4th International Workshop on High-Resolution Water Quality Monitoring and Analysis

31st of May – 2nd of June 2021

Swedish University of Agricultural Sciences, Uppsala

SLU

Swedish University of Agricultural Sciences

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Welcome

Welcome to the 4th International Workshop on High-Resolution Water Quality Monitoring and Analysis!

A year overdue due to the Covid-19 pandemic, we are finally gathered to celebrate cutting edge research and technological innovation in high-resolution monitoring.

We hope that the workshop will provide a much needed forum for sharing experiences and establishing best practice in application of sensor technology in water quality studies, sharing knowledge of hydrochemical processes in diverse catchments and stimulating future collaborations between the workshop's participants. High-resolution water quality technology provides opportunities for conducting joint experiments in different catchments and establishing long-term water quality experiments and monitoring networks which bridge the gap between regulatory monitoring, e.g. for compliance with the Water Framework Directive, and short-term research monitoring efforts in single catchments. In this way, high-resolution water quality monitoring can lead to further advancements in catchment science, by integrating understanding of solutes and particulates behaviour across spatial (from stream reaches to stream networks and between catchments) and temporal scales (from storm events, seasons to decades), and their extrapolation beyond single catchment inference. We hope that the workshop will explore these synergies and opportunities provided by the high-resolution technology and will pave the way for international research and exchange of experience.

Please make full use of our online platform, watch pre-recorded presentation videos, comment, ask questions and share ideas. With 3 keynote and 36 regular presentations, we are convinced you will find something interesting and stimulating for your own research. Please mingle with nearly 150 participants from 15 countries including 22 PhD students attending a short course on high-resolution research and technology. We hope that despite its online format, the workshop will meet your expectations and you will be even more convinced to visit us in Uppsala in the future.

The Scientific Committee

Scientific description

This scientific meeting follows a series of workshops previously held in Magdeburg (2014), Sandbjerg (2016) and Clonakilty (2018). The general focus is on exploring recent technological and scientific advances in water quality measurements allowing for high-resolution determination of chemicals in water with a range of instruments deployed *in situ* (optical sensors, passive samplers, wet-chemistry analysers and lab-on-a-chip). These new technologies have brought new insights into mechanistic understanding of catchment and stream processes and are progressively utilised to evaluate the effectiveness of water management efforts.

The objective of the workshop is therefore to discuss how these new technologies and data can further advance catchment science and contribute to water resources management. This comprises evaluation of hydrological and biogeochemical responses on time-scales of individual storm events, seasons and in the long-term, and linking them to natural and anthropogenic drivers and impacts. Specifically, the workshop will address topics from instrument deployment, data collection, analysis and modelling to interpretation of hydrochemical signals and processes for individual catchments and catchment typologies.

The workshop will be held over 3 days and consist of 3 keynote lectures, 36 contributed oral presentations, a 3 discussion sessions. The specific themes of the workshop are:

- New advances in high-resolution water quality monitoring – keynote by Prof. James Kirchner.
- Extracting hydrochemical patterns and modelling of high-resolution data – keynote by Prof. Nandita Basu.
- Understanding hydrochemical and biogeochemical processes from high-resolution data – keynote by Prof. Helen Jarvie.

Keynote speakers

Professor **James Kirchner** (Department of Environmental Systems Science, ETH Zürich, Switzerland). Professor of Earth and Planetary Science and Goldman Distinguished Professor for the Physical Sciences, Emeritus University of California, Berkeley. Professor Kirchner is a world-leading hydrologist, geomorphologist and biogeochemist pioneering research areas of catchment hydrology & geochemistry, geomorphology and Earth surface processes, and analysis of environmental data. Professor Kirchner has published over 200 scientific articles on hydrology, geomorphology and biogeochemistry.

Professor **Nandita Basu** (Department of Earth and Environmental Sciences, University of Waterloo, Canada). Associate Professor, Water Sustainability and Ecohydrology. Professor Basu studies the role of humans in modifying water availability and quality through changing land use and climate, providing innovative solutions to water sustainability challenges. Professor Basu has published over 100 scientific articles on hydrology and biogeochemistry.

Professor **Helen Jarvie** (Water Institute and Department of Geography and Environmental Management, University of Waterloo, Canada). Professor Jarvie joined the Water Institute at the University of Waterloo in 2020, as Professor of Water and Global Environmental Change. Before relocating to Canada, she worked for the UK Centre for Ecology and Hydrology for 25 years. She holds Visiting Professorships in Fluvial Sciences at the University of Arkansas, USA, in Environmental Chemistry at Plymouth University, UK, and in Water Quality Science at the University of Tokyo, Japan. Professor Jarvie's research focuses on stream biogeochemistry, nutrient cycling and water quality, from watershed to global perspectives. Professor Jarvie has published over 140 scientific articles on surface water chemistry, river water quality and nutrient cycling.

Scientific committee

Dr **Magdalena Bieroza**, Workshop Organiser, Associate Professor in Water Quality Management and Senior Lecturer in Water Quality in Agricultural Landscapes (Department of Soil and Environment, SLU). Her research focuses on catchment- and reach-scale nutrient, sediment and organic matter dynamics in agricultural catchments, high-temporal resolution stream biogeochemical responses and water quality monitoring using on-line *in situ* sensors.

Dr **Jens Fölster** (Department of Aquatic Sciences and Assessment). His research focuses on evaluation of water quality data from the national environmental monitoring programs.

Emma Lannergård, PhD student (Department of Aquatic Sciences and Assessment, SLU). Her project aims to improve catchment-scale understanding of mobilisation and transport of phosphorus in streams.

Dr **Martyn Futter**, Associate Professor in Water Quality (Department of Aquatic Sciences and Assessment, SLU). Research interests: organic carbon, water quality modelling, macronutrient responses in rivers, and implementation of circular economy for water quality improvements.

Dr **Katarina Kyllmar** (Department of Soil and Environment, SLU). Her research focuses on environmental monitoring and assessment at the small agricultural catchment scale, including development of methods for water quality data collection and assessment.

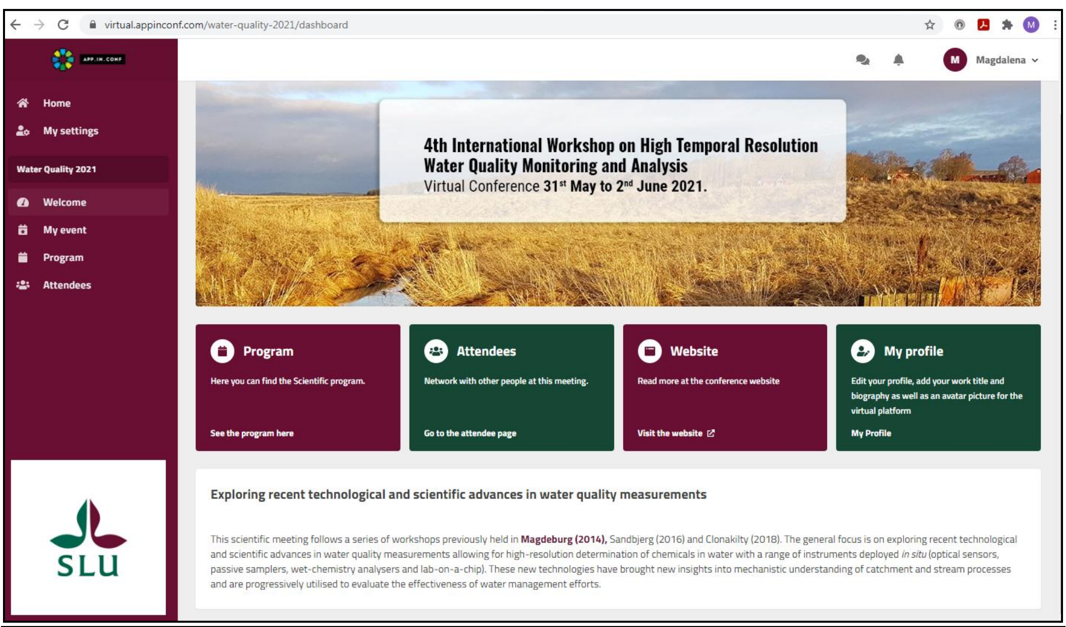
Professor **Stephan Köhler** (Department of Aquatic Sciences and Assessment, SLU). His research focuses on use of high-resolution water quality monitoring in drinking water treatment.

Online resources

Please visit our website https://www.slu.se/waterquality for further information about the workshop.

To access the online platform, please go to https://virtual.appinconf.com/ and select the workshop by putting the code 'waterquality2021'.

In the online platform, you can access the programme, read abstracts, watch video presentations, comment, ask questions and discuss.



Scientific programme

Session 1: New advances in high-resolution water quality monitoring

Chair person: Magdalena Bieroza — Mon 31st May 2021

Welcome to HighRes2021 — 12:15-12:30

1. **Alex Beaton** (National Oceanography Centre) — 12:30-12:45
   Lab-on-chip chemical sensors for automated high-resolution measurements in remote locations
2. **Per-Erik Mellander** (TEAGASC) — 12:45-13:00
   Critical pathways and critical times: apportioning nutrient transfer pathways in 10-years of continuous hydro-chemistry data
3. **Paul Floury** (Extralab) — 13:00-13:15
   Data management: From the lab on the field, through data treatment to the scientific model, can we work entirely remotely and in real time?

5 minutes break

4. **Astrid Harjung** (International Atomic Energy Agency) — 13:20-13:35
   A combined temporal resolution approach to monitor pollution sources in large rivers with nitrate isotopes
5. **Hari Ram Upadhayay** (Rothamsted Research) — 13:35-13:50
   Dynamics of fluvial hydro-sedimentological, nutrient and floc size responses during the UK extreme wet winter of 2019-2020
6. **Alexander Wiorek** (KTH) — 13:50-14:05
   Polyaniline Films as Electrochemical-Proton Pump for Alkalinity Detection

5 minutes break

7. **Julia Arndt** (German Federal Institute of Hydrology) — 14:10-14:25
   Beyond current routine: A close-to-real-time monitoring station at the river Rhine, Germany
8. **Liang Yu** (University of Amsterdam) — 14:25-14:40
   Drivers of nitrogen and phosphorus dynamics in a groundwater-fed urban catchment revealed by high-frequency monitoring

9. **Niklas Strömbeck** (LUODE) 14:40-14:55
   Nitrate optical sensors: overview of existing technology, their stability and pitfalls

30 minutes break

10. **Carolin Winter** (UFZ) 15:25-15:40
    Making a short story long: The impact of long-term runoff event characteristics on high frequency nitrate export
11. **Sofie Van't Veen** (Aarhus University/EnviDan) 15:40-15:55
    Experiences with high resolution monitoring of nitrate concentrations in three Danish headwater streams
12. **Yu Ting Chen** (University of Windsor) 15:55-16:10
    The impacts of biofouling on state-of-the-art automated phosphorus sensors during long-term deployment in Lakes and Rivers

5 minutes break

13. **James Kirchner** (ETH) – keynote speaker 16:15-17:00
    Exploring mechanisms and timescales of transport and hydrological response, using high-frequency chemical, isotopic, and hydrometric time series

5 minutes break

14. Discussion Session 1 17:00-17:45

Session 2: Extracting hydrochemical patterns and modelling of high-resolution data

