#### 1 Response to anonymous referee #1

We are grateful for the valuable general comments and the many detailed comments given in the annotated manuscript. We have in the revised manuscript followed the suggestions for shortening of the manuscript by deleting repetitions and being more precise in the wording of sentences. We have also followed the suggested strengthening of the connection to the application of high frequency monitoring to land and water management. In specific we have revised the manuscript according to the following:

8 The paper is an introduction to a special issue. As such it needs to introduce the subject of the 9 special issue, state its relevance, and indicate how the special issue came to be. These aspects 10 are all covered in the paper.

11 That being said, it takes some effort for the uninitiated to grasp some elements of the paper.
12 Jargon from applied water quality research is used freely. While the terminology within that

13 context is quite clear, the various buzzwords have very different meaning in other contexts,

and I would like to see this source of ambiguity removed by making the phrasing moreprecise and specific.

We have checked the text throughout the paper, defined terms in the context and rephrasedwhere necessary.

18 I think the paper can be shortened quite a bit. There is some repetition in there, and the 19 information density is low in some sections, with filler words used to start sentences, and text 20 devoted to state the obvious. Particularly the Aristotelian categorizing in section 2 was tedious 21 to read. This is not to say the list should go entirely, but probably it can be presented more 22 concisely.

23 We have made the section 2 more concise in the revised manuscript.

24 'I like the very explicit connection to the applications of the science, and would even advocate 25 for strengthening that by more clearly identifying the stakeholders and the main actors in the 26 areas of land and water management and legislation that are going to be the main users of this 27 research.'

We have identified stakeholders and actors in land and water management in the introductionof the paper.

P1. L0: Sometimes, paragraphs are separated by white lines, and in ohter cases the next
paragraph starts on the next line (without identation or white line). Please check the format
guidelines and make everything consistent.

- 4 We have checked the guidelines and made everything consistent.
- 5

P1. L0: The reference list seems to break up last names: van der Velde becomes 'Velde, van
der', for instance. In the text this is then referred to as Velde. This is very confusing - please
keep last names in tact, spaces and upper/lower case included.

9 We have checked all references and made them consistent.

10

11 P1. L0: For a paper that introduces a special issue there are a lot of self-citations.

12 The main references in the list are contributions to the EGU sessions "Monitoring Strategies:

13 temporal trends in groundwater and surface water quality and quantity". We have to cite all

14 relevant abstracts from these sessions.

15

P1. L12: The abstract requires some inside knowledge to be comprehensible. It could use a few more elaboration about what exactly is meant since several terms ('management', 'monitoring', 'mitigation', to name a few) are meaningful in many contexts, and could be misleading for those readers who are familiar with these terms from other backgrounds.

We have checked the terms throughout the whole text and have tried to define them in thiscontext.

22

23 P1. Line 20: management of what? ...land and water management...?

- 24 See previous reply.
- 25
- 26 P1. L24: scales of what?
- 27 We have added: 'of nutrient dynamics'

1	P1. L24: I presume those relates to high-frequency monitoring of nutrients.
2	Yes. We have added this to the text.
3	
4	P1. l27: plural vs singular. I think plural is better here.
5	Agreed – we have changed accordingly.
6	
7	P2. L2: This is awkward - it reads like the reversal is adverse. Please rephrase.
8	We have rephrased in the revised manuscript.
9	
10	P2. L2: are concerned
11	Agree- we have changed accordingly.
12	
13	P2. L7: skip, it is implied in the remainder of the sentence
14	Agreed – done in the revised manuscript.
15	
16	P2, L.18: Later in the text you say there are 10.
17	Should be $10 -$ we have checked for that in the revised manuscript.
18	
19	P2, 123: Please be specific
20	Minutes to weeks
21	
22	P2.124: Donald Trump talks a lot about management too. What is being managed, and by
23	whom?
24	We have defined management in this context.

1 P3.16: This tandem of terms appears a few times in the paper but is never really specified. I

2 can guess what it refers to, but that's only because I am reasonably well versed in the field.

3 The link to EU directives for instance is made very explicitly, and the rest of the paper does

4 not refer to national legislation or regional (ground-)water authorities at all. In fact, the only

5 stakeholder that have been mentioned explicitly so far are scientists.

6 We have defined management and policy in this context (see previous point)

7

8 P3. L13: If F.C. Geer in the refrerence list is the same person as the first author, what 9 happened to 'van'?

10 We have made the references consistent.

11

12 P3. L15: 'depend on' ?

- 13 Might be better. We have changed it accordingly.
- 14
- 15 P3. L17 20: This is very useful!
- 16 Thanks!
- 17
- 18 P3. L24: I do not think this is a word.
- 19 Increase of the concentration

20

- P3. L29-30: ...physically-based sensors and measurements with time intervals that are
   constant or inversely proportional to the flow rate.
- 23 Agree, Changed accordingly.
- 24
- 25 By the way: what is a physically-based sensor? Are they not all?
- 26 Yes indeed. In contrast to chemical analysis.

