

High resolution monitoring of nutrients in groundwater and surface waters: process understanding, quantification of loads and concentrations and management applications

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Abstract

Four sessions on “Monitoring Strategies: temporal trends in groundwater and surface water quality and quantity” at the EGU-conferences in 2012, 2013, 2014 and 2015 and a special issue of HESS form the background for this overview of the current state of high resolution monitoring of nutrients. The overview includes a summary of technologies applied in high frequency monitoring of nutrients in the special issue. Moreover, we present a new assessment of the objectives behind high frequency monitoring as classified into three main groups: i) Improved understanding of the underlying hydrological, chemical and biological processes (PU); ii) quantification of true nutrient concentrations and loads (Q); iii) operational management, including evaluation of the effects of mitigation measures (M). The contributions in the special issue focus on the implementation of high frequency monitoring within the broader context of policy making and management of water in Europe for support of EU Directives such as the Water Framework Directive, the Groundwater Directive and the Nitrates Directive. The overview presented enabled us to highlight the typical objectives encountered in the application of high frequency monitoring and to reflect on future developments and research needs in this growing field of expertise.

1

2 **1 Introduction**

3 The presence and dynamic behavior of nutrients in groundwater and surface water is an
4 important issue in water management, in particular in areas with intensive agriculture. This is,
5 for example, reflected in EU directives such as the Nitrates Directive (EU 1991), the Water
6 Framework Directive (*WFD*; EU 2000), the Groundwater Directive (*GWD*; EU 2006) and the
7 Monitoring Directive (EU, 2009). Member states are obliged to monitor and report on the
8 environmental status of the water bodies and, if necessary, take measures to establish adverse
9 trend reversal. As far as nutrients are concerned, the European directives focus on aquatic
10 ecosystems and groundwater-dependent ecosystems. In order to meet the obligations,
11 monitoring programs have to cover a range of water quantity, water quality and ecological
12 parameters, and an understanding of dynamic nutrient processes is required for these
13 programs to be efficient and cost effective. However, the design of monitoring strategies is
14 often hampered by limited knowledge of, for instance, nutrient responses to weather
15 conditions, land use and agricultural practices. Moreover, the behavior of nutrients shows
16 large variability in both space and time (see, e.g., Campbell et al., 2015, and Goyenola et al.,
17 2015).

18 To satisfy the increasing demand for knowledge and information on the dynamic behavior of
19 nutrients, the past 10-15 years have seen a rapid development of observation devices and
20 technologies for high resolution monitoring of nutrients and other solutes and isotopes at
21 affordable cost, encouraging researchers and other stakeholders to perform studies in
22 experimental as well as operational settings. Thus, vast amounts of research data have been
23 collected on various water quality variables, allowing the study of relevant biogeochemical
24 processes and enabling comparisons between the results obtained by the use of different
25 monitoring devices. Thus, awareness has increased about the advantage of using high
26 resolution nutrient monitoring as complementary tool next to traditional low frequency
27 monitoring. The sessions on “Monitoring Strategies: temporal trends in groundwater and
28 surface water quality and quantity” at the EGU-conferences in 2012, 2013, 2014 and 2015
29 clearly showed that high frequency monitoring and strategies for nutrient monitoring are
30 subjects that attract great interest. Part of the work presented at these sessions is now gathered
31 in the 10 papers included in this special issue of HESS, which aims to provide an overview of
32 the current state of high resolution monitoring of nutrients, identify important knowledge gaps

1 and to pinpoint future research needs and potential application of high resolution monitoring
2 in the management of groundwater and surface water resources. The main research questions
3 addressed are:

- 4 - What does the new monitoring technology have to offer and how can we develop an
5 optimal monitoring strategy?
- 6 - Can we assess and quantify the transport processes of nutrients, in particular at the
7 short time scale?
- 8 - How can we use high frequency nutrient monitoring to achieve our management
9 goals?