Chair person: Jens Fölster — Tue 1st of June 2021

1. **Judith Benet-Bayo** (BOKU) — 12:30-12:45
   Pattern recognition in stream water quality for the detection and classification of pollution events
2. **Emma Lannergård** (SLU) — 12:45-13:00
   Interpreting turbidity-flow hysteresis analysis in a meso-scale catchment: the importance of intermediate event discharge
3. **Michael Hutchins** (CEH) — 13:00-13:15
   Coupling new developments in high-resolution monitoring with process based modelling to better understand water quality in river networks

5 minutes break

4. **Reza Haghi** (James Hutton Institute) — 13:20-13:35
   Evaluating the application of UV-Vis spectroscopy for simultaneous detection of nitrate, DOC and phosphorus and for chemical 'water quality fingerprinting'
5. **Camilla Negri** (TEAGASC/James Hutton Institute) — 13:35-13:50
   High-resolution hydro-chemo-metrics monitoring to inform data sparse catchment modelling
6. **Devanshi Pathak** (CEH) — 13:50-14:05
   High-resolution river water quality modelling to estimate ecosystem metabolism in a lowland river

5 minutes break

7. **Felipe Saavedra** (UFZ) — 14:10-14:25
   Disentangling scatter in C-Q relationships: the role of runoff events types
8. **Eva Skarbøvik** (NIBIO) — 14:25-14:40
   Use of data from sensors in national monitoring programmes – pros and cons
9. **Shannon Speir** (University of Notre Dame) — 14:40-14:55
   Storm size and hydrologic modification influence nitrate mobilization and transport in agricultural watersheds

30 minutes break

10. **Maria Kämäri** (Finnish Environment Institute, SYKE) 15:25-15:40
High-resolution stream water quality monitoring to detect effects of structure liming on suspended solids and phosphorus leaching from agricultural catchments
11. **Abagael Pruitt** (University of Notre Dame) 15:40-15:55
Winter cover crops reduce stream sediment export during storm
12. **Colin Cooke** (University of Alberta) 15:55-16:10
Rapid changes in water quality following a large Boreal Forest wildfire

5 minutes break

13. **Nandita Basu** (University of Waterloo) – keynote speaker 16:15-17:00
High Resolution hydrochemistry provides critical insight into scale and land use controls on nitrogen dynamics

5 minutes break

14. Discussion Session 2 17:00-17:45

Session 3: Understanding hydrochemical and biogeochemical processes

Chair person: Emma Lannergård Wed 2nd of June 2021

1. **Susana Bernal** (CEAB-CSIC) 12:30-12:45
   Stream metabolism as a source of carbon dioxide to the atmosphere in two hydrologically contrasting Mediterranean streams
2. **Magdalena Bieroza** (SLU) 12:45-13:00
   Can high-resolution water quality data help to understand the interplay between stream hydrological flushing and biogeochemical cycling?
3. **Jason Galloway** (TEAGASC) 13:00-13:15
   Factors governing the relationship between nutrient source pressure and nutrient transfer in six Irish agricultural catchments

5 minutes break

4. **Danny Croghan** (University of Oulu) 13:20-13:35
   Seasonal controls on sub-Arctic river total organic carbon dynamics revealed by high frequency monitoring
5. **Remi Dupas** (INRAE) 13:35-13:50
   Flowpaths controls on high spatial resolution water chemistry profiles
6. **Michael Rode** (UFZ) 13:50-14:05
   Nitrate retention in a large stream across variable flow conditions using continues high-frequency data

5 minutes break

7. **Marcus Wallin** (SLU) 14:10-14:25
   CO2 dynamics in low-land streams driven by hydrology and primary production
8. **Xiaolin Zhang** (UFZ) 14:25-14:40
   Evaluation of in-stream nitrate retention dynamics based on high-frequency measurements in high order stream reaches (central Germany)
9. **Jakob Benish** (TU Dresden) 14:40-14:55
   Would short-term online-monitoring improve the current WFD-sampling strategy?

30 minutes break

10. **Victoria Barcala** (Deltares) 15:25-15:40
    High-resolution monitoring of legacy transport at the farm scale
11. **Lukas Hallberg** (SLU) 15:40-15:55
    Understanding the role of spatio-temporal patterns on hydrochemical processes in two-stage ditches to reduce eutrophication
12. **Anna Vincent** (University of Notre Dame) 15:55-16:10
    Influence of storms on ecosystem metabolism in two agricultural watersheds

5 minutes break

13. **Helen Jarvie** (University of Waterloo) **–** keynote speaker 16:15-17:00
    High-resolution in-situ hydrochemistry: exploring nutrient cycling processes

5 minutes break

14. Discussion Session 3 17:00-17:45

Abstracts

Exploring mechanisms and timescales of transport and hydrological response, using high-frequency chemical, isotopic, and hydrometric time series

James Kirchner

ETH Zürich, Switzerland

Catchment processes are nonlinear and nonstationary. As a result, each mm of rain that falls on a catchment may affect streamflow differently, depending on how that individual parcel of rainfall fits into the sequence of past and future precipitation. Characterizing catchments' hydrologic behavior (as distinct from modeling the consequences of individual precipitation scenarios) requires tools for abstracting general patterns from this complex nonstationary rainfall-runoff relationship. Here I present two data-driven, model-independent methods – ensemble rainfall-runoff distributions and ensemble hydrograph separation – for characterizing catchments' responses to precipitation inputs.

Ensemble hydrograph separation is thematically related to, but distinct from, conventional hydrograph separation. It uses tracer time series to estimate both "backward" transit time distributions (the fraction of streamflow that originated as rainfall at different lag times in the past) and "forward" transit time distributions (the fraction of rainfall that will become future streamflow following different time lags). It can separately quantify catchments' transport behavior under different catchment conditions, and different types and intensities of precipitation. Thus it can be used to quantify nonlinearities in catchment transport behavior.

Ensemble rainfall-runoff distributions are thematically related to conventional unit hydrographs, but with key conceptual and mathematical differences. One important difference is that they can separately quantify the characteristic impulse response to different intensities of precipitation, falling under different catchment antecedent conditions. Thus they can be used to map out nonlinear patterns in catchment hydrologic response, directly from data.

Using both techniques jointly allows one to quantify the velocity and celerity of transport and runoff generation at the catchment scale, and also to quantify how they respond to catchment characteristics and hydrometeorological forcing. When combined with high-frequency chemical data, they can also shed light on how flowpaths vary during catchment response to precipitation. This presentation will briefly introduce these techniques and illustrate them using data from several experimental catchments.

High Resolution hydrochemistry provides critical insight into scale and land use controls on nitrogen dynamics

Nandita Basu

University of Waterloo, Canada

The Upper Mississippi River Basin is the largest source of reactive nitrogen (N) to the Gulf of Mexico. Concentration-discharge (C-Q) relationships offer a means to understand both the terrestrial sources that generate this reactive N and the in-stream processes that transform it. Progress has been made on identifying land use controls on C-Q dynamics. However, the impact of basin size and river network structure on C-Q relationships is not well characterized. Here, we show, using high-resolution nitrate concentration data, that tile drainage is a dominant control on C-Q dynamics, with increasing drainage density contributing to more chemostatic C-Q behavior. We further find that concentration variability increases, relative to discharge variability, with increasing basin size across six orders of magnitude, and this pattern is attributed to different spatial correlation structures for C and Q. Our results show how land use and river network structure jointly control riverine N export.

High-resolution in-situ hydrochemistry: exploring nutrient cycling processes

Helen Jarvie

University of Waterloo, Canada

Nutrients (nitrogen, N, and phosphorus, P) from agriculture and domestic wastewater, are a major source of water-quality impairment. Biogeochemical processes along the land-river continuum play an important role in regulating downstream nutrient transport: mediating nutrient supplies to downstream aquatic ecosystems and thereby influencing downstream water quality and trophic status. These biogeochemical processes vary temporally and spatially, between streams, and along the river continuum. Nutrient cycling processes are often quantified from relatively short-term, localized measurements (e.g., from benthic chambers and sediment-P sorption experiments), which can be difficult to extrapolate in space and time. The deployment of continuous, high-resolution in-situ hydrochemical sensors offers opportunities to explore the net effects of biogeochemical processes on nutrient fluxes - and how these change over time - from river-reach to watershed scales. Case studies from Canada, the U.S. and the U.K. will illustrate how combining high-frequency measurements of stream metabolism (analysis of diurnal dissolved oxygen curves to calculate rates of primary production and respiration), with high-resolution P, N and C measurements, can be used to apportion net biogeochemical process controls on downstream nutrient transfers. These studies reveal reciprocal interactions between stream metabolism and nutrient dynamics: how changing nutrient inputs can impact stream metabolism, and how shifts in stream metabolism influence nutrient retention, recycling and downstream nutrient transport. Combining high-resolution in-situ sensor measurements with long-term hydrochemical monitoring can also uncover converging climatic and biogeochemical drivers of nutrient retention and release, across a hierarchy of temporal scales, from decadal and seasonal to subdaily. These high-resolution hydrochemical fingerprints of coupled nutrient cycles are helping to identify the functional capacity of fluvial systems to amplify or diminish downstream nutrient transfers, and the implications for eutrophication of receiving waters.

Lab-on-chip chemical sensors for automated high-resolution measurements in remote locations

Alex Beaton

National Oceanography Centre, United Kingdom

High resolution chemical data can provide unprecedented insights into hydrological and biogeochemical processes. Chemical sensors have an exciting future in delivering these datasets, but must be capable of providing a high level of analytical performance and measurement stability during field deployment. The National Oceanography Centre in Southampton has developed a family of miniaturised lab-on-chip (LOC) chemical analysers for multiple aquatic chemical parameters (including phosphate, silicate, nitrate, dissolved iron, manganese, pH, DIC and total alkalinity). These sensors combine sensitive wet chemistry assays with microfluidic technology, allowing long term (up to one year), high frequency and high performance (nanomolar detection levels) measurements. Onboard calibration standards allow the sensors to correct for drift and retain accuracy for several months. Low power requirements and small physical size mean that the sensors can deployed in remote locations away from mains power or other infrastructure. The sensors have been deployed in a large range of aquatic environments, including rivers, lakes, estuaries, glacial meltwater, coastal environments, surface seawater and the deep ocean. This talk will review data from multiple sensor deployments (covering several of the parameters and environments listed above), and discuss how the sensors can be used to advance catchment science and aid water resource management.

Critical pathways and critical times: apportioning nutrient transfer pathways in 10-years of continuous hydro-chemistry data

Per-Erik Mellander[1], Jason Galloway[1] and Phil Jordan[2]

[1]TEAGASC, Ireland
[2]Ulster University, Northern Ireland

The physical settings of the agricultural landscape largely control the nutrient transfer pathways, associated transformation process along the pathways, and the timing of delivery. Changes in weather and agronomic pressures will further influence the dynamics within the system. Consideration of specific information on temporal and spatial variability in the most representative flows and active nutrient transfer pathways may improve the implementation of targeted and effective mitigation schemes to manage diffuse pollution.

The aim of this study was to identify and quantify critical pathways and times of phosphorus (P) and nitrogen (N) delivery in two hydrologically contrasting agricultural river catchments. Both in southeast Ireland, the *Ballycanew catchment* ($12km^2$) is dominated by poorly-drained soils and has a “flashy” hydrology and the *Castledockerell catchment* ($11km^2$) is dominated by well-drained soils and a fissured bedrock and is mainly groundwater driven. Ten-years of sub-hourly hydro-chemistry data were used to quantify the loads and concentrations of Reactive P (RP), Total P (TP) and nitrate-N in apportioned transfer pathways. Using hydrograph and loadograph separation techniques these pathways were baseflow (BF), elevated event baseflow (eBF), interflow (IF) and quick flow (QF).