1	P4, 11: This selection has a lot of lists, which makes it tedious to read at times. This can
2	probably be shortened or otherwise be made more appealing. The information density is not
3	always that high.
4	We have shortened the text and tried to make it more to the point.
5	
6	P4. L13. All this sounds quantitative, very hydrological. Yet in the next sentence you bring in
7	solute concentrations. How are these sentences linked?
8	High frequent monitoring is relevant for understanding quantitative flow as well as nutrient
9	transport. We have clarified in the revised manuscript.
10	
11	P4. L13: of what?
12	Of fluxes and concentrations
13	
14	P4. L22: van der Velde.
15	See previous reply.
16	
10	
10	P4. L25: to what?
	P4. L25: to what? To rainfall events, water management measures and other driving forces.
17	
17 18 19	
17 18	To rainfall events, water management measures and other driving forces.
17 18 19 20	To rainfall events, water management measures and other driving forces. P4. L25: I do not think ground waters should be plural. Perhaps repalce by 'surface and
17 18 19 20 21	To rainfall events, water management measures and other driving forces. P4. L25: I do not think ground waters should be plural. Perhaps repalce by 'surface and groundwater bodies.'
17 18 19 20 21 22	To rainfall events, water management measures and other driving forces. P4. L25: I do not think ground waters should be plural. Perhaps repalce by 'surface and groundwater bodies.'
<ol> <li>17</li> <li>18</li> <li>19</li> <li>20</li> <li>21</li> <li>22</li> <li>23</li> </ol>	To rainfall events, water management measures and other driving forces. P4. L25: I do not think ground waters should be plural. Perhaps repalce by 'surface and groundwater bodies.' Agree.
<ol> <li>17</li> <li>18</li> <li>19</li> <li>20</li> <li>21</li> <li>22</li> <li>23</li> <li>24</li> </ol>	To rainfall events, water management measures and other driving forces. P4. L25: I do not think ground waters should be plural. Perhaps repalce by 'surface and groundwater bodies.' Agree. P6. L1 What does this mean?

1	Agree.	We	have	changed	it	accord	ingl	y.
	0						0	2

- 2
- 3 P7. L6-7: Is this not obvious?
- 4 We have skipped this sentence.
- 5
- 6 P7, 19-10: Repetitive
- 7 We have skipped this sentence
- 8
- 9 P7. L13: Filler words can be skipped.
- 10 Agreed
- 11
- 12 P7. L14: Phrased like this, one wonders how it could be otherwise why would one prefer a
- 13 time series wiht a low reolsution over one wiht a high resolution?
- 14 What we mean to say is that high resolution time series open new possibilities that are also
- 15 useful for longer term monitoring objectives. We have changed the text to make this more
- 16 clear in the revised manuscript.
- 17
- 18 P7. L26: high-pass filter?
- 19 Yes, we will add this term.

20

- 21 P8. L10: Typo.
- 22 We have corrected this in the revised manuscript.
- 23
- 24 P8. L12: Confusing, please rephrase.
- 25 We have rephrased in the revised manuscript.

1	P8. L13: low-pass filter?	This creates a nice	constrast with 3.1	(high-pass	filtering), but	you
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2 do not at all highlight this. On first reading I even thought it was repetitive.

3 Yes, we have added the term low pass filter in the revised manuscript.
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5	P8. L21:	Filler	words,	shorten	or	skip
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- 6 Agree. We have skipped it in the revised manuscript.
- 7
- 8 P8. L24: You just list them in Table 2.
- 9 Changed to 'list'
- 10
- 11 P9. Table 2: Change accordingly.
- 12 We have changed in the revised manuscript.
- 13 P9. L4: Indeed 10 papers.
- 14 Agree.
- 15
- 16 P10. L19: explain abbreviations.
- 17 Agree
- 18
- 19 P10. L26: Is it not the other way around?
- 20 We have rephrased to make it more clear.
- 21
- 22 P10. L28 -29: These are stakeholders that can be identified (along with others) earlier in the
- paper. and This is the first time in the paper that the term management receives a clearqualification. This needs to be done much earlier in the paper.
- 25 We have defined earlier in the introduction section about meaning of management.
- 26
- 27

#### 1 Response to Anonymous Referee #2

2 We are grateful for the valuable comments given by the referee.

3 <sup>c</sup>Considering that the manuscript is an introductory paper that should give an overview of the 4 general topic, it efficiently covers the state of the art on the subject. Nonetheless, I found two 5 things that should be better addressed: a) there is a redundancy of classification and 6 schematics that creates some confusion and makes the manuscript very repetitive. The most 7 redundant part is the one on the time scales that: it is introduced and discussed from Line 10 8 to 27 in Page 3, section 1, then used for characterizing each monitoring objectives in section 9 2, and then again discussed in detail in a dedicated section (3). My suggestion is to shorten the 10 manuscript by completing removing section 3. All the information contained in this section 11 have been discussed in section 2, where they are very useful because directly relate the time 12 scales to the monitoring objectives. There is no reason to repeat them in the next section with 13 a different scheme. '

We have followed the suggestions in the revised manuscript for shortening of the manuscript
by deleting repetitions and rearranging in the manuscript to overcome the problems
highlighted above in section 3.