10

11

12 **2 Monitoring objectives**

13 An overview of monitoring objectives and time scales for high frequency nutrient monitoring
14 is given in Table 1. We distinguished between three main groups of monitoring objectives:

- 15 - To improve our understanding of the underlying hydrological, chemical and biological
16 processes determining temporal and spatial patterns in nutrients (PU).
- 17 - To quantify nutrient loads and concentrations (Q).
- 18 - To support operational water and environmental management, including evaluation of the
19 effects of mitigation measures and predictions (M).

20 It should be noted that some papers address more than one of these overall objectives.

21

2.1

22 **Hydrological, chemical and biological process understanding**

23 Kirchner et al. (2004) addressed the new opportunities of high resolution monitoring for
24 understanding the functioning of catchments, and they foresaw a new era of technical
25 progress and study of actual data, making full profit of the newly acquired spectrum of signals
26 from very short to longer time scales. A decade later, a large number of papers and
27 presentations, including those at the EGU sessions, have demonstrated that process

1 understanding has indeed improved significantly. We have made a subdivision of the
2 monitoring objectives focusing on process understanding:

- 3 • *PU1: Understanding flow regimes and nutrient dynamics.* These studies focus on the
4 behavior of one variable at a time in order to characterize flow regimes, flow and
5 concentration dynamics, hysteresis effects and extreme values of nutrient
6 concentrations and loads. Typically, high frequency monitoring via its high resolution
7 allows characterization of the concentration changes. Thus, the rising limb of the
8 hydrograph represents the short-scale transport processes. Examples can be found in
9 Goyenola et al. (2015) and Outram et al. (2014).
- 10 • *PU2: Characterization of transport routes and time scales.* These studies aim to detect
11 flow routes, groundwater-surface water interactions and travel time distributions with
12 emphasis on the interactions between variables in different hydrological
13 compartments, in particular those between groundwater and surface water. The added
14 value of high frequency monitoring is its ability to distinguish between fast and slow
15 flow components (see Poulsen et al. 2015b, Shreshta et al. 2013, Rozemeijer et al.
16 2010a, 2012). High frequency monitoring has also stimulated the development of new
17 approaches to characterize the transient nature of travel time distributions (Velde et al.
18 2010, Botter et al. 2011, Hrachowitz et al. 2015).
- 19 • *PU3: Characterization of retention processes.* These studies aim to gain insight into
20 the attenuation and retention processes determining the response of nutrients to driving
21 forces such as rainfall events, in both surface and ground water. High frequency
22 monitoring may, for example, reveal clear day-night cycles in nutrient concentrations,
23 contributing to the unraveling of retention and primary production processes in surface
24 waters (see, e.g., Rode et al. 2013). Quantifying denitrification processes using N-
25 isotopes together with calibration of flow models using nitrate and discharge data is a
26 promising approach when studying PU2 and PU3 objectives combined (Shershta et al.
27 2.2 2013).

28 **Quantification of loads and concentrations**

29 Q type monitoring objectives focus not on identifying and understanding the processes but on
30 the quantification of specified quantities, such as averages, probabilities and proportions of
31 exceedance of water quality standards. Typically, such objectives relate to policy
32 development and operational management, in particular relative to EU directives such as the