Active N and P transfer pathways were largely dictated by the soil drainage. For the same runoff the RP load was 5 times higher, and TP load 3 times higher in *Ballycanew catchment* compared to the *Castledockerell catchment*. More specifically, the QF pathways dominated and transferred half of the RP and TP loss, and mostly in winter. However, the *Castledockerell catchment* had 3 times higher NO_3-N loss and 64% of that was transferred in BF, and mostly in winter. In the *Ballycanew catchment* critical pathways and times for elevated concentrations were: BF in summer and QF and IF in spring for RP; QF and eBF all year for TP; and QF and eBF in summer-autumn for nitrate-N. In the *Castledockerell catchment* it was: QF and eBF in summer for RP; QF and eBF in spring and summer for TP; and BF, eBF and QF all year (more elevated in spring and autumn) for nitrate-N. Both increasing and decreasing trends in concentrations were apparent in specific pathways and times. For example, in the *Ballycanew catchment* over the 10 year period, RP, TP and nitrate-N concentrations increased successively for the month of March and decreased in QF in July. In the *Castledockerell catchment* the nitrate-N concentrations increased successively in QF in March and RP and TP decreased in QF in July.

This seasonality in specific pathways may guide strategies to mitigate nutrient loss to water. For example, increasing trends in both N and P concentrations in the two rivers were largely linked to trends in *BF* concentration in both catchment types. However, pulses in QF and eBF may be linked to both weather and agronomy and changes were more apparent in spring and summer.

Data management: From the lab on the field, through data treatment to the scientific model, can we work entirely remotely and in real time?

Paul Floury, Antoine Dolant, Fatma Miled, Samantha Mazzei

Extralab Society, France www.extralab-system.com

Several online analysers and field-analysers have since decades provided a wealth of information for water quality monitoring at high frequency combining with a regular sampling to the laboratory. Recently improvements on laboratory instruments (more self-tuned and user friendly) and the deployment of the 4G network and soon 5G open a considerable possibility to manage remotely a full laboratory. This meets a strong scientific interest. The potential on high frequency measurements of all parameters open up new lines of inquiry that have previously been largely inaccessible. In this way, since 2017 three laboratories called Riverlab are deployed in France in a network of research institutes. Today Riverlabs are deployed in the word on CZO in China or USA. This constitutes a decentralised connected laboratories network. These Riverlabs can perform measurement of all concentration of major dissolved species and physico-chemical parameters in less than 30 minutes on a natural waters like river, regardless of their quality. A new limitation is coming out from this new decentralised laboratories network about how can we manage all data. Unlike probes or auto-samplers, where data or samples can be collected and treat regularly, such field laboratory like Riverlab requires a permanent attention and to work continuously in remote to perform acceptable and accurate results. It forces us to totally rethink the conception of a laboratory. In a conventional laboratory, water samples come to the laboratory to be analysed and then results to the scientists to be explored. In our laboratory conception, this chain of measurements from sampling to scientific models has to be rethought at 180 degrees. Since a year, we are deploying on the Riverlabs network an online software on Extralab. This software is designed to gather remotely all tasks necessary to supply like a conventional laboratory. This software is building in constant collaboration with teams engaged. This software allows scientists to:

1. Collect in real time all results coming from all instruments and probes regardless the model or brand

2. Treat data through methods apply to filter data continuously according to the best practices and qualification, with a calibration and blank/standard control remotely performed in parallel

3. A platform to visualise, explore and apply matrix calculation in real time and provide a first overview on data

4. The end point of this solution is to directly apply scientific model through an online IDE on the platform to perform calculation on the dataset instead of download the data.

This platform is a new virtual space where all Riverlabs workers can meet and share each other their experiences and problems/solutions. Such solutions are aiming to feed platforms already deployed to connect data together like Hydroshare in the USA or Theia-OZCAR and eLter at European scale. This will conduct to entirely digitalise the data acquisition. We will present how we work continuously through this platform. We open to discussion the potential of such software solution: Is it an optimised remote control or a real deep revolution on our conception of a laboratory?

A combined temporal resolution approach to monitor pollution sources in large rivers with nitrate isotopes

Astrid Harjung, Ioannis Matiatos, Yuliya Vystavna, Jodie Miller

International Atomic Energy Agency, Austria

Analysis of nitrate 15N/14N and 18O/16O ratios have become more accessible over the last couple of years thanks to improved reduction methods of nitrate into nitrous oxide. This has significant implications for monitoring of water quality because these data can provide important insights into sources and processing of nitrate. However, the ability to differentiate nitrate sources is limited by (i) mixing and biogeochemical processes, such as organic decay and nitrification, changing the initial nitrate isotope source and (ii) the fact that two important contributors to nitrate pollution, manure and septic waste, cannot be easily discriminated, both organic, and need to be discriminated by other tracers. Emerging contaminants, such as pharmaceuticals are ideal tracers to help differentiate animal from anthropogenic wastes. In a preliminary study of the Danube river basin, we were able to show that the isotopic composition of nitrate in river water correlated with wastewater indicators, such as caffeine. However, temporal resolution is needed to evaluate if nitrate isotopes in combination with other emerging contaminants can be used as source indicators of nitrate pollution in large river systems. The Danube river in Vienna is well monitored via numerous stations, with real-time discharge and basic chemistry data easily accessible. For this proof-of-concept, we will conduct routine weekly sampling for stable water and nitrate isotopes, as well as, basic chemistry parameters and ions at one of these monitoring stations. Additional sampling campaigns are planned to be conducted to capture behaviour during extreme events, such as high discharge flood events. Because pharmaceuticals and pesticides typically occur in very low concentrations, the objective will be to couple an isotope sampling program with time integrated passive sampling techniques. Passive sampling techniques provide time-weighted average concentrations of pharmaceuticals and pesticides over the deployment period. Based on existing information this period in the Danube will be less than one week. We expect that pharmaceuticals for human and veterinary applications and pesticides, can confirm the dominance of agricultural, industrial or urban source of nitrate pollution. To investigate the influence of N-cycling in the nitrate isotope values in 24h, our nitrate isotope sampling will be performed twice on each sampling date to cover diel cycles. Results of this pilot project will be used to establish monitoring strategies to understand the mixing of water and contaminants in large, transboundary river systems.

Dynamics of fluvial hydro-sedimentological, nutrient and floc size responses during the UK extreme wet winter of 2019-2020

Hari Ram Upadhayay, Steven J. Granger, Adrian L. Collins

Rothamsted Research, United Kingdom

The floc size distribution of suspended sediment is a critical driver for in-channel sedimentation and sediment-associated contaminant and nutrient transfer and fate in river catchments. Real-time, *in situ*, floc size characterisation is possible using available laser technology but, to date, limited high resolution floc data have been published for fluvial systems in general and, in particular, those draining upland extensive peaty grassland catchments. In response to this evidence gap, suspended sediment floc size distribution and turbidity were characterised at 15-minute intervals using Laser In-Situ Scattering and Transmissometry (LISST) diffraction and a YSI turbidity sonde for six storm events between October 2019 and February 2020 in the upper River Taw (15 km^2) observatory catchment in SW England. Maximum storm event discharges ranged between 4.3 to 20.0 m^3s^{-1}, with corresponding total suspended solid concentrations (TSS) ranging from 5.7 mg L^{-1} to 47.0 mg L^{-1} and storm event TSS fluxes ranging from 0.55 t (0.04 t km^{-2}) to 44.1 t (2.9 t km^{-2}). Clockwise hysteretic loops (HI = 0.18–0.48) were observed between TSS and Q and the sediment flushing index was highest in the early autumn (0.93) and during the highest (storm Dennis) monitored discharge event (0.85). The proportion of POM to TSS was highly variable (5–89%), with an average of 25% across the monitored discharge events. Particulate organic matter (POM) fluxes during the storm events ranged between 0.14 t (0.01 t km^{-2}) and 11.27 t (0.74 t km^{-2}). The fine-grained tail (D10 and D16) of the floc size distributions decreased during hydrograph rising limbs, with the finest floc sizes associated with the highest TN and TP concentrations at peak flows. The D50 floc size ranged between 95 µm and 382 µm. Collectively, the results suggest that dynamic interactions between wet ground and extreme rainfall event can flush significant amounts of sediment, nutrients and POM from the relatively undisturbed extensive grassland upland catchment.

Polyaniline Films as Electrochemical-Proton Pump for Alkalinity Detection

Alexander Wiorek, Maria Cuartero, Gaston A. Crespo

Alkalinity is arguably one of the most important parameters for monitoring water quality, affecting proliferation of microorganisms and sensitivity for water acidification, among others. Alkalinity refers to all titratable components down to pH 4, where the carbonates (HCO^{3-} and CO_3^{2-}) usually has the largest contribution, making it highly dependent on the partial pressure of carbon dioxide. Thus, water samples removed from its source and analyzed under a different atmosphere are likely to be altered and show an alkalinity different from the true value. Therefore, almost all measurements today are carried out on-site. Here, an automatic in situ titration for alkalinity detection would be beneficial, allowing the sample to be analyzed without removing it from its source.

To solve this problem, we recently provided the first evidence of using the conductive polymer polyaniline (PANI) as a source of protons for in-situ titrations. We also demonstrate how this new insight allows for the utilization of PANI as an electrochemically tuned proton pump capable of rapid protonation of confined thin layer samples of natural waters (30-40 s to titrate sea water samples), proving its analytical significance. This is achieved by using two faced planar electrodes, where the PANI-film on one of the electrodes works as a proton pump, and the opposing electrode is a pH-sensor also based on PANI. The sensing strategy is based on a perturbation of the sample pH accomplished by electrochemically controlled release of protons from the PANI-film, and the pH is monitored versus injected charge, which is used instead of volume of added titrant. The sample alkalinity is then deduced by comparison with titrations standards of known bicarbonate-concentration. The developed device is tested on 7 different sea water samples obtained from different locations in the Stockholm archipelago, providing comparable results to those obtained by standard methods. We also demonstrate how the PANI-film can be utilized in samples of higher alkalinities, where it is capable of titrating samples in the range of 0.5-20 mM acid equivalents.

This work holds a two-fold significance: i) all-solid-state electrode materials may be implemented and utilized into miniaturized analytical devices, as illustrated in our work, or ii) implemented into a submersible probe for rapid acidification of thin layer samples for alkalinity detection or pretreatments for other electrochemical sensors by adjustment of the sample pH.

Beyond current routine: A close-to-real-time monitoring station at the river Rhine, Germany

Julia Arndt, Julia S. Kirchner, Anna-Lena Gerloff, Alex Zavarsky, Kevin S. Jewell, Michael P. Schlüsener, Arne Wick, Lars Duester

German Federal Institute of Hydrology, Germany

The River Rhine, one of the largest rivers in Europe, connects six nations from Switzerland to the Netherlands. This waterway includes some of the most densely populated areas in Europe and therefore needs to balance different requirements for water management concerning societal, economic, as well as ecological functions. As demand on these resources grows, close-to-real-time monitoring with high-frequency sampling is becoming increasingly important at the river Rhine for a fast detection of unattended chemical releases (early warning systems) as well as for a better understanding of sudden changes in chemical water quality of the river system (e.g. by temperature, water flow, rain events or anthropogenic activity). Analytes include nutrients, major and trace elements, as well as organic substances. An online monitoring and data evaluation decreases reaction times and increases the basis for evidence-based decision making.