17

18 'b) Moreover, some efforts should be directed to extend outlooks in section 5 where most of 19 the space is dedicated to a summary of what described in the previous sections. The 20 expectations that readers have in an overview paper are to receive some inspiring and exciting 21 viewpoints on future technical, research and management challenges; they are very limited in 22 this version of the manuscript.'

We have extended the outlook in section 5 of the revised manuscript by inclusion of a few
more viewpoints on future technical, research and especially management challenges in
section 5:

High frequency data will in the future assist in achieving a better understanding about instream processes such as nitrogen and phosphorus assimilation, sedimentation and resuspension processes. Moreover, water quality models will be challenged when calibrated against high frequency data which in turn will force models to be more dynamic (run at lower time steps) and improve their internal process descriptions. High frequency monitoring data will also be able to assist water managers in getting a true
picture of nutrient loadings and sources that will enable River Basin managers to implement
more targeted and thereby cost-effective decisions when fulfilling the requirement under the
EU Directives directed at water management such as the Water Framework Directive, the
Nitrates Directive and the Groundwater Directive.

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

- 8 [2]{ Department of Physical Geography, Faculty of Geosciences, Utrecht University, P.O.
- 9 Box 80115, 3508 TC Utrecht, the Netherlands}
- 10 [3] { Department of Bioscience, Aarhus University, Vejlsøvej 25, 8600 Silkeborg, Denmark }
- 11 Correspondence to: B. Kronvang (bkr@bios.au.dk) and H.P. Broers (hans-
- 12 peter.broers@tno.nl)
- 13

#### 14 Abstract

15 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 16 17 issue of HESS form the background for this overview of the current state of high resolution 18 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 19 20 assessment of the objectives behind high frequency monitoring as classified into three main 21 groups: i) Improved understanding of the underlying hydrological, chemical and biological 22 processes (PU); ii) quantification of true nutrient concentrations and loads (Q); iii) operational 23 management, including evaluation of the effects of mitigation measures (M). The 24 contributions in the special issue focus on the implementation of high frequency monitoring 25 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 26 Nitrate Directive. The overview presented based on the special issue and the presentations at 27 28 the four EGU sessions enabled us to highlight the typical objectives encountered in the 29 application of high frequency monitoring to support EU Directives, to assess the temporal and Field Code Changed

spatial scales and to reflect on future developments and research needs in this growing field of
 expertise.

3

#### 4 1 Introduction

5 The presence and dynamic behavior of nutrients in groundwater and surface water are-is an 6 important issue in water management, in particular in areas with intensive agriculture. This is, 7 for example, reflected in EU directives such as the Nitrates Directive (EU 1991), the Water 8 Framework Directive (WFD; EU 2000), the Groundwater Directive (GWD; EU 2006) and the 9 Monitoring Directive (EU, 2009). Member states are obliged to monitor and report on the 10 environmental status of the water bodies and, if necessary, take measures to establish adverse trend reversal. As far as nutrients are concerned, the European directives focus on aquatic 11 12 ecosystems and groundwater-dependent ecosystems. In order to meet the obligations, 13 monitoring programmesprograms have to cover a range of water quantity, water quality and ecological parameters, and an understanding of dynamic nutrient processes is required for 14 these programmesprograms to be efficient and cost effective. However, the design of 15 16 monitoring strategies is often hampered by limited knowledge of, for instance, nutrient responses to weather conditions, land use and agricultural practices. Moreover, the dynamic 17 18 behavior of nutrients shows large variability in both space and time (see, e.g., Campbell et al., 19 2015, and Goyenola et al., 2015).

20 To satisfy the increasing demand for knowledge and information on the dynamic behavior of 21 nutrients, the past 10-15 years have seen a rapid development of observation devices and 22 technologies for high resolution monitoring of nutrients and other solutes and isotopes at 23 affordable cost, encouraging researchers and other stakeholders to perform studies in 24 experimental as well as operational settings. Thus, vast amounts of research data have been 25 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 26 27 monitoring devices. Thus, awareness has increased about the advantage of using high 28 resolution nutrient monitoring as complementary tool next to traditional low frequency 29 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 30 clearly showed that high frequency monitoring and strategies for nutrient monitoring are 31 32 subjects that attract great interest. Part of the work presented at these sessions is now gathered

in the <u>12-10</u> papers included in this special issue of HESS, which aims to provide an overview 1 2 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 3 4 monitoring in the management of groundwater and surface water resources. The main 5 research questions addressed are:

#### 6

What does the new monitoring technology have to offer and how can we develop an 7 optimal monitoring strategy?

