



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

5 **F. C. van Geer<sup>1,2</sup>, B. Kronvang<sup>3</sup> and H. P. Broers<sup>1</sup>**

[1]{TNO – Geological Survey of the Netherlands, PO Box 80015, 3508 TA, Utrecht, The Netherlands}

[2]{ Department of Physical Geography, Faculty of Geosciences, Utrecht University, P.O. Box 80115, 3508 TC Utrecht, the Netherlands}

[3]{ Department of Bioscience, Aarhus University, Vejlshøvej 25, 8600 Silkeborg, Denmark }

10 Correspondence to: B. Kronvang ([bkr@bios.au.dk](mailto:bkr@bios.au.dk)) and H.P. Broers ([hans-peter.broers@tno.nl](mailto:hans-peter.broers@tno.nl))

## 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 in Europe for support of EU Directives such as the Water Framework Directive, the Groundwater Directive and the Nitrate Directive. The overview presented based on the special issue and the presentations at the four EGU sessions enabled us to highlight the typical objectives encountered in the application of high frequency monitoring to support EU Directives, to assess the temporal and spatial scales and to reflect on future developments and research needs in this growing field of expertise.

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## 1 Introduction

The presence and dynamic behavior of nutrients in groundwater and surface water are an important issue in water management, in particular in areas with intensive agriculture. This is, for example, reflected in EU directives such as the Nitrates Directive (EU 1991), the Water Framework Directive (*WFD*; EU 2000), the Groundwater Directive (*GWD*; EU



2006) and the Monitoring Directive (EU, 2009). Member states are obliged to monitor and report on the environmental status of the water bodies and, if necessary, take measures to establish adverse trend reversal. As far as nutrients concern, the European directives focus on aquatic ecosystems and groundwater-dependent ecosystems. In order to meet the obligations, monitoring programmes have to cover a range of water quantity, water quality and ecological parameters, and an understanding of dynamic nutrient processes is required for these programmes to be efficient and cost effective. However, the design of monitoring strategies is often hampered by limited knowledge of, for instance, nutrient responses to weather conditions, land use and agricultural practices. Moreover, the dynamic behavior of nutrients shows large variability in both space and time (see, e.g., Campbell et al., 2015, and Goyenola et al., 2015).

To satisfy the increasing demand for knowledge and information on the dynamic behavior of nutrients, the past 10-15 years have seen a rapid development of observation devices and technologies for high resolution monitoring of nutrients and other solutes and isotopes at affordable cost, encouraging researchers and other stakeholders to perform studies in experimental as well as operational settings. Thus, vast amounts of research data have been collected on various water quality variables, allowing the study of relevant biogeochemical processes and enabling comparisons between the results obtained by the use of different monitoring devices. Thus, awareness has increased about the advantage of using high resolution nutrient monitoring as complementary tool next to traditional low frequency monitoring. The sessions on “Monitoring Strategies: temporal trends in groundwater and surface water quality and quantity” at the EGU-conferences in 2012, 2013, 2014 and 2015 clearly showed that high frequency monitoring and strategies for nutrient monitoring are subjects that attract great interest. Part of the work presented at these sessions is now gathered in the 12 papers included in this special issue of HESS, which aims to provide an overview of the current state of high resolution monitoring of nutrients, identify important knowledge gaps and to pinpoint future research needs and potential application of high resolution monitoring in the management of groundwater and surface water resources. The main research questions addressed are:

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

In order to address these questions we categorized the papers in this special issue, the abstracts of the EGU sessions and some recent key papers according to the monitoring objective studied and the time scale considered. The overview should not be regarded as complete or exhaustive, but the EGU session presentations and the resulting papers in this special issue and elsewhere enable us to describe the typical objectives of high frequency monitoring, to assess temporal and spatial scales and reflect on the future development and research needs within this growing field of expertise. An overview of monitoring objectives and time scales for high frequency nutrient monitoring is given in Table 1. We distinguished between three groups of monitoring objectives:



1. To improve our understanding of the underlying hydrological, chemical and biological processes determining temporal and spatial patterns in nutrients (PU). The main focus is analysis of processes in complex systems.
2. To quantify nutrient loads and concentrations (Q). Here, the focus is not on system functioning but on the values and characteristics (including uncertainties) observed.
3. To support operational management, including evaluation of the effects of mitigation measures and predictions (M). The focus is directed at the implementation of high frequency monitoring within the broader context of policy making and management.