An experimental and prototype testing monitoring station, supplementary to the regular Koblenz Rhine station (km 590), was designed and set up to go beyond current monitoring routines as far as possible by real-time monitoring. Water from the Rhine is pumped to the station for prototype real-world testing, without interfering the regular monitoring activities. As an example, online and atline techniques are already compared for nutrients by online ion chromatography (IC) to sensor results since December 2020. Colorimetric methods will be added by mid-2021 for comparison purposes (method robustness and precision).

Set up of the automated close-to-real-time monitoring is in progress for major and trace elements analyzed by inductively coupled plasma mass spectrometry (ICP-QMS) and a non-target screening for organic compounds based on liquid chromatography quadruple time-of-flight mass spectrometry (LC-QToF-MS). At the moment, automated workflows for sample preparation and instrument calibration are being developed, including optimization and the development of robust algorithms for an automated data processing and evaluation of the non-target data. The future recorded data serves as basic system input to support users to understand and to timely react to internal or external system changes and anomalies.

The contribution describes the principle philosophy and needs behind the monitoring station setup and allows to sneak peek on current developments.

Drivers of nitrogen and phosphorus dynamics in a groundwater-fed urban catchment revealed by high-frequency monitoring

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Eutrophication of water bodies has been a problem causing severe degradation of water quality in cities. To gain mechanistic understanding of the temporal dynamics of nitrogen (N) and phosphorus (P) in a groundwater-fed low-lying urban polder, we applied high-frequency monitoring in Geuzenveld, a polder in the city of Amsterdam. The high-frequency monitoring equipment was installed at the pumping station where water leaves the polder. From March 2016 to June 2017, total phosphorus (TP), ammonium (NH4), turbidity, electrical conductivity (EC), and water temperature were measured at intervals of less than 20 min. We discussed the results at three timescales: annual scale, rain event scale, and single pumping event scale. Mixing of upwelling groundwater (main source of N and P) and runoff from precipitation on pavements and roofs was the dominant hydrological process governing the temporal pattern of the EC, while N and P fluxes from the polder were also regulated by primary production and iron transformations. In our groundwater-seepage controlled catchment, NH_4 appeared to be the dominant form of N with surface water concentrations in the range of 2–6 mg N L^{-1}, which stems from production in an organic-rich subsurface. The concentrations of NH_4 in the surface water were governed by the mixing process in autumn and winter and were reduced down to 0.1 mg N L^{-1} during the algal growing season in spring. The depletion of dissolved NH_4 in spring suggests uptake by primary producers, consistent with high concentrations of chlorophyll *a*, O_2, and suspended solids during this period. Total P and turbidity were high during winter (range 0.5–2.5 mg P L^{-1} and 200–1800 FNU, respectively) due to the release of P and reduced iron from anoxic sediment to the water column, where Fe^{2+} was rapidly oxidized and precipitated

as iron oxides which contributed to turbidity. In the other seasons, P is retained in the sediment by sorption to precipitated iron oxides. Nitrogen is exported from the polder to the receiving waters throughout the whole year, mostly in the form of NH_4 but in the form of organic N in spring. P leaves the polder mainly during winter, primarily associated with $Fe(OH)_3$ colloids and as dissolved P. Based on this new understanding of the dynamics of N and P in this low-lying urban catchment, we suggested management strategies that may effectively control and reduce eutrophication in urban polders and receiving downstream waters.

Nitrate optical sensors: overview of existing technology, their stability and pitfalls

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Optical nitrate sensors for measuring water quality in natural waters have been available for almost 15 years, but are still not very commonly used. Depending on monitoring needs and available instruments, different implementation models exist and the technology still evolves. Based on our own and partners' experiences with nitrate optical sensors, we present a brief overview of some different implementation models, their designs, practicalities and show collected data with a special focus on nitrate measurements in aquatic systems.

Making a short story long: The impact of long-term runoff event characteristics on high frequency nitrate export

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High riverine nitrate concentrations threaten the health of aquatic ecosystems and drinking water quality. Runoff events play a dominant role for the mobilization and transport of nitrate and their role might even increase with progressive climate change. The advent of high-frequency sensors for nitrate concentrations enabled detailed analysis of nitrate transport during runoff events and highlighted their disproportional contribution to total nitrate export but also their large inter- and intra-annual variability. Moreover, the number of analyzed events is often limited due to relatively short measurement periods. On the contrary, precipitation and discharge data at daily resolution are typically available over far longer periods and allow for the characterization of runoff events on the long-term. Here, we combine long-term runoff event characteristics with nitrate export characteristics identified in recent high-frequency measurements to draw conclusions on the relationship between runoff event characteristics and nitrate transport beyond the limited period of high frequency measurements. To this end, we used a recently developed approach from Tarasova et al. (2020) to classify runoff events using daily long-term data (1955 – 2017) from six contrasting mesoscale catchments. In combination with that, we characterized event-driven nitrate export from high-frequency data (2013 – 2017) and analyzed the relationship between runoff event characteristics and nitrate export patterns. We found a strong positive correlation between event-specific median nitrate concentrations (Cmedian) and median discharge (Qmedian), implying that nitrate concentrations and exported loads increase if Qmedian increases. This relationship significantly changed for large snow- or rainfall-induced events with high antecedent soil moisture, where only a small or no increase of Cmedian with Qmedian was observed. Event-specific CQ slopes

(slope of nitrate concentration and discharge relationships in logarithmic domain) showed a large variability for small rainfall-induced events, mainly under dry antecedent soil moisture conditions, while they approach a narrow range of slightly positive CQ slopes for larger events. A part of the heterogeneity in CQ slopes for small events can be explained by their temporal organization (defined by the ratio of maximum precipitation rate and precipitation volume). Intensity-dominated events have significantly higher CQ slopes in some of the catchments, indicating a higher mobilization potential than volume-dominated events. On the long term, the fraction of snow-related events between January and April decreased, same as antecedent soil moisture between May and September. These trends might cause a redistribution of nitrate loads between winter and spring and an increase in the variability of nitrate concentrations during summer and autumn.

Tarasova, L., Basso, S., Wendi, D., Viglione, A., Kumar, R., & Merz, R. (2020). A process-based framework to characterize and classify runoff events: The event typology of Germany. Water Resources Research, 56(5), e2019WR026951.

Experiences with high resolution monitoring of nitrate concentrations in three Danish headwater streams

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This study investigates the use of the Nitrate sensor (NITRATAX plus sensor from HACH) in three small Danish headwater streams over a period of 4 years. The nitrate sensor works according to the UV measuring principle. It was installed in Jegstrup stream in 2016 (catchment area: 2173 ha, 64% agricultural area and nitrate concentrations from 0.9-2.3 mg N/l), in Saltø stream in 2017 and 2018 (catchment area: 3737 ha, 77% agricultural area and nitrate concentrations from 0.005-23 mg N/l) and in Horndrup stream continuously from 2019 to 2021 (catchment area: 548 ha, 73% agricultural area and nitrate concentrations from 0.44-8 mg N/l). We defined four overall factors that may affect the sensor measurement in the streams: Zero offset of a sensor, sensor drift, sensor interference and sensor disturbances. In Jegstrup stream, we found challenges with zero offset of the sensor measurements, which may be due to a high concentration of dissolved iron in the stream. However, it can also be because UV light from the sun interfered with the measurements of nitrate. In Saltø stream and Horndrup stream, we experienced data problems being mainly related to sensor disturbances. In both Saltø stream and Horndrup stream, was the sensor in general measuring higher nitrate concentrations than the concentrations measured in the laboratory from grab water sampling. The deviation is greatest at low nitrate concentrations. This is probably due to sensor interference with either organic matter, suspended sediment or UV light from the sun. In both streams, we found robust correlations between nitrate concentrations measured with the sensor and grab samples (R^2> 0.95). It is therefore possible to calibrate the sensor measurements, in order to transform the concentration of nitrate measured with the sensor comparable to the concentrations measured in the laboratory. Moreover, we analysed the differences between calculation of the nitrate transport based on traditional grab samples taken every fortnight and nitrate sensor measurements every 5 minutes. The results from Horndrup stream shows that deviations vary highly between months and can result in both an underestimation of monthly nitrate transport of up to 36%, and an overestimation of up to 18%.

Lastly, the sensor measurements of nitrate provide optimal opportunities for more in-depth knowledge of the response and dynamics of nitrate sources and concentrations in the streams draining the catchments studied and selected representative examples of these behaviours will be shown.

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The impacts of biofouling on state-of-the-art automated phosphorus sensors during long-term deployment in Lakes and Rivers

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Application of in-situ high-frequency phosphorus (P) sensors have provided invaluable insights into identification of sources, transport pathways and in-stream metabolism processes within watersheds. Wet chemistry techniques have been widely applied in autonomous P monitoring and incorporated into microfluidic systems due to their robust performance in analyses and inexpensive cost in component materials. Until recently however, autonomous monitoring of total and dissolved phosphorus (TP and TDP) fractions were restricted to riverine systems in close proximity to mains electricity, due to high power requirements associated with analytical digestion techniques. State-of-the-art automated wet chemical analysers (WIZ Probes) used in this study overcome the deployment challenges by adopting low power digestion methods supplied by solar power from discrete portable units, allowing in-situ analyses to be performed on floating platforms in remote areas, such as lakes. Data retrieved from these regions can broaden our understanding of nutrient dynamics and freshwater biogeochemical processes. In 2019, the aforementioned sensors were deployed to measure three fractions of phosphorus (P); total phosphorus (TP), total dissolved phosphorus (TDP) and soluble reactive phosphorus (SRP) in-situ over an 8-month period at four sites in Southern Ontario, Canada which represent a wide range of P concentrations. To ensure data consistency and accuracy during long-term monitoring, the effects of instrument biofouling were closely examined, an issue which has remained largely unresolved in the past despite recent technological advances. The four sensors were calibrated using chemical standards both in the field and the lab, validated with fortnightly grab samples, and the representativeness of real-time data under a range of biofouling conditions were evaluated.

The results of this study indicate that sensor biofouling during long-term deployment can desensitize instrument measurements, with greatest impacts on instruments operating in highly turbid environments. Temporal changes in calibration curves suggest that equilibrium P concentrations (EPC_0) of sediments

accumulating inside filters can elicit a rapid exchange of dissolved P (SRP, TDP) with the water sample. Data drift increases when sample concentrations are further away from a filter's EPC_0 values. As a result, this demonstrates in-situ sensors should ideally be dedicated to a specific waterbody type defined by similar EPC_0 values unless filters are frequently replaced or renovated. It is recommended that in order to ensure accuracy in in-situ monitoring of TP, TDP and SRP during long-term deployment, preliminary site trials should be conducted to ascertain sediment EPC_0; the extent of biofouling should be monitored; and/or frequent grab samples taken for post-deployment validation. The findings will be of interest to any studies using in-situ phosphorus monitoring techniques for SRP or TDP; which furthermore will prove useful in research, for example, addressing drivers of harmful algal bloom events supplemented by other high-resolution hydrological data and parameters.

Pattern recognition in stream water quality for the detection and classification of pollution events

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The field of water quality monitoring is experiencing a transition, where off-line labor-intensive laboratory analyses are being substituted by online sensors, which are often based on optical measurements such as spectrometry. Several online sensors are often installed in one monitoring station to measure multiple parameters which together describe the overall water quality.