1 EU Nitrates Directive (EU 1991) and the Water Framework Directive (EU 2000). Q type
2 objectives are divided into:

- 3 • *Q1: Assessment of typical or average concentrations, solute loads and export of*
4 *solute towards downstream waters.* Low frequency monitoring can give an estimate
5 of average concentrations and discharges over a time period via interpolation.
6 However, nutrient concentrations and discharges are frequently correlated. Short
7 duration concentration peaks likely go undetected using low frequency monitoring,
8 which implies that load estimates based on low frequency monitoring are typically
9 biased and too low (Rozemeijer et al. 2010a, Cassidy & Jordan 2011, Audet et al.
10 2014, Goyenola et al. 2015, Skeffington et al. 2015). In contrast, high frequency
11 monitoring reduces the bias in concentration distributions derived from under-
12 sampling of the concentration time series. (e.g. Jordan et al. 2007, Rozemeijer et al.
13 2010b, Ernstsens et al. 2015, Campbell et al. 2015). High frequency monitoring may
14 also reveal artefacts produced by the fact that regular sampling is normally undertaken
15 in the daytime, thus typically not capturing differences between daytime and night-
16 time fluxes (Neal et al. 2012, Van der Grift et al. 2016).
- 17 • *Q2: Assessment of temporal trends, quantification of trend slopes and identification of*
18 *trend directions.* High resolution monitoring, in combination with time series from
19 regular low frequency monitoring, may help to reveal the structure of water quality
20 time series, thereby allowing testing the significance of trends both deterministically
21 (e.g. Van der Grift et al. 2016) and statistically (Lloyd et al. 2014, Rozemeijer et al.
22 2014), for example using spectral analysis methods (Aubert et al. 2013, Blauw et al.
23 2013).
- 24 • *Q3: Testing compliance with water quality standards, such as WFD Environmental*
25 *Quality Standards.* This involves testing the frequency of exceedance of standards or
26 quantifying the probability of exceedance. High frequency monitoring improves these
27 aims by adding information on extreme values and short-term peaks impacting the
28 regular evaluation of exceedances in low frequency programs. Skeffington et al.
29 (2015b) clearly demonstrate that the classification of WFD Chemical and Ecological
30 Status is strongly influenced by sampling frequency and time of sampling during the
31 year and over the day.

- 1 • *Q4: Water and matter balances and sources.* Detection of (pollution) sources is often
2 difficult to capture in natural catchment systems, but high frequency monitoring can
3 add short time scale information on dilution or accumulation rates which helps source
4 apportionment and adds to improving water and mass balances (see Van der Grift et
5 al. 2016, Aubert et al. 2013b, Goyenola et al. 2015, Rozemeijer et al. 2010b).
- 6 • *Q5: Comparison of monitoring equipment.* Several recent studies endeavor to answer
7 the question of how high frequency monitoring equipment may supplement the
8 existing monitoring tools. The central question is ‘what are the possibilities of new
9 equipment?’ Examples of comparisons of new monitoring equipment used in surface
10 water and groundwater monitoring are found in Audet et al. (2014), Huebsch et al.
11 (2015), Jordan et al. (2013) and Rozemeijer et al. (2010c).

12 **Operational (real time) management – effects and predictions**

13 ^{2.3} The central aim of the M type monitoring objectives is an evaluation of the impact of water
14 and environmental management measures as well as climate change on nutrient transport. M
15 type objectives typically involve the reaction of the catchment to man-made or natural
16 changes of nutrient sources and the hydrological functioning or the biogeochemistry of the
17 system. We have defined three subgroups:

- 18 • *M1: Management and mitigation of point sources.* High frequency monitoring can
19 reveal any changes in the short-term reaction of the catchment to changes in nutrient
20 inputs, hydrology or biogeochemistry. Besides revealing the time-dependent nutrient
21 inputs from, for instance, sewage treatment facilities or leaking septic tanks (Wade et
22 al. 2012), the effects of mitigating measures can be followed by assessing changes in
23 the duration or frequency of nutrient peaks in the time series before and after their
24 implementation. Examples are given in Campbell et al. (2015) and Greene et al.
25 (2011).
- 26 • *M2: Management and mitigation of diffuse sources.* Mitigation measures for nutrients
27 in agricultural areas typically involve some kind of land use management or changes
28 in the hydrological functioning of the system. Despite the establishment of high
29 frequency monitoring, the effects of mitigation measures are often difficult to separate
30 from those of natural variability created by meteorological conditions or from spatial
31 variations in governing variables such as soil types and subsurface reactivity.