It should be noted that some papers address more than one of these overall objectives. Section 2 of this overview discusses monitoring objectives and section 3 information scales.

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Table 1 shows the monitoring objectives relative to the temporal scale of the research. The scale at which information is required is termed “information scale”. Information scale is important when designing monitoring systems and choosing the methods and goals for data processing (Broers 2002, Geer et al. 2006). For instance, selection of monitoring equipment and choice of methods for data smoothing require a properly defined information scale, and the papers and abstracts are therefore grouped according to this (X-axis, Table 1). For each monitoring objective, the required information may differ relative to the scale at which the information is needed. The following three temporal scales are considered:

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

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Specific monitoring objectives may require a specific information scale. This we illustrate for the monitoring objective ‘characterizing groundwater surface water interaction’. Typically, analysis of the response of nitrate concentrations in surface water to rainfall events is of short temporal scale (minutes or hours); however, extension of the scale may be relevant if including the shallow groundwater flow leading to dilution or up-concentration depending on hydrological and subsoil conditions (e.g. Rozemeijer & Broers 2007). To estimate average loads from shallow groundwater towards surface water during the growing season, the information scale required will involve one or several seasons. To evaluate the long-term sustainability of groundwater-dependent aquatic ecosystems in a WFD assessment, the information scale may cover several years or decades. A more detailed description of information scales is given in Section 3.

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The past decades have seen a rapid development of monitoring equipment, including methods for *in situ* analysis, physically based sensors and time or flow proportional measurements. In Section 4, we briefly describe the monitoring equipment used in the contributions included in Table 1. Finally, in Section 5, we discuss the current state and give an outlook to future developments.

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## 2 Monitoring objectives

### 2.1 Hydrological, chemical and biological process understanding

The new methods of high frequency monitoring are applied to fulfil various objectives. The objectives treated here are those included in Table 1. The overall objective of the PU group is to gain more detailed insight into the relevant hydrological, chemical and biological processes determining nutrient behavior in catchments. Kirchner et al. (2004) addressed the new opportunities of high resolution monitoring for understanding the functioning of catchments, and they foresaw a new era of technical progress and study of actual data, making full profit of the newly acquired spectrum of signals from very short to longer time scales. A decade later, a large number of papers and presentations, including those at the EGU sessions, have demonstrated that process understanding has indeed improved significantly. We have made a subdivision of the monitoring objectives focusing on process understanding:

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



## 2.2 Quantification of loads and concentrations

The central aim of the Q type monitoring objectives is quantification of loads and concentrations. Here, the focus is not on understanding the processes but on the quantification of specified quantities, such as averages, probabilities and proportions of exceedance of water quality standards. Typically, such objectives relate to policy development and operational management, in particular relative to EU directives such as the EU Nitrates Directive (EU 1991) and the Water Framework Directive (EU 2000). Q type objectives are divided into:

- *Q1: Typical concentrations, loads and exports.* Assessment of typical or average concentrations, solute loads and export of solutes towards downstream waters. Low frequency monitoring can give a reasonable estimate of average concentrations and discharges over a time period via interpolation. However, nutrient concentrations and discharges are frequently correlated. Short duration concentration peaks likely go undetected using low frequency monitoring, which implies that load estimates based on low frequency monitoring are typically biased and too low (Rozemeijer et al. 2010a, Cassidy & Jordan 2011, Audet et al. 2014, Goyenola et al. 2015, Skeffington et al. 2015). In contrast, high frequency monitoring reduces the bias in concentration distributions derived from under sampling of the concentration time series. (e.g. Jordan et al. 2007, Rozemeijer et al. 2010b, Ernsten et al. 2015, Campbell et al. 2015). High frequency monitoring may also reveal artefacts produced by the fact that regular sampling is normally undertaken in the daytime, thus typically not capturing differences between daytime and night-time fluxes (Neal et al. 2012, Grift et al. 2016).
- *Q2: Trend assessment.* Assessment of temporal trends, quantification of trend slopes and identification of trend directions are the objectives of many monitoring programmes or research studies. High resolution monitoring, in combination with time series from regular low frequency monitoring, may help to reveal the structure of water quality time series, thereby allowing testing the significance of trends both deterministically (e.g. Van der Grift et al. 2016) and statistically (Lloyd et al. 2014, Rozemeijer et al. 2014), for example using spectral analysis methods (Aubert et al. 2013, Blauw et al. 2013).
- *Q3: Compliance with water quality standards.* Testing compliance with water quality standards, such as WFD Environmental Quality Standards, is another important aim of many monitoring programmes, typically involving testing the frequency of exceedance of standards or quantifying the probability of exceedance. High frequency monitoring improves these aims by adding information on extreme values and short-term peaks impacting the regular evaluation of exceedances in low frequency programmes. Skeffington et al. (2015b) clearly demonstrate that the classification of WFD Chemical and Ecological Status is strongly influenced by sampling frequency and time of sampling during the year and over the day.



