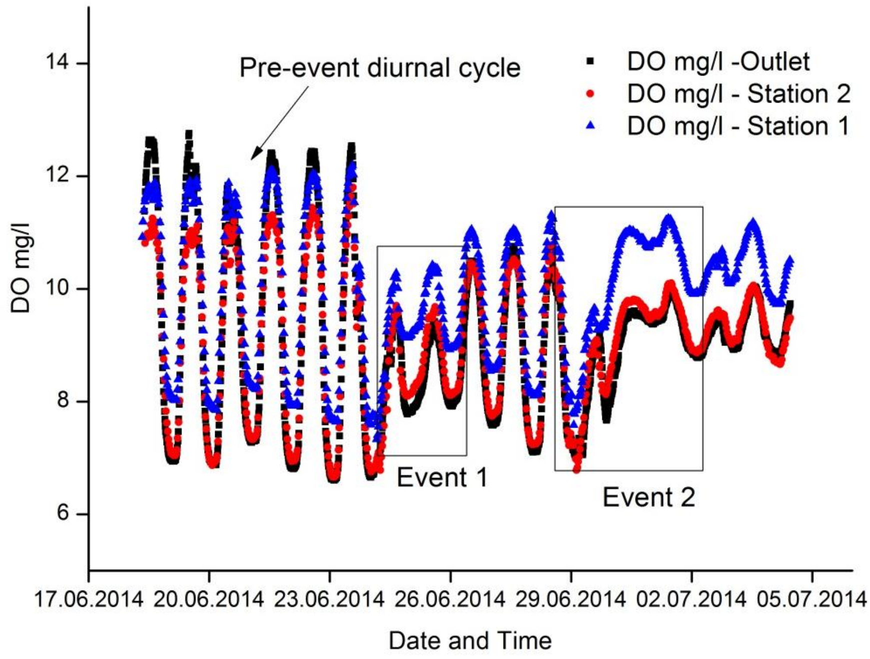

Figure 6 The DO time series in the sampling stations. The decrease in the DO diurnal variation during Event 1 and Event 2 are shown in the boxes.

6.4.4 Outlook - Recommendation for further studies

In this chapter, two sample storm events with varying discharge peaks – event 1 (Q_{peak}= 81 m^3/s) and event 2 ($Q_{oeak=}$ 150 m^3/s) were considered and the effect of these events on various water quality parameters was analyzed. An increase in discharge resulted in a decrease of EC by dilution at all monitoring stations during both events. A delay between the peak discharge (Q_{peak}) and maximum dilution of EC (EC_{min}) was observed at all monitoring stations. During the bigger event (Event 2), the delay between Q_{peak} and EC_{min} was shorter than that of the smaller event (Event 1). The decrease of EC by dilution was observed to be nearly the same for both events between 30-35% at the outlet and between 44 and 48% at the stations 1 and 2.

Following the increase in discharge, a temperature decrease of between 15 and 18% was observed at all the stations during Event 1 and between 25 and 40% at all stations during event 2. The bigger event caused a greater decrease in temperature in the river. An increase in turbidity was observed following the increase in discharge, the turbidity peak was observed in less than 3 hours following the Q_{peak} in all the stations during both the events. The turbidity peak at the upstream station 1 was nearly twice that observed at the restored site (at Station 2). The peak turbidity values corresponded to the magnitude of the peak discharge, with higher turbidity values being observed during event 2 than during event 1. The turbidity was found to be inversely correlated to the DO during event 1, thereby affecting the diurnal variability of DO. A reduction in the diurnal variability of DO was observed during both the events.

Thus the major water quality parameters were affected by the storm events and the magnitude of the event was found to play a significant role in altering the parameters. In addition, the restored section with its broader sections and lower flood velocities, was observed to have lower turbidity values. Further studies with continuous monitoring of several events of varying discharge regimes in the lower part of the Thur River incorporating the measurement of nutrients and dissolved organic matter (DOC), are also recommended to better understand the effect of storm events on water quality.

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