1 Examples of monitoring the effects of mitigation measures in diffuse pollution settings
2 are given in Campbell et al. (2015), Ernstsen et al. (2015), Van der Grift et al. (2015)
3 and Rozemeijer et al. (2016), all included in this special issue, and Greene et al.
4 (2011). Given the slower dynamics of groundwater, other techniques such as age
5 dating and lower monitoring frequencies are usually applied to reveal trends following
6 implementation of mitigation measures (Broers & Van der Grift 2004, Visser et al.
7 2007, 2009, Hansen et al. 2012, 2013).

- 8 • *M3: Climate change and mitigation measures.* High frequency monitoring helps
9 reveal the impact of and adaptations to climate change by capturing changes in the
10 hydrological and hydro chemical response to rainfall events and testing whether the
11 projected changes in catchment behavior actually occur. Examples are given in
12 Graeber et al. (2015) and Goyenola et al. (2015).

14 **3 Information time scales**

15 The scale at which information is required is termed “information scale”. Information scale is
16 important when designing monitoring systems and choosing the methods and goals for data
17 processing (Broers 2002, Van Geer et al. 2006). For instance, selection of monitoring
18 equipment and choice of methods for data smoothing require a properly defined information
19 scale, and the papers and abstracts are therefore grouped according to this (Table 1). For each
20 monitoring objective, the required information depends on the scale at which the information
21 is needed. The following three temporal scales are considered:

- 22 - Short-scale dynamics and extreme events (minutes to weeks).
- 23 - Seasonal and annual patterns (months to several years).
- 24 - Longer term behavior and trends (years to decades).

25 Specific monitoring objectives may require a specific information scale. This we illustrate for
26 the monitoring objective ‘characterizing groundwater surface water interaction’. Typically,
27 analysis of the response of nitrate concentrations in surface water to rainfall events is of short
28 temporal scale (minutes or hours). To estimate average loads from shallow groundwater
29 towards surface water during the growing season, the information scale required will involve
30 one or several seasons. To evaluate the long-term sustainability of groundwater-dependent

1 aquatic ecosystems in a WFD assessment, the information scale may cover several years or
2 decades.

3 Irrespective of the time scale of the monitoring objective, observations contain variations at
4 all time scales and the gathered data have to be processed and statistically filtered in order to
5 obtain the correct trend information or system characteristics at the desired time scale (e.g.
6 Lloyd et al. 2014).

7 **Short time scales**

8 Obviously, to obtain information at short time scales, high frequent monitoring is required
9 and data processing will include high pass filters. Concentrations and loads of nutrients
10 frequently show rapid changes over time as a result of rainfall events, emissions of effluents
11 from point sources and unintended losses of manure or pesticides during application. Often,
12 these rapid changes occur at time scales less than one hour and high frequency monitoring is
13 required in order to capture peaks and extreme values that would go undetected if applying
14 only low frequency monitoring (cf. Campbell et al. 2015, Skeffington et al. 2015b, Van der
15 Grift et al. 2016).

16 Also, if assessing the statistical characteristics of the concentration or the load of a solute (e.g.
17 average and percentile values or the frequency of exceedance of a threshold), high frequency
18 monitoring is a valuable tool. In principle, statistical characteristics can be determined from
19 low frequency observations provided that the monitoring period is sufficiently long. However,
20 in many cases the system shows statistically non-stationary behavior over longer periods of
21 time due to, for example, changes in land use management. High frequency monitoring,
22 enables the estimation of trend characteristics in shorter periods, being less sensible for
23 longer-term trends (e.g. Lloyd et al. 2014). Many studies focus on the interactions between
24 groundwater and surface water, in particular the different flow paths of nutrients towards the
25 surface water (cf. Poulsen et al. 2015b, Rozemeijer et al. 2010b). The weather conditions
26 appear to be the major driving force for the temporal distribution of fluxes along the different
27 flow paths, including quick components like discharges from point sources, tile drain water
28 and overland flow and slow components such as discharges from deeper groundwater. The
29 quick components have response times in the order of magnitude of hours, days or weeks.
30 Therefore, the response of nutrient fluxes and loads to precipitation is a complex function
31 (e.g. Van der Velde et al. 2010). To estimate this complex response function and to unravel

1 the contributions of the different flow paths, high frequency monitoring is a prerequisite (cf.
2 Campbell et al. 2015).