- *Q4: Water and matter balances and sources.* Source appointment is often difficult to capture in natural catchment systems, but high frequency monitoring can add short time scale information on dilution or accumulation rates (see van der Grift et al. 2016, Aubert et al. 2013b, Goyenola et al. 2015, Rozemeijer et al. 2010b).
- *Q5: Comparison of monitoring equipment.* Several recent studies endeavor to answer the question of how high frequency monitoring equipment may supplement the existing monitoring tools. The central question is ‘what are the possibilities of new equipment?’ Examples of comparisons of new monitoring equipment used in surface water and groundwater monitoring are found in Audet et al. (2014), Huebsch et al. (2015), Jordan et al. (2013) and Rozemeijer et al. (2010c).

### 2.3 Operational (real time) management – effects and predictions

10 The central aim of the M type monitoring objectives is an evaluation of the impact of management measures and climate change on nutrient transport. M type objectives typically involve the reaction of the catchment to man-made or natural changes of nutrient sources and the hydrological functioning or the biogeochemistry of the system. We have defined three subgroups:

- 15 • *M1: Management and mitigation of point sources.* High frequency monitoring can reveal any changes in the short-term reaction of the catchment to changes in nutrient inputs, hydrology or biogeochemistry. Besides revealing the time-dependent nutrient inputs from, for instance, sewage treatment facilities or leaking septic tanks (Wade et al. 2012), the effects of mitigating measures can be followed by assessing changes in the duration or frequency of nutrient peaks in the time series before and after their implementation. An example is given in Campbell et al. (2015) and Greene et al. (2011).
- 20 • *M2: Management and mitigation of diffuse sources.* Mitigation measures for nutrients in agricultural areas typically involve some kind of land use management or changes in the hydrological functioning of the system. Despite the establishment of high frequency monitoring, the effects of mitigation measures are often difficult to separate from those of natural variability created by meteorological conditions. Examples of monitoring the effects of mitigation measures in diffuse pollution settings are given in Campbell et al. (2015), Ernstsens et al. (2015), Van der Grift et al. (2015) and Rozemeijer et al. (2016), all included in this special issue, and Greene et al. (2011). Given the slower dynamics of groundwater, other techniques such as age dating and lower monitoring frequencies are usually applied to reveal trends following implementation of mitigation measures (Broers & van der Grift 2004, Visser et al. 2007, 2009, Hansen et al. 2012, 2013).
- 25 • *M3: Climate change and mitigation measures.* High frequency monitoring helps reveal the impact of and adaptations to climate change by capturing changes in the hydrological and hydrochemical response to rainfall
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events and testing whether the projected changes in catchment behavior actually occur. Examples are given in Graeber et al. (2015) and Goyenola et al. (2015).

### 3 Information time scales

5 Monitoring programmes produce time series of nutrient concentrations, discharge, precipitation and other relevant variables. These time series are processed in order to compute the dynamic characteristics and to extract the desired information for the objective specified in the monitoring programme. The dynamics of the hydrological and chemical observations vary at time scales ranging from minutes to decades depending on the solute monitored. Most frequently, the objective of a monitoring programme is related to a specified time scale. For example, the response of nitrate concentrations in surface water to a rainfall event is a short scale event (in the order of hours to days), whereas meeting the objectives of the WFD has a longer time scale (years to decades). Irrespective of the monitoring objective, observations contain variations at all time scales and the gathered data have to be processed and statistically filtered in order to obtain the correct trend information or system characteristics at the desired time scale (e.g. Lloyd et al. 2014). Within a data processing perspective, we distinguish between three time scales (events, seasonal and annual and long term) where high resolution time series might be preferred over low resolution time series.