- 8 - Can we assess and quantify the transport processes of nutrients, in particular at the 9 short time scale?
- 10 How can we use high frequency nutrient monitoring to achieve our management 11 goals?

12 In order to address these questions we categorized the papers in this special issue, the 13 abstracts of the EGU sessions and some recent key papers according to the monitoring objective studied (Section 2) and the time scale considered (Section 3). The overview should 14 not be regarded as complete or exhaustive, but the EGU session presentations and the 15 resulting papers in this special issue and elsewhere enable us to describe the typical objectives 16 17 of high frequency monitoring, to assess temporal and spatial scales and reflect on the future 18 development and research needs within this growing field of expertise. An overview of 19 monitoring objectives and time scales for high frequency nutrient monitoring is given in Table 1. We distinguished between three groups of monitoring objectives: 20

- To improve our understanding of the underlying hydrological, chemical and biological 21 22 processes determining temporal and spatial patterns in nutrients (PU). The main focus is 23 analysis of processes in complex systems.
- 24 To quantify nutrient loads and concentrations (Q). Here, the focus is not on system 2 functioning but on the values and characteristics (including uncertainties) observed. 25

To support operational management, including evaluation of the effects of mitigation 26 3 27 measures and predictions (M). The focus is directed at the implementation of high frequency 28 monitoring within the broader context of policy making and management.

- 29 It should be noted that some papers address more than one of these overall objectives. Section
- 30 2 of this overview discusses monitoring objectives and section 3 information scales.

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2 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 3 4 important when designing monitoring systems and choosing the methods and goals for data 5 processing (Broers 2002, Geer et al. 2006). For instance, selection of monitoring equipment 6 and choice of methods for data smoothing require a properly defined information scale, and 7 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 8 9 information is needed. The following three temporal seales are considered:

10 - Short-scale dynamics and extreme events (minutes to weeks).

Seasonal and annual patterns (months to several years).

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12 Longer term behavior and trends (years to decades).

Specific monitoring objectives may require a specific information scale. This we illustrate for 14 the monitoring objective 'characterizing groundwater surface water interaction'. Typically, 15 analysis of the response of nitrate concentrations in surface water to rainfall events is of short 16 temporal scale (minutes or hours); however, extension of the scale may be relevant if 17 18 including the shallow groundwater flow leading to dilution or up-concentration depending on 19 hydrological and subsoil conditions (e.g. Rozemeijer & Broers 2007). To estimate average 20 loads from shallow groundwater towards surface water during the growing season, the 21 information scale required will involve one or several seasons. To evaluate the long-term 22 sustainability of groundwater dependent aquatic ecosystems in a WFD assessment, the information scale may cover several years or decades. A more detailed description of 23 24 information scales is given in Section 3.

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.

30

1

11

1	2Monitoring objectives
2	An overview of monitoring objectives and time scales for high frequency nutrient monitoring
3	is given in Table 1. We distinguished between three main groups of monitoring objectives:
4	- To improve our understanding of the underlying hydrological, chemical and biological
5	processes determining temporal and spatial patterns in nutrients (PU).
6	- To quantify nutrient loads and concentrations (Q).
7	- To support operational water and environmental management, including evaluation of the
8	effects of mitigation measures and predictions (M).
9	It should be noted that some papers address more than one of these overall objectives.
10	
11	2

#### 12 2.1 Hydrological, chemical and biological process understanding

13 The new methods of high frequency monitoring are applied to fulfil various objectives. The 14 objectives treated here are those included in Table 1. The overall objective of the PU group is 15 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 16 opportunities of high resolution monitoring for understanding the functioning of catchments, 17 18 and they foresaw a new era of technical progress and study of actual data, making full profit 19 of the newly acquired spectrum of signals from very short to longer time scales. A decade 20 later, a large number of papers and presentations, including those at the EGU sessions, have 21 demonstrated that process understanding has indeed improved significantly. We have made a 22 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\_and
 concentration dynamics, hysteresis effects and extreme values\_of\_nutrient
 concentrations and loads. 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).

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1 PU2: Characterization of transport routes and time scales. These studies aim to detect 2 flow routes, groundwater-surface water interactions and travel time distributions with 3 emphasis on the interactions between variables in different hydrological compartments, in particular those between groundwater and surface water. The added 4 5 value of high frequency monitoring is its ability to distinguish between fast and slow 6 flow components (see Poulsen et al. 2015b, Shreshta et al. 2013, Rozemeijer et al. 7 2010a, 2012). High frequency monitoring has also stimulated the development of new 8 approaches to characterize the transient nature of travel time distributions (Velde et al. 9 2010, Botter et al. 2011, Hrachowitz et al. 2015).