3 **Seasonal and annual patterns and long term behavior**

4 An example of an objective with a seasonal information scale is the estimation of average or
5 3.2 typical nutrient concentrations during the growing season. An example of a long-term
6 monitoring objective is found in the Water Framework Directive (WFD), which include
7 elucidating the trends in water quality status towards the 2027 compliance with good
8 chemical status and meeting the environmental objectives for aquatic and terrestrial
9 ecosystems (cf. Rozemeijer et al. 2014, Erntsen et al. 2015, Skeffington et al. 2015b). As to
10 groundwater, an equivalent time scale is required for demonstrating the trend reversal in
11 concentrations of nitrate (Visser et al. 2007). Although high frequency information (days to
12 weeks) is not required for the analysis of seasonal and annual patterns and long term behavior,
13 high frequent monitoring can be beneficial, because often statistical characteristics and input-
14 response relations can be inferred reliable from a shorter monitoring period. Individual
15 observations of water quality are the result of variation at a wide range of frequencies. High
16 frequency variations (noise) tend to obscure the low frequency signal. High frequency
17 monitoring enables filtering out the noise (low pass filter) during relatively short monitoring
18 periods in order to elucidate the long-term trend (Bierkens et al. 1999, Halliday et al. 2012,
19 Aubert et al. 2013, Lloyd et al. 2014, Van der Grift 2016).

20

21 **4 Monitoring equipment**

22 Several types of sensors have been developed in recent years. Some are based on *in situ*
23 laboratory (mobile or stationary) analysis of water samples, while others utilize, for instance,
24 light or infrared (UV) spectra to measure chemical parameters (e.g. turbidity, nitrate, DOM)
25 or materials capable of passive adsorption of chemicals (e.g. Sorbicells). Some sampling
26 methods produce point observations in time, whereas others derive flow- or time-weighted
27 concentrations over a time period. A number of studies (e.g. Rozemeijer et al. 2010c, Cassidy
28 and Jordan 2011, Jordan et al. 2013, Huebsch et al. 2015) compare several sampling
29 instruments and monitoring strategies (Table 2). Various continuous monitoring methods, in
30 particular those described in the papers presented in this special issue, are listed in Table 2.

31

1 Table 2: Overview of monitoring methods and instruments applied in the Session abstracts
 2 and Special Issue papers.

Monitoring methods	Instruments	References to papers in the special issue describing the results of studies in which the instruments were applied
Nitrate sensors	- scan spectrolyserTM ,scan Messtechnik GmbH, Austria - NITRATAX plus sc, Hach Lange GmbH, Germany - reagentless hyperspectral UV photometer (ProPS)	Huebsch et al. (2015) Van der Grift et al. (2016) Rozemeijer et al. (2010c) Wade et al. (2012) Heinz et al. (2014)
Phosphorus (total P, total reactive P)	Phosphax Sigma auto-analyzer, Hach Lange GmbH, Düsseldorf, Germany C	Campbell et al. (2015) Rozemeijer et al. (2016) Skeffington et al. (2015b) Van der Grift et al. (2016)
(Total reactive phosphorus, TRP), nitrite (NO ₂) and ammonium (NH ₄)	Systea Micromac C	Wade et al. (2012)
Passive samplers	SorbiCell-samplers (De Jonge & Rothenberg, 2005)	Rozemeijer et al. (2010c, 2015) Audet et al. (2014)
Turbidity	OBS sensor, Campbell Scientific	Van der Grift et al. (2016)
Automatic samplers	Isco sampler; Sigmatax sampler	Goyenola et al. (2015) Audet et al. (2014) Van der Grift et al. (2016)
O ₂ , pH, temperature conductivity, turbidity and chlorophyll	- YSI 6600 multi-parameter sonde	Skeffington et al. (2015b) Wade et al. (2012)
Conductivity, temperature	CTD-diver (Van Essen Instruments, Delft, the Netherlands)	Van der Grift et al. (2016)
¹⁸ O, ² H	Wavelength-Scanned Cavity Ring Down Spectrometry System (WS-CRDS) L2120-i Picarro	Heinz et al. (2014)