#### 3.1 Short time scales

Concentrations and loads of nutrients frequently show rapid changes over time as a result of rainfall events, emissions of effluents from point sources and unintended losses of manure or pesticides during application. Often, these rapid changes occur at time scales less than one hour and high frequency monitoring is required in order to capture peaks and extreme values that would go undetected if applying only low frequency monitoring (cf. Campbell et al. 2015, Skeffington et al. 2015b, Van der Grift et al. 2015).

Also, if assessing the statistical characteristics of the concentration or the load of a solute (e.g. average and percentile values or the frequency of exceedance of a threshold), high frequency monitoring is a valuable tool. In principle, statistical characteristics can be determined from low frequency observations provided that the monitoring period is sufficiently long. However, in many cases the system shows statistically non-stationary behavior over longer periods of time due to, for example, changes in land use management. With high frequency observations, we can obtain more reliable estimates of the trend characteristics for shorter periods, permitting filtering out longer-term trends (e.g. Lloyd et al. 2014). Many studies focus on the interactions between groundwater and surface water, in particular the different flow paths of nutrients towards the surface water (cf. Poulsen et al. 2015b, Rozemeijer et al. 2010b). The weather conditions appear to be the major driving force for the temporal distribution of fluxes along the different flow paths, including quick components like discharges from point sources, tile drain water and overland flow and slow components such as discharges from deeper groundwater. The quick components have response times in the order of magnitude of hours, days or weeks. Therefore, the response of nutrient



fluxes and loads to precipitation is a complex function (e.g. Velde et al. 2010). To estimate this complex response function and to unravel the contributions of the different flow paths, high frequency monitoring is a prerequisite (cf. Campbell et al. 2015).

### 3.2 Seasonal and annual patterns and long term behavior

5 In many studies the aim is not to identify short-term dynamics but to reveal longer-term patterns, distinguishing between periodic (seasonal) patterns and long-term trends. An example of a policy-relevant objective with a seasonal information scale is the estimation of average or typical nutrient concentrations during the growing season. Long-term monitoring objectives of the Water Framework Directive (WFD) include elucidating the trends in water quality status towards the 2027 compliance with good chemical status and meeting the environmental objectives for aquatic and terrestrial ecosystems. (cf. 10 Rozmeijer et al. 2014, Erntsen et al. 2015, Skeffington et al. 2015b). As to groundwater, an equivalent time scale is required for demonstrating the trend reversal in concentrations of nitrate (Visser et al. 2007). Individual observations of water quality might be prone to all frequencies and high frequency variations (noise) that tend to obscure the low frequency signal. High frequency monitoring enables filtering out the noise occurring during relatively short monitoring periods in order to elucidate the long-term trend (Bierkens et al. 1999, Halliday et al. 2012, Aubert et al. 2013, van der Grift 2015).

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## 4 Monitoring equipment

Several types of sensors have been developed in recent years. Some are based on *in situ* laboratory (mobile or stationary) analysis of water samples, while others utilize, for instance, light or infrared (UV) spectra to measure chemical parameters (e.g. turbidity, nitrate, DOM) or materials capable of passive adsorption of chemicals (e.g. Sorbicells). Some sampling 20 methods produce point observations in time, whereas others derive flow- or time-weighted concentrations over a time period. All methods have advantages and disadvantages, and some studies (e.g. Rozemeijer et al. 2010c, Cassidy and Jordan 2011, Jordan et al. 2013, Huebsch et al. 2015) compare several sampling instruments and monitoring strategies (Table 2). Below various continuous monitoring methods, in particular those described in the papers presented in this special issue (overview in Table 2), are described.