10 PU3: Characterization of retention processes ... These studies aim to gain insight into the attenuation and retention processes determining the response of nutrients to driving 11 forces such as rainfall events, in both surface and ground waters. High frequency 12 13 monitoring may, for example, reveal clear day-night cycles in nutrient concentrations, 14 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-15 isotopes together with calibration of flow models using nitrate and discharge data is a 16 17 promising approach when studying PU2 and PU3 objectives combined (Shershta et al. 18 2013).

19 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 identifying and 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 an 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

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1 undetected using low frequency monitoring, which implies that load estimates based 2 on low frequency monitoring are typically biased and too low (Rozemeijer et al. 3 2010a, Cassidy & Jordan 2011, Audet et al. 2014, Goyenola et al. 2015, Skeffington et 4 al. 2015). In contrast, high frequency monitoring reduces the bias in concentration distributions derived from under sampling of the concentration time series. (e.g. 5 Jordan et al. 2007, Rozemeijer et al. 2010b, Ernstsen et al. 2015, Campbell et al. 6 7 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 8 9 differences between daytime and night-time fluxes (Neal et al. 2012, Van der Grift et 10 al. 2016).

11 Q2: Trend assessment. Assessment of temporal trends, quantification of trend slopes and identification of trend directions, are the objectives of many monitoring 12 programmes or research studies. High resolution monitoring, in combination with time 13 14 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 15 16 deterministically (e.g. Van der Grift et al. 2016) and statistically (Lloyd et al. 2014, 17 Rozemeijer et al. 2014), for example using spectral analysis methods (Aubert et al. 2013, Blauw et al. 2013). 18

- 19 Q3:-Compliance with water quality standards. Testing compliance with water quality standards, such as WFD Environmental Quality Standards. r is another important aim 20 of many monitoring programmes, typically This involving involves testing the 21 22 frequency of exceedance of standards or quantifying the probability of exceedance. 23 High frequency monitoring improves these aims by adding information on extreme 24 values and short-term peaks impacting the regular evaluation of exceedances in low 25 frequency programmesprograms. Skeffington et al. (2015b) clearly demonstrate that the classification of WFD Chemical and Ecological Status is strongly influenced by 26 27 sampling frequency and time of sampling during the year and over the day.
- Q4: Water and matter balances and sources. Detection of (pollution) sSource
   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 which helps source apportionment and adds to improving water

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- 1and mass balances (see van-Van der Grift et al. 2016, Aubert et al. 2013b, Goyenola et2al. 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).

#### 9 2.3 Operational (real time) management – effects and predictions

The central aim of the M type monitoring objectives is an evaluation of the impact of <u>water</u> and <u>environmental</u> management measures <u>and as well as</u> 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 16 17 inputs, hydrology or biogeochemistry. Besides revealing the time-dependent nutrient 18 inputs from, for instance, sewage treatment facilities or leaking septic tanks (Wade et 19 al. 2012), the effects of mitigating measures can be followed by assessing changes in 20 the duration or frequency of nutrient peaks in the time series before and after their 21 implementation. An example Examples are is given in Campbell et al. (2015) and Greene et al. (2011). 22
- M2: Management and mitigation of diffuse sources. Mitigation measures for nutrients 23 24 in agricultural areas typically involve some kind of land use management or changes 25 in the hydrological functioning of the system. Despite the establishment of high 26 frequency monitoring, the effects of mitigation measures are often difficult to separate 27 from those of natural variability created by meteorological conditions or from spatial variations in governing variables such as soil types and subsurface reactivity. 28 29 Examples of monitoring the effects of mitigation measures in diffuse pollution settings 30 are given in Campbell et al. (2015), Ernstsen et al. (2015), Van der Grift et al. (2015) 31 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 & <u>van-Van</u> der Grift 2004, Visser et
 al. 2007, 2009, Hansen et al. 2012, 2013).

- *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 hydro chemical response to rainfall 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).
- 10

21

#### 11 **3** Information time scales

12 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 13 14 processing (Broers 2002, Van Geer et al. 2006). For instance, selection of monitoring equipment and choice of methods for data smoothing require a properly defined information 15 scale, and the papers and abstracts are therefore grouped according to this (Table 1). For each 16 17 monitoring objective, the required information depends on the scale at which the information is needed. The following three temporal scales are considered: 18 19 Short-scale dynamics and extreme events (minutes to weeks). Seasonal and annual patterns (months to several years). 20

Longer term behavior and trends (years to decades).

22 Specific monitoring objectives may require a specific information scale. This we illustrate for the monitoring objective 'characterizing groundwater surface water interaction'. Typically, 23 24 analysis of the response of nitrate concentrations in surface water to rainfall events is of short 25 temporal scale (minutes or hours). To estimate average loads from shallow groundwater 26 towards surface water during the growing season, the information scale required will involve 27 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 28 29 decades.