3

4 **5 Conclusions and future outlook**

5 Based on the observations and findings described at the 5 EGU sessions together with the 10
 6 papers included in the present special issue, some general conclusions can be drawn.

7 Several research groups in Europe and beyond are undertaking pilot studies on the use of high
 8 frequency monitoring of nutrients. During the past decades, there has been growing awareness
 9 of the fact that the quality of the aquatic environment is threatened by high concentrations and
 10 loads of nutrients in groundwater and surface water. At the same time, development of
 11 observation equipment enabling high frequency monitoring at affordable cost has been
 12 extensive and, accordingly, assessment and quantification of the dynamic behavior of
 13 nutrients at very small time scales (minutes to hours) are now feasible. Most testing has been
 14 devoted to process understanding (PU) and quantification of concentrations and loads (Q)
 15 (Table 1).,Quantification of concentrations and loads to be used in the status assessments

1 required by the EU Water Framework Directive has received much attention by several
2 European research groups during the last five years. However, only few papers and
3 contributions cover aspects of the monitoring effects of river basin management plans that
4 have been implemented to reduce pollution by nutrients or climate change impacts. Although
5 full-scale application of high frequency monitoring at national or regional scale may not
6 always be reported in scientific papers, we believe that its use in operational water
7 management is still limited. The papers listed in Table 1 show that different monitoring
8 methods have been successfully implemented and tested and it is a step forward towards
9 implementation of these kinds of applications in national or regional monitoring programs in
10 the coming years.

11 Some papers present comparisons between different observation methods and equipment, and
12 others discuss the technical issues related to the observation devices, and it appears that
13 sensors and other equipment have measurement errors differing from those of traditional
14 laboratory analyses. This may, for example, be due to the required regular calibration and the
15 often high maintenance effort of equipment.

16 High frequency monitoring produces time series that enable us to unravel the transport
17 processes of nutrients, for example the contribution of different flow routes or the ratio
18 between statistically stationary fluctuations and structural trends. The fast-growing amount of
19 data requires development of new analysis techniques to handle the large data sets. The error
20 statistics of the new equipment in combination with the large amount of data require also new
21 techniques for QA/QC.

22 Research into high frequency nutrient monitoring will continue. Here, we focus on the
23 development expected for the near future:

24 Today, high frequency monitoring of nutrients is subject to research and pilot studies, but we
25 expect a transition from research to implementation in operational practice. This transition
26 requires the design of efficient and cost-effective monitoring programs, for which research is
27 needed to identify the best combination of observation devices and how to best integrate the
28 data from these devices with dynamic models describing the evolution of nutrients in time and
29 space. Well-defined monitoring objectives are prerequisite for optimum monitoring strategies
30 (observation devices, spatial and temporal distribution) .