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Table 2: Overview of monitoring methods and instruments applied in the Session abstracts 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                            |
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| Nitrate sensors  | - s::can spectro::lyserTM ,s::can Messtechnik GmbH, Austria<br>- NITRATAX plus sc, Hach Lange GmbH, Germany<br>- reagentless hyperspectral UV photometer (ProPS) | <b>Huebsch et al. (2015)</b><br><b>Van der Grift et al. (2015)</b><br>Rozemeijer et al. (2010c)<br>Wade et al. (2012)<br>Heinz et al. (2014) |
| Phosphorus (total P, total reactive P)   | Phosphax Sigma auto-analyzer Hach Lange GmbH, Düsseldorf, Germany C  | <b>Campbell et al. (2015)</b><br><b>Rozemeijer et al. (2016)</b><br><b>Skeffington et al. (2015b)</b><br><b>van der Grift et al. (2015)</b>  |
| (Total reactive phosphorus, TRP), nitrite (NO <sub>2</sub> ) and ammonium (NH <sub>4</sub> ) | Systea Micromac C  | Wade et al. (2012)   |
| Passive samplers   | SorbiCell-samplers (De Jonge & Rothenberg, 2005)   | <b>Rozemeijer et al. (2010c, 2015)</b><br><b>Audet et al. (2014)</b>   |
| Turbidity  | OBS sensor, Campbell Scientific  | <b>van der Grift et al. (2015)</b>   |
| Automatic samplers   | Isco sampler; Sigmatax sampler   | <b>Goyenola et al. (2015)</b><br><b>Audet et al. (2014)</b><br><b>Van der Grift et al. (2015)</b>  |
| O <sub>2</sub> , pH, temperature conductivity, turbidity and chlorophyll                     | - YSI 6600 multi-parameter sonde   | <b>Skeffington et al. (2015b)</b><br>Wade et al. (2012)  |
| Conductivity, temperature  | CTD-diver (Van Essen Instruments, Delft, the Netherlands)  | <b>Van der Grift et al. (2015)</b>   |
| <sup>18</sup> O, <sup>2</sup> H  | Wavelength-Scanned Cavity Ring Down Spectrometry System (WS-CRDS) L2120-i Picarro  | Heinz et al. (2014)  |

## 5 Conclusions and future outlook

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

Several research groups in Europe and beyond are undertaking pilot studies on the use of high frequency monitoring of nutrients. During the past decades, there has been growing awareness of the fact that the quality of the aquatic environment is threatened by high concentrations and loads of nutrients in groundwater and surface water. At the same time, development of observation equipment enabling high frequency monitoring at affordable cost has been extensive and, accordingly, assessment and quantification of the dynamic behavior of nutrients at very small time scales (minutes to hours) are now feasible. Most papers and abstracts on the subject published in the past 10 years have been prepared by research groups exploring the possibilities of high frequency monitoring of processes at small temporal scale; thus, most papers in Table 1 concern process understanding (PU) and quantification of concentrations and loads (Q). The new opportunities increase our



understanding of flow regimes, dynamics and hydrological extremes, flow routes and interactions between flow components as well as attenuation and retention processes in surface and ground waters. During the last five years, quantification of concentrations and loads to be used in the status assessments required by the WFD has received much attention by several European research groups. However, only few papers and contributions cover aspects of the monitoring effects of river basin management plans that have been implemented to reduce pollution by nutrients or climate change impacts. Although full-scale application of high frequency monitoring at national or regional scale is often not reported in scientific papers, we believe that its use in operational management is still limited. The papers listed in Table 1 show that different monitoring methods have been successfully implemented and tested and it is a step forward towards implementation of these kinds of applications in national or regional monitoring programmes in the coming years.

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

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High frequency monitoring produces time series that enable us to unravel the transport processes of nutrients, for example the contribution of different flow routes or the ratio between statistically stationary fluctuations and structural trends. The fast-growing amount of data requires development of new analysis techniques to handle the large data sets (e.g. Aubert et al. 2014; van der Grift et al. 2016). The error statistics of the new equipment in combination with the large amount of data require also new techniques for QA/QC.

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

Today, high frequency monitoring of nutrients is subject to research and pilot studies, but we expect a transition from research to implementation in operational practice. This transition requires efficient and cost-effective monitoring programmes and to design optimum programmes, research is needed to identify the best combination of observation devices and how to best integrate the data from these devices with dynamic models describing the evolution of nutrients in time and space. Optimum monitoring strategies (observation devices, spatial and temporal distribution) should be tuned to/translated into well-defined monitoring objectives (Lloyd et al. 2014).