1 Monitoring programmes produce time series of nutrient concentrations, discharge, 2 precipitation and other relevant variables. These time series are processed in order to compute 3 the dynamic characteristics and to extract the desired information for the objective specified 4 in the monitoring programme. The dynamics of the hydrological and chemical observations 5 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 6 example, the response of nitrate concentrations in surface water to a rainfall event is a short 7 8 scale event (in the order of hours to days), whereas meeting the objectives of the WFD has a 9 longer time scale (years to decades). Irrespective of the time scale of the monitoring objective, 10 observations contain variations at all time scales and the gathered data have to be processed 11 and statistically filtered in order to obtain the correct trend information or system 12 characteristics at the desired time scale (e.g. Lloyd et al. 2014). Within a data processing 13 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. 14

#### 15 3.1 Short time scales

Obviously, to obtain information at short time scales, high frequent monitoring is required 16 and data processing will include high pass filters. Concentrations and loads of nutrients 17 18 frequently show rapid changes over time as a result of rainfall events, emissions of effluents 19 from point sources and unintended losses of manure or pesticides during application. Often, 20 these rapid changes occur at time scales less than one hour and high frequency monitoring is 21 required in order to capture peaks and extreme values that would go undetected if applying 22 only low frequency monitoring (cf. Campbell et al. 2015, Skeffington et al. 2015b, Van der 23 Grift et al. 20156).

24 Also, if assessing the statistical characteristics of the concentration or the load of a solute (e.g. 25 average and percentile values or the frequency of exceedance of a threshold), high frequency 26 monitoring is a valuable tool. In principle, statistical characteristics can be determined from 27 low frequency observations provided that the monitoring period is sufficiently long. However, 28 in many cases the system shows statistically non-stationary behavior over longer periods of 29 time due to, for example, changes in land use management. With highHigh frequency monitoringobservations, we can obtain more reliable estimates of theenables the estimation of 30 trend characteristics for in shorter periods, permitting filtering outbeing less sensible for 31 longer-term trends (e.g. Lloyd et al. 2014). Many studies focus on the interactions between 32

1 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 2 3 appear to be the major driving force for the temporal distribution of fluxes along the different 4 flow paths, including quick components like discharges from point sources, tile drain water 5 and overland flow and slow components such as discharges from deeper groundwater. The 6 quick components have response times in the order of magnitude of hours, days or weeks. 7 Therefore, the response of nutrient fluxes and loads to precipitation is a complex function 8 (e.g. Van der Velde et al. 2010). To estimate this complex response function and to unravel 9 the contributions of the different flow paths, high frequency monitoring is a prerequisite (cf. 10 Campbell et al. 2015).

#### 11 3.2 Seasonal and annual patterns and long term behavior

12 In many studies the aim is not to identify short term dynamics but to reveal longer term 13 patterns, distinguishing between periodic (seasonal) patterns and long term trends. An 14 example of a policy relevant an objective with a seasonal information scale is the estimation 15 of average or typical nutrient concentrations during the growing season. An example of a Long-term monitoring objectives is found in of the Water Framework Directive (WFD), 16 17 which 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 18 19 ecosystems, (cf. Rozemeijer 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 20 concentrations of nitrate (Visser et al. 2007). Although high frequency information (days to 21 22 weeks) is not required for the analysis of seasonal and annual patterns and long term behavior, 23 high frequent monitoring can be beneficial, because often statistical characteristics and inputresponse relations can be inferred reliable from a shorter monitoring period. Individual 24 25 observations of water quality might be prone to are the result of variation at a wide range all-of frequencies. and hHigh frequency variations (noise) that tend to obscure the low frequency 26 27 signal. High frequency monitoring enables filtering out the noise (low pass filter) occurring 28 during relatively short monitoring periods in order to elucidate the long-term trend (Bierkens 29 et al. 1999, Halliday et al. 2012, Aubert et al. 2013, Lloyd et al. 2014, van Van der Grift 201**5**6). 30

#### 1 4 Monitoring equipment

2 Several types of sensors have been developed in recent years. Some are based on in situ 3 laboratory (mobile or stationary) analysis of water samples, while others utilize, for instance, 4 light or infrared (UV) spectra to measure chemical parameters (e.g. turbidity, nitrate, DOM) 5 or materials capable of passive adsorption of chemicals (e.g. Sorbicells). Some sampling 6 methods produce point observations in time, whereas others derive flow- or time-weighted 7 concentrations over a time period. All methods have advantages and disadvantages, and sA 8 number of Some studies (e.g. Rozemeijer et al. 2010c, Cassidy and Jordan 2011, Jordan et al. 9 2013, Huebsch et al. 2015) compare several sampling instruments and monitoring strategies 10 (Table 2). Below vVarious continuous monitoring methods, in particular those described in 11 the papers presented in this special issue (overview in Table 2), are describedlisted in Table 2.