31 High frequency monitoring will become part of the routine work flow of agencies within
32 groundwater and surface water quality management and vast amounts of data will be

1 generated. Often long time series are necessary, for example to assess trends over longer
2 periods of time. Therefore, a robust system for data storage, QA/QC and easy access data
3 availability is of great importance (e.g. Neal et al.2011).Today, data processing (e.g. to assess
4 trends) is hampered by the short duration of the time series. However, with increasing
5 availability of long time series, application of advanced statistical time series analysis
6 methods becomes feasible (Lloyd et al. 2014). We expect that more research will be
7 conducted into the application of statistically based techniques, such as transfer function -
8 noise models, to deduce the characteristics of the series and to quantify the relationship with
9 other hydrological variables (e.g. Van der Grift et al. 2016). Examples of characteristics may
10 be typical seasonal behavior, the memory of the system and the trend. Examples of
11 relationships are the response of nutrients to meteorological variables or to water
12 management. Such time series analysis techniques will have applications in studying the
13 effects of climate change on the functioning of catchments, e.g. by elucidating the changing
14 response times of water and solutes towards precipitation and drought events.

15 High frequency data will in the future assist in achieving a better understanding about in-
16 stream processes such as nitrogen and phosphorus assimilation, sedimentation and
17 resuspension processes. Moreover, water quality models will be challenged when calibrated
18 against high frequency data which in turn will force models to be more dynamic (run at lower
19 time steps) and improve their internal process descriptions.

20 High frequency monitoring data will also be able to assist water managers in getting a true
21 picture of nutrient loadings and sources that will enable River Basin managers to implement
22 more targeted and thereby cost-effective decisions when fulfilling the requirement under the
23 EU Directives directed at water management such as the Water Framework Directive, the
24 Nitrates Directive and the Groundwater Directive.

25 The future will likely see more emphasis on multi-variable analysis, in which monitoring set-
26 up, data collection and data processing are not made for one variable at a time but within a
27 multi-variate framework. Such a framework can include the dynamic modelling of travel
28 times, the age dating of contributing flow routes (e.g. Gilmore et al. 2016) and the inclusion
29 of other tracers of flow processes that can be monitored at high resolution, including isotopes
30 of water ($^{18}\text{O}/^2\text{H}$) and products of radioactive decay in the subsurface (e.g. ^{222}Rn).

31 Future research into observation devices will probably concentrate on the combination of
32 different types of high frequency sensors to improve our knowledge of biogeochemical

1 processes, such as nitrate attenuation processes, phosphorus retention, in groundwater and
2 surface waters. Development of equipment (sensors) will likely continue in the coming years,
3 in particular to create cost effective, more precise and more robust and low-maintenance
4 monitoring devices.