Online monitoring allows for time-resolved measurements and provides a framework for the development of tools for automatic data analysis, including early warning systems for water contamination. In fact, several companies have developed their own event detection algorithms, which analyse the changes in water quality and trigger an alarm when an anomaly is detected. In the past years, online monitoring and event detection for water quality has been widely implemented for industrial control and monitoring of water supply networks. However, its application in monitoring natural freshwater bodies has been widely neglected.

This study focuses on the application of existing online monitoring sensors and event detection tools in a highly polluted river. Parallelly to the analysis of the data recorded by the studied monitoring station, a method has been developed which generally describes the workflow that has to be followed for stream water quality event detection and classification (SWQ-EDC).

The SWQ-EDC method has been developed to be universal, i.e., appropriate for different water quality standards. The proposed method has been developed under two premises: 1) that contamination causes a significant change in water quality, which can be detected in any water body independently from their original water quality, and 2) that different pollution types can be recognized in the detected events by the event detection system in a river monitoring station. Thus, the driving force of the SWQ-EDC method is the recognition of patterns in the water quality data and their interpretation to identify different pollution types.

The analysis of the recorded water quality data, and the development of the SWQ-EDC method has been divided in three main steps: data preprocessing, detection of pollution events and event classification. The first stage consists of a quality control assessment (QCA) followed by the application of statistical tools. The QCA is achieved through internal checks in the data provided by the station. The statistical tools include a correlation analysis, the computation of the missing values with multilinear regression, a principal component analysis and a study of the river behavior, which facilitates the extraction of the "normal pattern" in the river water quality. The second stage consists of the implementation of an event detection system. This is followed by the selection and description of the detected pollution events. In the third stage, artificial machine learning, i.e., clustering has been applied for the identification of pollution types.

As an outcome, 41 pollution events have been detected in the 4-month period where the monitoring station was active, and 3 different pollution types have been identified. Moreover, the SWQ-EDC method has been developed, which outlines how to analyze high-resolution data measured in-stream with in-situ sensors, to identify and classify pollution events.

Interpreting turbidity-flow hysteresis analysis in a meso-scale catchment: the importance of intermediate event discharge

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Evaluating differences in the temporal covariation of turbidity and discharge (i.e., hysteresis) can give insight about catchment processes and hydrological pathways affecting surface water quality. Using high frequency data to analyse a larger number of events over different seasons and conditions has previously shown promising results. For monitoring purposes, however, high frequency data are often collected on meso-scale (or larger) catchments where the connection between change in turbidity and discharge is not self-evident. Therefore, we evaluated high frequency turbidity-discharge hysteresis patterns for events extracted from a long term time series (2012-2019) representing all seasons, in a meso-scale northern agricultural catchment. 74 events were objectively defined by analysis of the hydrograph (implementation of specific criteria) and retained for further qualitative and quantitative analysis. During qualitative event analysis, three reoccurring patterns were identified. Events with low mean discharge (2 m^3/s) often showed short-term, quasi-periodic variation in turbidity, to a large extent disconnected from variation in discharge. Events with high maximum discharge (>15 m3/s) were often connected to spring flood or snow melt, and also showed a disconnection between turbidity and discharge. Events with intermediate flow (2-15 m^3/s) were the most informative when applying hysteresis indexes, since changes in turbidity and discharge were actually connected. Hysteresis indexes could be calculated on a subset of 60 events, where they showed heterogeneous responses: 23 events showed a clockwise response, 7 events an anti-clockwise response, 7 events a figure eight (clockwise-anticlockwise) response, 6 events an opposite figure eight pattern (anticlockwise-clockwise) and 17 a complex response. Clockwise hysteresis responses were connected to the wetter winter and spring seasons. Generally, changes in flow and turbidity were small for events displaying anti-clockwise hysteresis. For the figure eight patterns (ACA, CAC), some turbidity peaks were associated with precipitation. Complex patterns were generally observed during the summer low flows. The long term monitoring showed all kinds of responses, but it was at the intermediate discharge range where turbidity and discharge were clearly

connected, as opposed to low and high discharge events. The results showed that hysteresis analysis could improve process understanding and possibly aid in choosing the right management action for targeting a specific observed pattern, even in a meso-scale catchment.

Coupling new developments in high-resolution monitoring with process based modelling to better understand water quality in river networks

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High resolution monitoring plays a central role in advancing understanding of catchment-scale water quality as represented in process-based models. We illustrate the value of a river eutrophication model (QUESTOR) to quantify the sensitivity of the River Thames in southern England to various combinations of multiple pressures related to climate, population growth and river basin management. Combining optical fluorescent chlorophyll sensor measurements with microscopy and flow cytometry improves understanding of water quality sensitivity to phytoplankton dynamics. As a result, an hourly resolution model performs well over two years and shows that relationships between nutrient concentrations, chlorophyll and dissolved oxygen (DO) are not straightforward. Although light and residence time exert primary control, feedback between water quality and biology is apparent in a partially phosphorus-limited system. Moreover, autotroph photosynthesis and respiration can only explain a small part of DO response, as characterised using optical sensors. Thames modelling studies coupled with long-term high-resolution and periodic water quality monitoring have pinpointed medium-term increases in heterotrophic respiration which can give rise to conditions that are potentially damaging at higher trophic levels, especially during warm and dry summers. Climatic extremes are a probable driver of extended periods of increased sensitivity brought about by delivery to the river of degradable organic matter primarily of urban origin. Two recently-emerging high-resolution monitoring techniques will allow a step change in model development by enabling characterisation of organic matter in rivers and their bed sediments at a temporal resolution that was previously unattainable: (1) High-resolution fluorescent Dissolved Organic Matter sensors and excitation-emission fingerprinting techniques provide invaluable information on degradation rates in the water column. (2) By coupling rapid high spatio-temporal resolution acoustic doppler water velocity signals and phosphorescent DO measurements, aquatic eddy covariance equipment, sited just above the riverbed, can quantify benthic respiration rate. Given the success of hourly simulations, notably using hourly inputs solely from solar radiation and thereby in

the absence of comparably high resolution water inputs, combining QUESTOR with new monitoring techniques unlocks wider capabilities. These include: (1) better prediction of future conditions in response to change; (2) hindcasting hourly dynamics in rivers, not only to allow interpolation between monitoring sites but also to extend the record back to times before high-resolution measurements were available.

Evaluating the application of UV-Vis spectroscopy for simultaneous detection of nitrate, DOC and phosphorus and for chemical 'water quality fingerprinting'

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Understanding of water quality based on data with low temporal resolution can greatly under-estimate pollutant concentrations and loads, hindering cost-effective targeting of mitigation measures and understanding of environmental change. Optical probes have been successfully deployed in catchment observatories and by the waste-water industry for high-resolution monitoring of nitrate and dissolved organic carbon (DOC). In this project, we test the application of this technology for the simultaneous detection of nitrate, DOC and phosphorus. We develop new mathematical models to address the following questions:

1. Can we apply supervised chemometric approaches to monitor nitrate, DOC and phosphorus simultaneously in order to enable accurate high temporal resolution data acquisition at lower cost?

2. Can we derive a 'chemical fingerprint' to characterize the spatial variability of water quality in river catchments, based on the full range of UV-Vis spectra, as an indicator of 'ecosystem health'?

3. Can we identify unusual changes in composition of environmental water samples and in ecosystem health due to changes in the integrated 'chemical fingerprint'?

An sc::an UV-Visible spectrometer was employed to acquire ~200 spectra of water samples, including laboratory mixtures and field samples, over the wavelength range of 200 to 800 nm with an optical pathlength of 35 mm. The samples were collected from various locations during several seasons to cover spatial and temporal variability in water quality. The predictive performance of two regression methods - Partial least square (PLS) and support vector regression (SVR) methods was investigated, alongside the impact of different pre-processing methods on accuracy of PLS and SVR models. We evaluate the performance of UV-Vis spectroscopy technique in combination with chemometric approaches for accurate estimation of nitrate, DOC and phosphorus simultaneously in environmental water samples at different turbidity levels. To assess the spatial variability in water quality in river catchments using the UV-vis spectra, we used principal component analysis (PCA) to reduce the spectra dimension to generate a proper visualization of the experimental data. The UV-Vis spectrum of water samples from different catchments were recorded and the applicability of UV-Vis combined with PCA to detect water contamination events was investigated.

High-resolution hydro-chemo-metrics monitoring to inform data sparse catchment modelling

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Diffuse pollution of phosphorus (P) from agriculture is a major stressor on water quality in Ireland, where the Agricultural Catchments Programme (ACP) was initiated to evaluate the Good Agricultural Practice measures implemented under the EU Nitrates Directive. Within the ACP, extensive high-resolution monitoring and research have been put in place to understand the drivers and controls on nutrient loss in the agricultural landscape. The high-intensity monitoring strategy delivers a ten-year dataset from simultaneous high frequency monitoring of streamflow, phosphorus (P) and nitrogen (N) concentrations in surface and groundwater, mapped soil properties (drainage class and Soil Morgan P), landscape characteristics (i.e. land use and management, presence of mitigation measures and presence of point pollution sources) and ecological surveys within six Irish agricultural catchments. This information-rich dataset offers a unique opportunity for the understanding and modelling of catchment processes.

Bayesian Belief Networks (BBNs) are probabilistic graphical models that allow the integration of both quantitative and qualitative information from different sources (experimental data, model outputs and expert opinion) all in one model. Moreover, these models can be easily updated with new knowledge and can be applied with scarce datasets. Because of these characteristics, BBNs can be a powerful (and not fully exploited yet) tool in water quality and nutrient transport modelling, which is often hindered by constraints associated with data gathering and knowledge gaps.

In this study, a prototype spatial BBN was implemented to develop a Decision Support Tool for understanding the influence of land management on P pollution risk in four ACP catchments dominated by intensively farmed land with contrasting hydrology and land use. In the first stage of the study, the spatial BBN was constructed identifying the main drivers of P pollution based on previous findings from the ACP catchments. A second step involved the consultation of experts and stakeholders through a series of interviews aimed at eliciting their input. These stakeholders have expertise ranging from hydrology and hydrochemistry, land management and farm consulting, to policy and environmental modelling. At present, the BBN is being parameterized for a 12km2 catchment with mostly grassland on poorly drained soils.

Future research will be focussed on parameterizing and testing the BBN in three other ACP catchments, in order to compare model transferability. In addition, such parametrization will be pivotal to testing the model in data sparse catchments and possibly upscaling the tool to regional and national scale, as BBNs are particularly suited to provide national scale understanding as well as explicitly inform on the uncertainties regarding both the model and the data. Moreover, climate change and land use change modelled scenarios will be crucial to inform targeting of mitigation measures.