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High frequency monitoring will become part of the routine work flow of agencies within groundwater and surface water quality management and vast amounts of data will be generated. Often long time series are necessary, for example to assess trends over longer periods of time. Therefore, a robust system for data storage, QA/QC and data availability is of great importance. Long time series are valuable and should be easily accessible (Neal et al. 2011).

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Today, data processing (e.g. to assess trends) is hampered by the short duration of the time series. However, with increasing availability of long time series, application of advanced statistical time series analysis methods becomes feasible. We expect that more research will be conducted into the application of statistically based techniques, such as time series models, to



deduce the characteristics of the series and to quantify the relationship with other hydrological variables (e.g. van der Grift et al, 2016). Examples of characteristics may be typical seasonal behaviour, the memory of the system and the trend. Examples of relationships are the response of nutrients to meteorological variables or to water management. The future will likely see more emphasis on multi-variable analysis, in which monitoring set-up, data collection and data processing are not made for one variable at a time but within a multi-variate framework. Such a framework can include the dynamic modelling of travel times, the age dating of contributing flow routes (e.g. Gilmore et al. 2016) and the inclusion of other tracers of flow processes that can be monitored at high resolution, including isotopes of water ( $^{18}\text{O}/^2\text{H}$ ) and products of radioactive decay in the subsurface (e.g.  $^{222}\text{Rn}$ ).

Future research into observation devices will probably concentrate on the combination of different types of high frequency sensors to improve our knowledge of biogeochemical processes, such as nitrate attenuation processes, phosphorus retention, in groundwater and surface waters. Development of equipment (sensors) will likely continue in the coming years, in particular to create cost effective, more precise and more robust monitoring devices.

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**Table 1: Overview of monitoring objectives and time scales for high frequency nutrient monitoring**

| <i><b>Bold references appear in this Special Issue</b></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)   |
|--|--|--|--|---|
| <b>Hydrological, chemical and biological process understanding</b> | PU1; Flow regimes and dynamics, hysteresis effects, extremes                                     | <b>Poulsen et al. (2015b)</b><br>Poulsen et al. (2015a)<br>Outram et al. (2014)<br>Jordan et al. (2014)<br>Wade et al. (2012)<br>Oosterwoud (2014)<br>Neal et al. (2012)<br>Kirchner et al. (2004)   | <b>Goyenola et al. (2015)</b><br><b>Van der Grift et al. (2015)</b><br>Halliday et al. (2014)<br>Jordan et al. (2012)<br>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)<br>Van der Velde et al. (2010)<br>Wade et al. (2013)<br>Kirchner et al. (2004)  | <b>Poulsen et al. (2015b)</b><br>Shrestha et al. (2013)<br>Van der Velde et al. (2012, 2013)<br>Van der Vlugt et al. (2014) Yu et al. (2015)<br>Neal et al. (2011)   |   |
|  | PU3; Attenuation and retention processes – surface and ground waters                             | Rode et al. (2012, 2013)<br>Bierzoa and Heathwaite (2013)<br>Halliday et al. (2014a)<br>Neal et al. (2012)<br>Kirchner et al. (2004)   | Rode et al. (2012,2013, 2014)<br>Shrestha et al. (2013)<br>Windolf et al. (2011)<br>Wade et al. (2012)<br>Halliday et al. (2014a)<br>Neal et al. (2011, 2012)  | <b>Ernstsen et al. (2015)</b>   |
| <b>Quantification of loads and concentrations</b>                  | Q1; Assessment of concentrations, loads, export to downstream waters (lakes, rivers, estuaries)  | <b>Campbell et al. (2015)</b><br><b>Graeber et al. (2015)</b><br>Wade et al. (2012)<br>Lloyd et al. (2012)<br>Jordan et al. (2014)<br>Ovesen et al. (2012,2013)<br>Rozemeijer et al. (2010, 2013)<br>Halliday et al. (2012)<br>Cassidy and Jordan (2011) | <b>Campbell et al. (2015)</b><br><b>Ernstsen et al. (2015)</b><br><b>Goyenola et al. (2015)</b><br><b>Graeber et al. (2015)</b><br><b>Van der Grift et al. (2015)</b><br><b>Rozemeijer et al. (2016)</b><br>Wade et al. (2012)<br>Halliday et al. (2012)<br>Lloyd et al. (2012)<br>Ovesen et al. (2013)<br>Wade et al. (2012)<br>Bierzoa et al. (2013, 2014)<br>Jordan et al. (2012, 2014)<br>Oosterwoud (2014)<br>Poulsen et al. (2014)<br>Yu et al. (2015) | <b>Ernstsen (2015)</b><br>Windolf et al. (2014)<br>Kronvang et al. (2013)<br>Greene et al. (2011) |