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#### 16 Table 2: Overview of monitoring methods and instruments applied in the Session abstracts

#### 17 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	<ul> <li>- s:+can spectro:+lyserTM ,s:+can</li> <li>Messtechnik GmbH, Austria</li> <li>- NITRATAX plus sc, Hach Lange GmbH,</li> <li>Germany</li> <li>reagentless hyperspectral UV</li> <li>photometer (ProPS)</li> </ul>	Huebsch et al. (2015) Van der Grift et al. (20156) Rozemeijer et al. (2010c) Wade et al. (2012) Heinz et al. (2014)		Formatted: Dutch (Netherlands)
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) <del>van Van</del> der Grift et al. (201 <u>6</u> 5)		Formatted: French (France)
(Total reactive phosphorus, TRP), nitrite ( $NO_2$ ) and ammonium ( $NH_4$ )	Systea Micromac C	Wade et al. (2012)	i	
Passive samplers	SorbiCell-samplers (De Jonge & Rothenberg, 2005)	Rozemeijer et al. (2010c, 2015) Audet et al. (2014)	i	
Turbidity	OBS sensor, Campbell Scientific	van- <u>Van</u> der Grift et al. (201 <u>6</u> 5)		Formatted: Dutch (Netherlands)
Automatic samplers	Isco sampler; Sigmatax sampler	Goyenola et al. (2015) Audet et al. (2014)		Formatted: Dutch (Netherlands)
O <sub>2</sub> , pH, temperature conductivity, turbidity and chlorophyll	- YSI 6600 multi-parameter sonde	Van der Grift et al. (20165)           Skeffington et al. (2015b)           Wade et al. (2012)		Formatted: French (France) Formatted: French (France)

Conductivity, temperature	CTD-diver (Van Essen Instruments, Delft, the Netherlands)	Van der Grift et al. (201 <u>6</u> 5)
<sup>18</sup> O, <sup>2</sup> H	Wavelength-Scanned Cavity Ring Down Spectrometry System (WS-CRDS) L2120-i Picarro	Heinz et al. (2014)

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#### 2 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.

5 Several research groups in Europe and beyond are undertaking pilot studies on the use of high 6 frequency monitoring of nutrients. During the past decades, there has been growing awareness 7 of the fact that the quality of the aquatic environment is threatened by high concentrations and 8 loads of nutrients in groundwater and surface water. At the same time, development of 9 observation equipment enabling high frequency monitoring at affordable cost has been 10 extensive and, accordingly, assessment and quantification of the dynamic behavior of 11 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 12 13 exploring the possibilities of high frequency monitoring of processes at small temporal scale; 14 thus, Mmost testing has been devoted papers in Table 1 concern to process understanding (PU)1 and quantification of concentrations and loads (Q)) (Table 1). The new opportunities 15 increase our understanding of flow regimes, dynamics and hydrological extremes, flow routes 16 and interactions between flow components as well as attenuation and retention processes in 17 surface and ground waters. During the last five years, qQuantification of concentrations and 18 19 loads to be used in the status assessments required by the EU Water Framework Directive has 20 received much attention by several European research groups during the last five years. 21 However, only few papers and contributions cover aspects of the monitoring effects of river 22 basin management plans that have been implemented to reduce pollution by nutrients or 23 climate change impacts. Although full-scale application of high frequency monitoring at 24 national or regional scale may not always beis often not reported in scientific papers, we 25 believe that its use in operational water management is still limited. The papers listed in Table 26 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 27 28 regional monitoring programmesprograms in the coming years.

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.

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 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.

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

14 Today, high frequency monitoring of nutrients is subject to research and pilot studies, but we 15 expect a transition from research to implementation in operational practice. This transition 16 requires the design of efficient and cost-effective monitoring programmesprograms for whichand to design optimum programmesprograms, research is needed to identify the best 17 18 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. Well-defined 19 20 monitoring objectives are prerequisite for Ooptimum monitoring strategies (observation 21 devices, spatial and temporal distribution) should be tuned to/translated into well defined monitoring objectives (Lloyd et al. 2014). 22

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 <u>easy access</u> data availability is of great importance(e.g. Neal et al.2011). Long time series are valuable and should be easily accessible (Neal et al. 2011).

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 (Lloyd et al. 2014). We expect that more research will be conducted into the application of statistically based techniques, such as

1 transfer function - noisetime series models, to deduce the characteristics of the series and to 2 quantify the relationship with other hydrological variables (e.g. Van der Grift et al. 2016). 3 (e.g. van <u>Van\_der Grift et al, 2016</u>). Examples of characteristics may be typical seasonal 4 behaviour, the memory of the system and the trend. Examples of relationships are the 5 response of nutrients to meteorological variables or to water management. Such time series analysis techniques will have applications in studying the effects of climate change on the 6 7 functioning of catchments, e.g. by elucidating the changing response times of water and 8 solutes towards precipitation and drought events.