High-resolution river water quality modelling to estimate ecosystem metabolism in a lowland river

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In this study, we present a new approach to estimate ecosystem metabolism from high-resolution modelling of in-stream flows and water quality. To do so, we modify a process-based river model, QUESTOR (Quality Evaluation and Simulation Tool for River-systems), to predict flow, water temperature, dissolved oxygen, nutrients and phytoplankton concentrations at an hourly scale. The model is implemented along a 62 km long stretch in the lower River Thames in England using high-frequency water quality measurements from two years (2013-2014). Conventional methods of metabolism modelling do not specifically account for oxygen transport under varying flows and oxygen transformations due to biogeochemical processes. Our approach addresses both these challenges and allows us to study specific metabolic pathways such as photosynthetic production and respiration, reaeration, benthic oxygen demand, removal of biochemical oxygen demand (BOD) and nitrification that may influence diurnal dissolved oxygen variation in the river. We also analyse the sensitivity of estimated metabolism rates to multiple environmental controls using empirical modelling techniques such as random forests and generalised least squares regression. We observe that the lower River Thames is a primarily autotrophic system from mid-spring to mid-summer during the biomass growing season and represents heterotrophy during the rest of the year. Ecosystem respiration at the upstream end of the network is mainly driven by oxygen loss through BOD decay, autotrophic respiration and nitrification (total 97% of ecosystem respiration). Downstream sites also display an important role of benthic oxygen demand (19%) in driving respiration in addition to the former processes (80%). Overall, our study demonstrates the utility of high-frequency data in river modelling to study ecosystem functioning and its sensitivity to flow and water quality controls.

Disentangling scatter in C-Q relationships: the role of runoff events types

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Diffuse sources of water contamination within catchments, such as agriculture, are a challenging problem for water quality management. Excess of nutrients (e.g., nitrate and phosphate) are harming ecosystems by producing eutrophication in water bodies and leading to biodiversity loss.

The relationship between solute concentrations and streamflow rates observed at catchment outlets provide useful information on hydrological functioning and biogeochemical transformations at catchment scale. The shape of concentration-discharge (C-Q) relationships encodes export regimes and determines the quantity of critical substances such as nutrients delivered to streams.

A significant scatter observed in the C-Q relationship might be related to hydrological event conditions at sampling time. Runoff events can be triggered by inducing events of different nature (e.g., rainfall, rain-on-snow, snow melt). Variable temporal dynamics and spatial structure of precipitation events within catchments as well as antecedent wetness states might lead to differences in dominant runoff generation processes among different events. These differences may in turn affect solute transport dynamics during an event, producing different C-Q export patterns. In this study we hypothesized that the differences in characteristics and generation processes of runoff events might explain the observed scatter in long-term C-Q relationships and thus assist in pinpointing sources and reactive transport mechanisms.

In this study, we analyzed the variability of nitrate export patterns of around 200 mesoscale German catchments under different event conditions. For this purpose, we have linked low-frequency nitrate concentration measurements from 1980 to 2014 with corresponding daily discharges and constructed a long-term C-Q relationship (linear regression in log space) for each catchment. In the next step, we used discrete series of separated and classified rainfall-runoff events

(Tarasova et al., 2020) to link concentration measurements to corresponding runoff events.

We grouped samples linked to each event class (e.g., rain-on-now, rainfall events during dry conditions, rainfall events during wet conditions) and quantified the deviation from the long-term C-Q relationship. For this purpose, we analyzed the residuals of the general C-Q relationship and the slope of C-Q linear regressions for samples grouped according to event class.

Preliminary results revealed distinctive differences in catchment export patterns among events of different types. These first results suggest that further investigation is needed to infer mechanistic processes that lead to differences in solute export patterns among different event types.

Tarasova, L., Basso, S., Wendi, D., Viglione, A., Kumar, R., & Merz, R. (2020). A process-based framework to characterize and classify runoff events: The event typology of Germany. Water Resources Research, 56(5), e2019WR026951.

Use of data from sensors in national monitoring programmes – pros and cons

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A frequently asked question by managers is if high-frequency sensors can substitute regular water quality data in national monitoring programmes. In this presentation we will compare experiences on this topic from several countries in Northern Europe. Our aim is to shed more light on the following questions:

• Could sensors be used as *substitutes* for regular monitoring parameters? If so, what new information and knowledge can sensors provide for national monitoring programs?

- what kind of sensors are best suited to be used in national monitoring programmes?

- how do we design and prioritise the station network?

- how do we conserve long-term data series if we substitute regular monitoring with sensor data?

- what additional data storage and quality control issues would arise?

• Is a better use of sensor data to provide *additional* information to national programmes, e.g. by improving load calculations or detecting possible maximum concentrations?

• Can sensors be used for detecting long-term change of drivers, or short-term change of management-induced impacts and measures?

• Are existing guidelines meeting our needs? Such needs may be rules for running, testing and calibration of sensors in national monitoring programmes across e.g. EU to facilitate comparisons of concentrations and loads (e.g., related to international commissions like HELCOM and OSPAR).

Storm size and hydrologic modification influence nitrate mobilization and transport in agricultural watersheds

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Solute transport in streams has been influenced by agriculturally-driven land use change and hydrologic modifications. Given anticipated shifts in hydrology associated with a changing climate, a clear understanding of the mechanisms driving nutrient export from agricultural watersheds will be critical in mitigating diffuse nutrient pollution. We used four years of high-frequency nitrate (NO_3--N) sensor data from two tile-drained, agricultural watersheds in Indiana to explore NO_3--N export patterns for 200 storms. We used concentration-discharge (C-Q) relationships, as well as the hysteresis index (HI) and flushing index (FI), to understand physicochemical controls on NO_3--N export across time scales. At both annual and seasonal time scales, we found NO3--N concentrations were largely chemostatic; however, patterns in FI suggested C-Q relationships for individual storms were highly variable, which may influence estimates of watershed-scale NO_3--N export. The predominance of counterclockwise hysteresis also suggests storm NO_3--N export was strongly driven by the mobilization of distal sources. In both watersheds, HI and FI values varied seasonally and with storm size, and patterns were linked to changes in hydrologic connectivity related to seasonal variation in subsurface tile drain flow. Variation in storm-specific NO_3--N yields was driven by event runoff, storm duration, and antecedent basin moisture, rather than antecedent precipitation, suggesting the landscape served to mediate the direct impact of precipitation on NO_3--N loss. Overall, we found that high-frequency NO_3--N data accurately documented the magnitude of the ecological challenge presented by storm-driven nutrient export in agricultural watersheds.

High frequency in situ monitoring of streams in two catchments shows that structure liming of fields reduces suspended solids leaching

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Structure lime treatment can reduce leaching of suspended sediments and attached particulate phosphorus (P) from agricultural clayey soils. However, large scale i.e. catchment scale experiments showing the potential positive impact of structure lime on suspended sediment and nutrient fluxes have been largely missing. Thus, a major research project was initiated in Finland in 2019 to study the effect of field scale structure liming on water quality and nutrient fluxes within two catchments.

The Kainu and Koolonoja catchment sizes are 111 ha and 269 ha, respectively. Fields account for 86 % of Kainu and 32 % of Koolonoja catchments. Altogether, 160 ha of fields owned by 20 farmers were treated with structure lime (6.5 tn ha^{-1}) during September 2020. The amount of quicklime (calcium oxide, CaO) was 18.6 % (more than 1 tn ha^{-1}) and the rest was ordinary lime (calcium carbonate, $CaCO_3$). The lime was incorporated to approximately 10 cm thick topsoil layer with a disc cultivator immediately after lime distribution.

Both water quality grab sampling (2-6 samples/month) and high-frequency sensor monitoring of turbidity, pH and conductivity was conducted. In addition, stream flow was determined based on water level data and rating curves. Monitoring of the two lime-treated catchments and a reference catchment with a size of 95 ha started already before the structure lime amendment.

The preliminary results indicate that the structure lime has immediately after amendment reduced soil loss and phosphorus leakages especially from the Kainu catchment, which has a high percentage of fields. The sensor monitoring period April 2020 – January 2021 was divided into two periods i.e. before and after lime treatment. The turbidity discharge relationship was analysed based on log transformed data. The slope of regression model between log transformed turbidity and log transformed discharge was lower after structure lime amendment in the Kainu catchment. The effect was not as clear in the Koolonoja catchment with a lower field percentage but still visible.

The water quality and runoff monitoring of the study site continues at least during the project period 2019-2021. Funding will be applied to continue the monitoring and study of the structure lime effects on water quality in this research site beyond 2021.

Winter cover crops reduce stream sediment export during storms

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Agricultural land use can increase soil erosion, especially during winter and spring storms, when fields are fallow. Loss of topsoil can decrease crop yields and lead to sedimentation of waterways and downstream lakes and reservoirs. Erosion results in financial losses for farmers, thus agricultural conservation practices targeted to reduce soil loss are needed. Winter cover crops are an increasingly popular practice and are planted in the off-season when fields would normally be bare; green cover can retain topsoil especially during storms or snowmelt. To quantify the impact of cover crops on stream sediment export, we deployed a Hach Hydrolab MS-5 at the outlets of two agricultural watersheds (Indiana, USA; dominated by >85% row crops) to collect continuous turbidity every 30 minutes. We then related these data to periodic grab samples for total suspended solids (TSS) to generate a multiyear record of daily TSS loads, interpolating any missing data using Loadflex modeling. Our low cover crop watershed, Kirkpatrick Ditch (KDW), had between 12-32% cover crop coverage over the multiyear study period, and our high cover crop watershed, Shatto Ditch (SDW), had up to 68% cover crop coverage. The watersheds differed in size with KDW draining 2630 ha while SDW drains 1330 ha, but KDW had on average 25% lower runoff than SDW over four water years (2017-2020). Despite less water leaving the watershed, annual TSS export from KDW (mean = 1137 kg/ha/yr) was almost seven times higher than from SDW (mean = 166 kg/ha/yr). In KDW, TSS export was more variable, and average export was strongly influenced by two years with very high flow events in winter and spring; 88% of annual TSS export left during these seasons. Similarly, in SDW 45% of TSS was lost during winter and 38% was exported during spring. When we partitioned TSS export by flow periods, TSS export during the top 10% of flows was higher in KDW than in SDW (KDW = 61%; SDW = 41%), and KDW exported ten-fold more TSS during the largest storms than did SDW (690 vs. 69 kg/hectare/year, respectively). As expected, variation in annual TSS export was influenced by watershed-specific runoff. TSS export was positively correlated with runoff in

KDW (R= 0.88), but in SDW increases in runoff did not lead to higher TSS export; SDW has very low incidence of overland flows, and also has higher cover crop coverage. Moreover, variation in annual TSS export was related to % cover crop coverage, but again this relationship was watershed-specific, the relationship was stronger for KDW (r^2 = 0.94) than for SDW (r^2 = 0.67). This research is the first to examine the effect of cover crops on storm driven TSS export, advancing our understanding of their utility in reducing sediment loss during vulnerable periods when fields are bare in winter and spring.

Rapid changes in water quality following a large Boreal Forest wildfire

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Wildfires at the edge of urban environments are becoming increasingly large and increasingly common. Recognizing the water quality impacts of these especially large wildfires is therefore emerging as a new priority for water resource managers. Following the devastating 2016 Fort McMurray wildfire in western Canada, we initiated a multi-faceted water quality monitoring program that included water quality sondes recording at 15-minute intervals. Continuous monitoring of flow and water quality showed distinct, precipitation-associated signatures of ash transport in rivers draining expansive (800–100,000 km2) and partially-burned (<1–22 % burned) watersheds, which were not evident in nearby unburned regions. Calibrating turbidity sensors to samples of both sediment and ash allowed us to quantify ash inputs to the river during these events. Our results offer lessons for other agencies deployed under difficult circumstances to quantify the impact of environmental emergencies.