5

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1 **Table 1: Overview of monitoring objectives and time scales for high**
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<i>Bold references appear in this Special Issue</i>		Short-scale dynamics and extreme events (minutes to weeks)	Seasonal and annual patterns (months to several years)	Longer term behaviour and trends (years to decades)
Hydrological, chemical and biological process understanding	PU1; Flow regimes and dynamics, hysteresis effects, extremes	Poulsen et al. (2015b) Poulsen et al. (2015a) Outram et al. (2014) Jordan et al. (2014) Wade et al. (2012) Oosterwoud (2014) Neal et al. (2012) Kirchner et al. (2004)	Goyenola et al. (2015) Van der Grift et al. (2016) Halliday et al. (2014) Jordan et al. (2012) Neal et al. (2011, 2012)	Neal et al. (2011)
	PU2; Detection of flow routes, groundwater-surface water interactions, travel time distributions	Rozemeijer et al. (2012) Van der Velde et al. (2010) Wade et al. (2013) Kirchner et al. (2004)	Poulsen et al. (2015b) Shrestha et al. (2013) Van der Velde et al. (2012, 2013) Van der Vlugt et al. (2014) Yu et al. (2015) Neal et al. (2011)	
	PU3; Attenuation and retention processes – surface and ground waters	Rode et al. (2012, 2013) Bierzoza and Heathwaite (2013) Halliday et al. (2014a) Neal et al. (2012) Kirchner et al. (2004)	Rode et al. (2012,2013, 2014) Shrestha et al. (2013) Windolf et al. (2011) Wade et al. (2012) Halliday et al. (2014a) Neal et al. (2011, 2012)	Ernstsen et al. (2015)
Quantification of loads and concentrations	Q1; Assessment of concentrations, loads, export to downstream waters (lakes, rivers, estuaries)	Campbell et al. (2015) Graeber et al. (2015) Wade et al. (2012) Lloyd et al. (2012) Jordan et al. (2014) Ovesen et al. (2012,(2013) Rozemeijer et al. (2010, 2013) Halliday et al. (2012) Cassidy and Jordan (2011)	Campbell et al. (2015) Ernstsen et al. (2015) Goyenola et al. (2015) Graeber et al. (2015) Van der Grift et al. (2016) Rozemeijer et al. (2016) Wade et al. (2012) Halliday et al. (2012) Lloyd et al. (2012) Ovesen et al. (2013) Wade et al. (2012) Bierzoza et al. (2013, 2014) Jordan et al. (2012, 2014) Oosterwoud (2014) Poulsen et al. (2014) Yu et al. (2015)	Ernstsen (2015) Windolf et al. (2014) Kronvang et al. (2013) Greene et al. (2011)
	Q2; Trend assessment, slopes and directions	Aubert et al. (2013) Lloyd et al. (2014)	Van der Grift et al. (2016) Aubert et al. (2013) Kirchner (2004) Lloyd et al. (2014) Blauw et al. (2013) Jordan et al. (2014)	Aubert et al. (2013) Halliday et al. (2012,2014a) Windolf et al. (2013,2014) Rozemeijer et al. (2014) Broers (2012) Hansen et al. (2012,2013) Broers and vd Grift (2004) Visser et al. (2007, 2009) Neal et al. (2011)
	Q3; Probability of exceedance, compliance with water quality standards	Skeffington et al. (2015) Campbell et al. (2015) Audet et al. (2014) Halliday et al. (2014b) Lloyd et al. (2013) Rode et al. (2014)	Skeffington et al. (2015) Ernstsen et al. (2015) Bierzoza et al. (2013,2014) Lloyd et al. (2012,2013) Jonczyk et al. (2014)	Ernstsen (2015) Halliday et al. (2014a)

	Q4; Water and matter balances, sources apportionment	Rode et al. (2014) Rozemeijer et al. (2010b) Aubert et al. (2013b)	Graeber et al. (2015) Goyenola et al. (2015) Van der Grift et al. (2016) Greene et al. (2011) Rozemeijer et al. (2010b) Aubert et al. (2013b) Wade et al. (2012) Jordan et al. (2014) Poulsen et al. (2014,2015a) Van der Vlugt et al.. (2014) Yu et al. (2015)	Ernstsen et al. (2015) Greene et al. (2011)
	Q5; Test and comparison of equipment	Heusch et al. (2015) Audet et al. (2014) Faucheux et al. (2013) Oosterwoud et al. (2014) Wade et al. (2012) Cassidy et al. (2012) Schneider et al. (2012) Stadler et al. (2015) Jomaa (2015) Heinz et al. (2014)	De Jonge et al. (2012) Vendelboe et al. (2015) Jordan et al. (2013) Rozemeijer et al. (2010c, 2013) Cassidy et al. (2012)	
Operational (real time) management – effects and adaptations	M1; Management and mitigation of point sources	Campbell et al. (2015)	Jordan et al. (2012)	Greene et al. (2011)
	M2; Management and mitigation of diffuse sources, land use management	Campbell et al. (2015) Melland et al. (2012) Heinz et al. (2014)	Rozemeijer et al. (2016) Campbell and Jordan (2013) Melland et al. (2013) Jordan et al. (2012) Quinn et al. (2015)	Ernstsen et al. (2015) Windolf et al. (2014) Greene et al. (2011)
	M3; Climate change impacts and adaptations	Graeber et al. (2015) Goyenola et al. (2015) Graeber et al. (2014)	Graeber et al. (2015) Goyenola et al. (2015) Graeber et al. (2014)	

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