|  |   |  |  |
|--|---|--|--|
| Q2; Trend assessment, slopes and directions                            | Aubert et al. (2013)<br>Lloyd et al. (2014)   | <b>Van der Grift et al. (2015)</b><br>Aubert et al. (2013)<br>Kirchner (2004)<br>Lloyd et al. (2014)<br>Blauw et al. (2013)<br>Jordan et al. (2014)  | Aubert et al. (2013)<br>Halliday et al. (2012,2014a)<br>Windolf et al. (2013,2014)<br>Rozemeijer et al. (2014)<br>Broers (2012)<br>Hansen et al. (2012,2013)<br>Broers & vd Grift (2004)<br>Visser et al. (2007, 2009)<br>Neal et al. (2011) |
| Q3; Probability of exceedance, compliance with water quality standards | <b>Skeffington et al. (2015)</b><br><b>Campbell et al. (2015)</b><br><b>Audet et al. (2014)</b><br>Halliday et al. (2014b)<br>Lloyd et al. (2013)<br>Rode et al. (2014)   | <b>Skeffington et al. (2015)</b><br><b>Ernstsen et al. (2015)</b><br>Bierzo et al. (2013,2014)<br>Lloyd et al. (2012,2013)<br>Jonczyk et al. (2014)  | <b>Ernstsen (2015)</b><br>Halliday et al. (2014a)  |
| Q4; Water and matter balances, sources apportionment                   | Rode et al. (2014)<br>Rozemeijer et al. (2010b)<br>Aubert et al. (2013b)  | <b>Graeber et al. (2015)</b><br><b>Goyenola et al. (2015)</b><br><b>Van der Grift et al. (2015)</b><br>Greene et al. (2011)<br>Rozemeijer et al. (2010b)<br>Aubert et al. (2013b)<br>Wade et al. (2012)<br>Jordan et al. (2014)<br>Poulsen et al. (2014,2015a)<br>Van der Vlugt et al.. (2014)<br>Yu et al. (2015) | <b>Ernstsen et al. (2015)</b><br>Greene et al. (2011)  |
| Q5; Test and comparison of equipment                                   | <b>Heusch et al. (2015)</b><br><b>Audet et al. (2014)</b><br>Faucheux et al. (2013)<br>Oosterwoud et al. (2014)<br>Wade et al. (2012)<br>Cassidy et al. (2012)<br>Schneider et al. (2012)<br>Stadler et al. (2015)<br>Jomaa (2015)<br>Heinz et al. (2014) | De Jonge et al. (2012)<br>Vendelboe et al. (2015)<br>Jordan et al. (2013)<br>Rozemeijer et al. (2010c, 2013)<br>Cassidy et al. (2012)  |  |
| M1; Management and mitigation of point sources                         | <b>Campbell et al. (2015)</b>   | Jordan et al. (2012)   | Greene et al. (2011)   |
| M2; Management and mitigation of diffuse sources, land use management  | <b>Campbell et al. (2015)</b><br>Melland et al. (2012)<br>Heinz et al. (2014)   | <b>Rozemeijer et al. (2016)</b><br>Campbell & Jordan (2013)<br>Melland et al. (2013)<br>Jordan et al. (2012)<br>Quinn et al. (2015)  | <b>Ernstsen et al. (2015)</b><br>Windolf et al. (2014)<br>Greene et al. (2011)   |
| M3; Climate change impacts and adaptations                             | <b>Graeber et al. (2015)</b><br><b>Goyenola et al. (2015)</b><br>Graeber et al. (2014)  | <b>Graeber et al. (2015)</b><br><b>Goyenola et al. (2015)</b><br>Graeber et al. (2014)   |  |
|  |   |  |  |