- 9 High frequency data will in the future assist in achieving a better understanding about in10 stream processes such as nitrogen and phosphorus assimilation, sedimentation and
  11 resuspension processes. Moreover, water quality models will be challenged when calibrated
  12 against high frequency data which in turn will force models to be more dynamic (run at lower
  13 time steps) and improve their internal process descriptions.
- High frequency monitoring data will also be able to assist water managers in getting a true
   picture of nutrient loadings and sources that will enable River Basin managers to implement
   more targeted and thereby cost-effective decisions when fulfilling the requirement under the
   EU Directives directed at water management such as the Water Framework Directive, the
   Nitrates Directive and the Groundwater Directive.

The future will likely see more emphasis on multi-variable analysis, in which monitoring setup, 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) (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 (<sup>18</sup>O/<sup>2</sup>H) and products of radioactive decay in the subsurface (e.g. <sup>222</sup>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 <u>and low-maintenance</u> monitoring devices.

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#### 2

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# Table 1: Overview of monitoring objectives and time scales for high

# frequency nutrient monitoring

Bold referen Issue	nces appear in this Special	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)		
ogical process	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)	<b>Goyenola et al. (2015)</b> Van der Grift et al. (20156) Halliday et al. (2014) Jordan et al. (2012) Neal et al. (2011, 2012)	Neal et al. (2011)		Formatted: Dutch (Netherlands)         Formatted: Dutch (Netherlands)         Formatted: Dutch (Netherlands)
Hydrological, chemical and <u>bi</u> ological process understanding	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)			Formatted: French (France)
Hydrological, ch understanding	PU3; Attenuation and retention processes – surface and ground waters	Rode et al. (2012, 2013) Bieroza 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)		
1	O1: Accossment of	Campbell et al. (2015)	Campbell et al. (2015)	Ernstsen (2015)	-	
1	Q1; Assessment of concentrations, loads,	Graeber et al. (2015)	Ernstsen et al. (2015)	Windolf et al. (2014	$\swarrow$	Formatted: French (France)
ļ	export to downstream	Wade et al. (2012) Lloyd et al. (2012)	Goyenola et al. (2015) Graeber et al. (2015)	Kronvang et al. (2013) Greene et al. (2011)	/	Formatted: Dutch (Netherlands)
	waters (lakes, rivers,	Jordan et al. (2014)	Van der Grift et al. (20165)			Formatted: Dutch (Netherlands)
ļ	estuaries)	Ovesen et al. (2012,(2013)	Rozemeijer et al. (2016) Wade et al. (2012)			Formatted: Dutch (Netherlands)
nd concentrations		Rozemeijer et al. (2010, 2013) Halliday et al. (2012) Cassidy and Jordan (2011)	Halliday et al. (2012) Lloyd et al. (2012) Ovesen et al. (2013) Wade et al. (2013) Bieroza et al. (2013, 2014) Jordan et al. (2012, 2014) Oosterwoud (2014) Poulsen et al. (2015)			Formatted: Dutch (Netherlands)
Quantification of loads and concentrations	Q2; Trend assessment, slopes and directions	Aubert et al. (2013) LLoyd et al. (2014	Van der Grift et al. (20165) 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)		Formatted: Dutch (Netherlands) Formatted: Dutch (Netherlands)

	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) Bieroza et al. (2013,2014) Lloyd et al. (2012,2013) Jonczyk et al. (2014)	Ernstsen (2015) Halliday et al. (2014a)	Formatted: French (France) Formatted: Dutch (Netherlands)
	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. (201 <u>6</u> 5) Greene et al. (2011) Rozemeijer et al. (2010b) Aubert et al. (2013b) Wade et al. (2012)	Ernstsen et al. (2015) Greene et al. (2011)	
			Jordan et al. (2014) Poulsen et al. (2014,2015a) Van der Vlugt et al (2014) Yu et al. (2015)		Formatted: Danish
	Q5; Test and comparison of equipment	Heubsch et al. (2015) Audet et al. (2014) Faucheux et al. (2013) Oosterwoud et al. (2014)	De Jonge et al. (2012) Vendelboe et al. (2015) Jordan et al. (2013) Rozemeijer et al. (2010c,		Formatted: French (France) Formatted: Dutch (Netherlands)
 		Wade et al. (2012) Cassidy et al. (2012) Schneider et al. (2012) Stadler et al. (2015) Jomaa (2015) Heinz et al. (2014)	2013) Cassidy et al. (2012)		
÷	M1; Management and mitigation of point sources	Campbell et al. (2015)	Jordan et al. (2012)	Greene et al. (2011)	Formatted: English (U.S.) Formatted: Indent: Left: 1.02 cm,
Operational (real	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 ∧ 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)	No bullets or numbering           Formatted: French (France)
Ö	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)		