Stream metabolism as a source of carbon dioxide to the atmosphere in two hydrologically contrasting Mediterranean streams

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Headwater streams are important control points for carbon dioxide (CO_2) emissions to the atmosphere, with relative contributions to CO_2 evasion fluxes of lateral groundwater inputs widely assumed to overwhelm those from in-stream metabolic processes. We tested this assumption in two Mediterranean headwater streamswith contrasting hydrological regimes: one perennial gaining stream, and one intermittent stream with seasonally losing reaches. Stream dissolved CO_2 and oxygen (O_2) concentrations were continuously analyzed during spring and early summer together with stream discharge, stream water temperature, and insolation. We used these data to analyze instantaneous and daily CO_2-O_2 exchange fluxes, and evaluate the contribution of in-stream net ecosystem production (NEP) to CO_2 evasion. In contrast to the widespread assumption that dissolved CO_2 evading from headwater streams comes primarily from lateral inflows (i.e., terrestrial export of CO_2), we found that NEP contributed substantially to total CO_2 evasion at the both sites, despite large differences in lateral groundwater inputs. Our study suggests that these headwater streams are not CO_2 chimneys to the atmosphere, but rather important venues for landscape organic carbon mineralization.We will discuss the potential mechanisms and processes responsible for this finding, particularly in light of the different hydrological and environmental conditions prevailing at each stream.

Can high-resolution water quality data help to understand the interplay between stream hydrological flushing and biogeochemical cycling?

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Understanding the interplay between hydrological flushing and biogeochemical cycling in streams is now possible owing to advances in high-frequency water quality measurements with *in situ* sensors. It is often assumed that storm events are periods when biogeochemical processes become suppressed and longitudinal transport of solutes and particulates dominates. However, high-frequency data suggest that diel cycles are a common feature of water quality time series and are often preserved during storm events, depending on their magnitude and timing. In this study, we mine a high-frequency dataset and use two key hydrochemical indices, hysteresis and flushing indices to evaluate the diversity of concentration-discharge relationships in an 3rd order agricultural stream. We show that mobilisation patterns, inferred from the hysteresis index, change on a seasonal basis, with a predominance of rapid mobilisation from surface and near stream sources during winter high-magnitude storm events and of delayed mobilisation from subsurface sources during summer low-magnitude storm events. Using Dynamic Harmonic Regression, we were able to separate concentration signals during storm events into hydrological flushing (using trend as a proxy) and biogeochemical cycling (using amplitude of a diel cycle as a proxy). Our results show that despite large storm to storm diversity in hydrochemical responses, storm event magnitude and timing have a critical role in controlling the type of mobilisation, flushing and cycling behaviour of each water quality constituent. Hydrochemical indices can be used to fingerprint the effect of hydrological disturbance on freshwater quality and can be useful in determining the impacts of global change on stream ecology.

Factors governing the relationship between nutrient source pressure and nutrient transfer in six Irish agricultural catchments

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Nutrient loads from agricultural sources can reduce water quality and contribute to impaired ecosystem functioning. In order to effectively manage and improve water quality is necessary to understand the processes that govern nutrient transport. The transfer of nutrients from agricultural sources to streams is controlled by a number of interacting factors which are both static (e.g. soil and bedrock type, thickness and permeability) and dynamic (e.g. climate, soil moisture deficit, depth to water table) and through time and space. Thus two catchments can be subject to similar source nutrient loadings yet vary in their response to source pressures.

The objective of this work was to understand the mechanisms which can cause a disparity between source nutrient loadings and nutrient flux and to expand upon the current conceptual model of the nutrient transfer continuum, with a focus on nitrate (N) and total reactive phosphorus (TRP). The “nutrient transfer continuum” (Haygarth et al., 2005) was used as a basis to develop a long-term coherent monitoring strategy of nutrient sources and hydrochemical metrics at high temporal resolution across six Irish agricultural catchments. Two hydrologically contrasting catchments with comparatively high source nutrient loadings (Timoleague and Ballycanew) were divided into 8 sub-catchments (ca. 1 km^2) corresponding to the water quality monitoring sites along the river network. Sub-catchments with similar source nutrient loadings were selected for comparison of nutrient concentrations in the stream water.

We found that sub-catchment characteristics such as soil type, antecedent weather conditions and geology dominated source nutrient loadings at this scale. In Ballycanew, a catchment characterised by poorly-drained soils, source nutrient loadings were not reflected in stream water N or TRP concentrations. However, in Timoleague, a catchment characterised by freely-draining soils, sub-catchments with higher nutrient loadings we also observed higher N and TRP stream water concentrations.

Our findings highlight the complexity of nutrient transfer and show that the benefits of a coherent monitoring strategy of catchment hydrochemistry are two-fold. First, knowledge and understanding of a catchment’s response to source pressure allows measures to be developed which target critical nutrient transfer pathways. Second, an understanding of a catchment’s hydrochemical responses is needed in order to accurately assess the efficacy of any measures employed because hydrological time lags and changing weather patterns could cause the misinterpretation of monitoring data. The results of this work will contribute to the development of improved catchment management policy.

Seasonal controls on sub-Arctic river total organic carbon dynamics revealed by high frequency monitoring

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In the sub-Arctic region, climate change is rapidly modifying the hydrometeorological conditions with implications for the export and processing of carbon from river catchments. Despite this important context, our understanding of TOC (Total Organic Carbon) dynamics at seasonal - daily timescales remains limited for sub-arctic headwaters. To address this research gap high-frequency data were collected from August 2019 to December 2020 in the Pallas catchment located next to Pallas-Ylläs National Park, Finland (68°02′N, 24°16′W). We measured high frequency in-stream TOC and in-stream stable water isotopes alongside a range of hydrometeorological variables at a 30-minute resolution using *in-situ* sensors with the aim of quantifying TOC dynamics, and identifying the main controls and processes influencing TOC in a sub-arctic headwater stream during different seasons. Q-C (discharge - concentration) relationships were used to identify seasonal differences and controls on TOC. Innovative isotope aided hydrological modelling was employed to assess TOC – water age relationships. Wavelet transforms and coherence were used to identify periodicity in the relationship between TOC and hydrometeorological predictors from which we were able to infer which processes influencing TOC were acting at different timescales.

Seasonal variability in the Q – TOC relationship was assessed using segmented regression. Results suggested the breakpoint (i.e. transition from chemostatic to chemodynamic behaviour) occurs at lower flow in spring compared to summer and winter, likely due to increased dilution and/or supply exhaustion during the snowmelt period compared to later seasons. Young water provides the bulk of streamflow in summer when precipitation is the major water source which is associated with higher TOC, however this alters to older water during winter, as the stream becomes increasingly groundwater dominated. Wavelet analysis identified TOC diel cycles from May - October highlighting the importance of in-stream carbon processing during this period. Flow meanwhile exhibited a strong in-phase relationship with TOC from May - December, after which TOC remained relatively static for the rest of Winter.

Our study highlights the distinct seasonal processes and controls on TOC dynamics in a sub-arctic stream. We highlight a shift from groundwater (older-water) dominance in winter, to younger-water becoming increasingly important in summer and autumn as surface and near-surface flow pathways are activated. Furthermore, we highlight clear seasonality for photodegradation and in-stream processing which is likely to exhibit marked changes in the future. With climate changing altering the timing and length of seasons and temperatures rise leading to hydrological shifts, this study can be used to assess the importance of the current controls on TOC in the sub-arctic.

Flowpaths controls on high spatial resolution water chemistry profiles

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High temporal resolution monitoring of multiple water quality parameters have become widespread in the last two decades. Today, the development of portable sensors also make it possible to monitor water chemistry at a high spatial resolution, with similar technical and scientific challenges. In this study, we measured nitrate, dissolved organic carbon (DOC), pH, conductivity, redox potential, temperature and O2, every 50 to 100m along 15 km of streams within six agricultural headwater catchments (1-3.5 km²). The objective was to identify nitrate emission and retention zones at a high spatial resolution, during four seasons: autumn rewetting, winter high-flow, spring recession and summer low-flow. Our results showed monotonic concentration profiles for nitrate and DOC, and opposite profiles for both parameters. The shape of the high-resolution concentration profiles remained the same across all seasons. Four catchments exhibited decreasing nitrate and increasing DOC from upstream to downstream, and two catchments exhibited increasing nitrate and decreasing DOC. These profiles did not reflect a longitudinal land use gradient. Discharge measurement at four locations in two of the catchments showed an increase in specific runoff from upstream to downstream. This upstream water deficit shows that the upstream monitoring points only captured the shallowest flowpaths, while the downstream points captured both shallow and deeper flowpaths. We conclude that high spatial resolution monitoring in headwater catchments can be used to decompose the water chemistry of shallow/near-stream flowpaths from that of deep/long-distance flowpaths.

Nitrate retention in a large stream across variable flow conditions using continues high-frequency data

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Stream networks can process nutrients during their transport from headwaters to downstream sites. These in-stream transformations retain considerable amounts of nutrients, e.g. nitrate, and therefore mitigate anthropogenic loading. Most nitrogen retention studies in streams concentrate on low flow conditions and consequently studies of nitrate retention during high flows are extremely rare. High-frequency measurements using in-situ UV sensors can improve nitrate retention estimates at variable flow conditions. In our study, we investigated a 27 km long agricultural stream reach of the 6th order Bode river, Germany, which is part of the TERENO Hydrological Observatory. We used 5 years of high-frequency (15min interval) nitrate and discharge data and conservative monthly-sampled manganese measurements. A mass balance approach was applied for analyzing nitrate retention of high flow events of varying size. Percentage nitrate retention could be detected amounting up to 17% of total loads. Nitrate retention showed a clear dependency on storm size and declined with increasing storm magnitude. Areal uptake rates were in similar ranges than those of low flow conditions. High flow events retained nitrate mostly during the growing seasons but those with considerable inundation of floodplains could also retain nitrate in winter. Only small runoff events revealed a clear clockwise C/Q hysteresis of the difference between upstream and downstream nitrate concentration, indicating the strongest nitrate retention at the beginning of the event. Our study shows that also large streams can retain nitrate during high flows, while the retention of nitrate may change rapidly in time and with discharge conditions. Therefore, high-frequency data are critical for improving our understanding of such retention processes.

CO_2 dynamics in low-land streams driven by hydrology and primary production

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Streams are known to be hotspots for emitting CO_2 to the atmosphere and are hence important components in landscape carbon balances. However, surprisingly little is known about the stream CO_2 dynamics and emissions in agricultural settings, a land-use type that globally cover ca 40% of the continental area. Here we present directly measured and continuous CO_2 concentration data from streams draining agriculture influenced catchments covering the full open-water season. The stream CO_2 concentrations were generally high compared with the literature but were also highly variable. The high dynamics covered a variety of different time-scales from seasonal to hourly, and with an interplay of hydrological and biological controls. The hydrological control was strong (although with both positive as well as negative influences dependent on season) and rapid in response to rainfall and snowmelt events. However, during growing-season baseflow and receding flow conditions, aquatic primary production seems to control the stream CO_2 dynamics resulting in elevated diel patterns. Given the observed high levels of CO_2 and its temporally variable nature, agricultural streams clearly need more attention in order to understand and incorporate these considerable dynamics in large scale extrapolations.

Evaluation of in-stream nitrate retention dynamics based on high-frequency measurements in high order stream reaches (central Germany)

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Streams are important conduits to transport nitrogen (N) from terrestrial landscape to the sea. In-stream nitrate retention in rivers vary spatiotemporally and are affected by many factors, including hydraulic (e.g., discharge variations), biotic (e.g., phytoplankton and periphyton) and weather conditions (e.g., temperature and light variations). Two-station mass balance approaches based on high-frequency measurements allow quantifying reach-scale nitrate retention dynamics. However, such in-situ measurements are limited to few river types (e.g., spring-fed rivers), which limit analysis of controlling factors across stream conditions. Here, we conducted multi-parameter high-frequency monitoring, including two in-situ station time series and in-between longitudinal profiling in three high order stream reaches in central Germany (i.e., the Bode (6th), the Weisse Elster (5th) and the Mulde (7th) river). Two-station mass balance results showed that net nitrate uptake rates differed largely among reaches with contrasting morphology, as well as between sampling dates, ranging from 16.4 to 315.4 mg $Nm^{-2}d^{-1}$. The magnitude of assimilatory and dissimilatory uptake varied from 13.6 to 56.4 and 2.8 to 282.3 mg $Nm^{-2}d^{-1}$, respectively. Unexpected increases of nitrate concentration at the downstream site were observed during some campaigns, which may have been caused by lateral inputs or highly fluctuating flow regime from upstream. Multiple environmental parameters (e.g., discharge, specific conductivity and pH) were helpful to further detect and explain the potential reasons. Longitudinal profiling provided straightforward evidence of the existence of lateral inputs and was helpful to distinguish the mixing signal along the reach, making reach-scale mass balance results more precise. In conclusion, the two-station method can well measure in-stream nitrate retention at the reach scale, but measurements are affected by unexpected meteorological variabilities (e.g., rainstorms) and other disturbances. Hence, long-term continuous multi-site measurements can compensate for monitoring intra- or

inter-annual in-stream nitrate dynamics, albeit it could be time- and labor-consuming.

Would short-term online-monitoring improve the current WFD-sampling strategy?

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The European Union Water Framework Directive (WFD) aims to achieve good ecological and chemical status of the member states' surface water bodies by 2027. An integrated guidance on chemical & biological monitoring has been established and is transferred into the law of the states (European Union, 2000, e.g. Bundesministeriumder Justiz und für Verbraucherschutz, 2016). This guidance requires to assess the water bodies' quality with its variability in time and space by providing sufficient samples that will be analysed for representative results. However, detailed methods are not specified, leaving large space and flexibility for member states in its implementation (Skeffington et al., 2015). We assessed this implementation in Saxony (Germany) by comparing real grab sampling data with data from online-monitoring sensor from five stations at four streams of different sizes (3 * 10 years and 2 * 3 years of data). Furthermore, we suggested and compared an alternative sampling strategy, where grab sampling is replaced by application of online sensors - but for a short measurement duration and frequency (1-5 days of measurement during once every month to every three months). Our study focuses on dissolved oxygen, nitrate nitrogen and chloride concentration as they can be easily measured with online monitoring devices. Results show, that the current sampling regime's error varies from year to year with a range of 0.65 – 42 %. Especially in large streams grab sampling tends to be more accurate in contrast to smaller and medium sized streams. Parameters that are affected by diurnal variations (e.g. dissolved oxygen), are a good example for errors in the current sampling regime, as around 1/3 of the investigated online results would cause a worse classification of the waterbody. In this cases the new strategy of continuous measurement for consecutive days is proposed and it could be shown, that higher accuracy can be achieved for some streams. In contrast to that, the same sampling strategy leads to even higher uncertainty in other streams. The optimal sampling regime for short-term online-monitoring is not uniform but dependent on investigated parameter and catchment characteristics. Once a good measurement duration and frequency is identified, short-term online-monitoring could improve the

current grab sampling strategy by a reduction of site visits without a loss of information.

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High-resolution monitoring of legacy transport at the farm scale

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Phosphorus (P) leaching from agriculture is a major driver of water eutrophication in downstream rivers and lakes. In drained lowland areas with intensive agriculture, a reduction in the fertilizer applications may be insufficient to improve the water quality in the short term as the P accumulated in the soil during decades of high fertilization may continue leaching for many years. A complementary approach to reduce P exports from agriculture is to implement edge-of-field mitigation measures at the farm scale. The selection of effective measures requires a detailed insight into the chemical and hydrological transport mechanisms. Here, we determined the main P sources, processes, and transport routes at the farm scale to support the selection of appropriate mitigation measures. We quantified the legacy P, the different P pools stored in the upper soil, and related it to the yearly P export downstream. To do this, we combined high-resolution monitoring data from the soil, groundwater, surface water, and ditch sediments. The legacy P in the topsoil was high, about 2,500 kg/ha. The predominant subsurface flow and the subsoils' P sorption capacity retained the P mobilized from the topsoil and explained the relative moderate flux of P to surface waters (0.04 kg/ha during the 2018-2019 drainage season). The dissolved P entering the drainage ditch via groundwater discharge was bound to iron-containing particles formed due to the oxidation of dissolved ferrous iron. Once leached from the soil to the drainage ditch, resuspension of P-rich sediment particles during flow peaks were the most important P transport mechanism (78%). Therefore, we expect that hydraulic constructions that reduce flow velocities and promote sedimentation of P-containing particles could reduce the export of P further downstream.

Understanding the role of spatio-temporal patterns on hydrochemical processes in two-stage ditches to reduce eutrophication

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Combating eutrophication requires holistic mitigation measures aimed at reducing agricultural losses of nitrogen (N) and phosphorus (P) from field sources to aquatic systems. This need will become critical in the future as increased flashiness, expected from changing climate and growing food demand, will further accelerate N and P pollution.

This project will advance the knowledge of processes governing nutrient and sediment retention in agricultural streams in Sweden by focusing on two-stage ditches (SD), a novel mitigation measure. Constructed SDs resemble naturalized streams with incised floodplains surrounding the main channel. The measure relies on hydrological and biogeochemical controls to reduce N, P and sediment losses by increasing the hydrological connectivity and reducing the water velocity during high flows. High temporal water quality monitoring is critical to unravel the spatio-temporal patterns in nutrient and sediment fluxes in SDs, compared with traditional trapezoidal ditches (TD). High temporal monitoring can further provide information of catchment delivery pathways that may influence the function of SDs.

Existing studies in the US and Finland have found that SDs can mitigate N, P and sediment losses, compared with TDs. However, this project is the first of its kind to deploy sub-hourly monitoring of nitrate, suspended solids and stream metabolism parameters in 10 different SDs in Swedish conditions over 3 years. The catchments are situated in two climatically different regions with diverse agricultural land use and soil characteristics.

In this presentation, we show the details of experimental setup and preliminary results. A sampling has been setup in SD reaches in Central Sweden with high temporal monitoring of discharge, turbidity, dissolved oxygen, dissolved organic matter and specific conductivity. This is coupled with monthly grab sample water quality monitoring. We discuss the relationship between concentration-discharge (c-q) during storm events, measured at upstream and downstream of SDs as well as c-q differences between catchments. These patterns will provide information of SDs capacity to buffer against nutrient and sediments losses during hydrological events. Furthermore, it will aid the understanding of how different catchment behavior influence SDs function and thus where the mitigation measure is most suitable.

Influence of storms on ecosystem metabolism in two agricultural watersheds

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Extensive alteration of land use in agricultural watersheds impacts ecosystem function in adjacent waterways. Agricultural streams are highly productive due to high light availability via their open canopies, and excess nutrient inputs from surrounding fields, but they remain susceptible to disturbance exacerbated by channelization and flashy hydrology. Stream metabolism, quantified as gross primary productivity (GPP) and ecosystem respiration (ER), reflects ecosystem function, and is responsive to environmental variation. Understanding the influence of storms on stream metabolism is increasingly important as precipitation patterns are expected to shift under future climate projections. During the 2016-2020 water years (October to September), we measured dissolved oxygen concentrations and temperature every 30 minutes using Hydrolab Minisondes deployed at the outlets of two agricultural watersheds (>85% row crops) in Indiana (USA). We explored the impact of storms on metabolism by modeling daily GPP and ER for three days before and after storms using the inverse modelling approach using one-station open channel metabolism run in R. With an initial analysis of metabolism for around 30 storms, we found that GPP rates varied by season (ANOVA, $p<0.001$), where GPP was highest during the spring (4.3±0.5 g O_2 m^{-2} d^{-1}), followed by summer (2.4±0.3 g O_2 m^{-2} d^{-1}) and winter (1.2±0.2 g O_2 m^{-2} d^{-1}), and lowest in fall (0.7±0.1 g O_2 m^{-2} d^{-1}). In contrast, we found ER was comparable among seasons (-5.7±0.8 g O_2 m^{-2} d^{-1}, ANOVA, $p>0.05$). We predicted that storms would disturb benthic biology and thus ecosystem metabolism would decline after each storm, relative to before, due to the scouring of fine sediments. For GPP, storms did not alter rates for 12/30 storms (t-tests; $p>0.05$), but where GPP was different after storms, only 8/18 storms decreased GPP (t-tests, $p<0.05$). For ER, storms did not alter rates for 16/30 storms, while for the remaining storms, data were evenly split between significant increases and decreases after storms (t-tests, $p<0.05$). We also used flow duration analysis to explore if storm size was related to pre vs post

responses. For the storms analyzed thus far, even the top 10% of storms did not consistently reduce GPP or ER post storm, suggesting that agricultural streams may be more resistant to disturbance from high flows despite being dominated by fine sediments. Moreover, interactions among seasonal patterns, storm size, and benthic biological activity will be critical to explore in order to explain the variation in the response of metabolism metrics to storms. We will also expand our analyses to compare metabolism in two watersheds with different flow characteristics. Long-term monitoring of dissolved oxygen can be used to identify changes in stream ecosystem function in response to storms, which may become more vulnerable with a change in storm frequency and intensity under a changing climate.

PhD course

High Temporal Resolution Water Quality Monitoring and Analysis

Post graduate course, 1.5 ECTS, Course leader Magdalena Bieroza (SLU)

This course is run together with the 4th International Workshop on High Temporal Resolution Water Quality Monitoring and Analysis held at SLU 31st of May-2nd of June 2021. The general focus of the course is on exploring recent technological and scientific advances in water quality measurements allowing for high-resolution determination of chemicals in water with a range of instruments. These new technologies have brought new insights into mechanistic understanding of catchment and stream processes and are progressively utilised to evaluate the effectiveness of water management efforts.

The objective of the course and the workshop are therefore to discuss how these new technologies and data can further advance catchment science and contribute to water resources management. This comprises evaluation of hydrological and biogeochemical responses on time-scales of individual storm events, seasons and in the long-term, and linking them to natural and anthropogenic drivers and impacts. Specifically, the workshop will address topics from instrument deployment, data collection, analysis and modelling to interpretation of hydrochemical signals and processes for individual catchments and catchment typologies.

Session 0: Introduction to high-resolution water quality monitoring and analysis, 12:30-16:15, Fri 28th May 2021

Session 1: New advances in high-resolution water quality monitoring, 12:15-17:45, Mon 31st May 2021

Session 2: Extracting hydrochemical patterns and modelling of high-resolution data, 12:30-17:45, Tue 1st of June 2021

Session 3: Understanding hydrochemical and biogeochemical processes, 12:30-17:45, Wed 2nd June 2021

Session 4: Unanswered questions in catchment science and water quality management, Synthesis of workshop findings, 12:30-16:15, Thu 3rd June 2021

Session 5: Planning joint publication, 12:30-15:10, Fri 4th June 2021

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