Reply on review of our manuscript HESS-2015-235 "High-frequency monitoring reveals nutrient sources and transport processes in an agriculture-dominated lowland water system"" by Reviewer #1, #2

Dear Editor,

We would like to thank the reviewers for their effort reviewing our manuscript and their valuable comments which we have taken in full consideration to improve our manuscript.

Below we will explain point by point how we dealt with their comments, arranged from Reviewer #1 to #2. The original reviewer comments are presented in *bold italic*. Our response is presented in normal text.

Beside the changes suggested by the reviewer we improved our paper on several other topics. The marked up manuscript version is added to at the end of this document.

Our revised manuscript can be found in a separate document. We hope our improvements will satisfy your demands and lead to acceptance of our paper.

Sincerely,

Bas van de Grift, on behalf of all authors

# Reviewer #1

#### Major comment

The study is about how to manage potential eutrophication in a highly-managed Polder system, using high-resolution monitoring. Unfortunately, this monitoring was only carried out from October to April, and so they have completely missed the period when high nutrients may pose a threat by impairing the ecology or causing algal problems. This issue needs to be addressed. What are the implications of not monitoring during the period when bloom risk, biological nutrient uptake and denitrification are at their peak? This seriously reduces the impact of this study.

We agree with reviewer #1 that the half year period of high frequency data are short for allowing a clear explanation of the hydrogeochemical behavior of the polder. The reason behind this half year period was that we started the measurement in Oct. 2014. At time of writing the manuscript, we only had data for a half year. However, we have continued the monitoring during and after writing of the manuscript until Oct 2015. So, at the moment we have a full year of high-frequency nutrient concentration at the polder outlet and we used this data series in the revised manuscript. Shortly, the NO<sub>3</sub> concentrations dropped to almost zero during April and continued to stay low until intensive precipitation events in August. TP concentrations gradually increased from begin June until the end of August and dropped upon the precipitation event in August.

We also have measured suspended sediment continuously (via turbidity) with an OBS sensor combined with SS measurements on grab samples and Total Reactive P during the period Oct. 2014-Oct. 2015. Our original idea was to write second, more hydraulically oriented paper with a focus on erosion and sedimentation of suspended sediment and P from the channel sediment. We realize that not including this data in our manuscript weakens our environmental interpretation of the nutrient behavior in the system and, therefore, added the suspended sediment data and TRP data to the revised version of the manuscript in support of our findings.

#### Minor comments

#### 8338.4. I'm not sure that this study is highly relevant. It is very site specific.

Highly relevant is a general statement that for improving the water quality it is important to gain insight in the hydrochemical function of the catchment. To our opinion this applies to all type of catchments, whether these are managed or not. In this manuscript we focus on the importance of short-scale events as thaw and rainstorms but also on seasonal dynamics on nutrient dynamics in an agricultural-dominated lowland catchment. This type of catchments can be found in many delta areas worldwide. Increasing system knowledge in such areas is therefore relevant.

#### 8338.11 Change to "losses via field drains after intensively...."

Agreed and changed to "losses via tube drains after intensively...."

8338.18. Change to "The rainfall induced. . ..."

Agreed and changed accordingly.

8338.20. Change to "but this may be then buffered". This study does not directly monitor the drain outputs and the data does not fully support this statement.

Agreed and changed accordingly.

8338.22. Change highly to primarily.

Agreed and changed accordingly.

8339.1. Change loads to concentration

To our opinion it is the nutrient loads that matters when considering thread functions of water bodies. Nutrient concentration can be seen as result parameters of loads in combination with biological nutrient uptake or release processes. For instance, dissolved P concentration can be low during spring algae blooms because it is all taken up by the algae. Therefore, we prefer to use loads in this sentence.

8339.3. Reference needed.

Agreed, we added a reference to Bouwman et al. (2013a)

8339.5. Change to "Aim to improve water quality"

Agreed and changed accordingly

8339.7. What other sources? Sewage effluent is a major one that doesn't get mentioned in throughout the paper.

We rephrased this into "other sources like sewage effluent".

There is a wastewater treatment plant located within our study area. The effluent discharge is with an average of 0.35 m3/sec low compared to the discharge from the polder. The TP concentration in the effluent is maximal 0.5 mg/l. The TP load from the wastewater treatment plant to the Lage Vaart in the period Oct-Apr equals approximately 2700 kg compared to the export load from the Lage Vaart to the Markermeer of 10500 kg in the same period. For NO3 this equals 8100 kg and 308000 kg NO3-N. There are no other sources of sewage effluent like septic tank to the surface water within the Lage Afdeling drainage area. We added this to the M&M section 2.1 and discussed the limited impact of sewage in section 4.1.

8340.20 "has revealed the presence"

Agreed and changed accordingly.

8340.23. Managed, rather than human controlled?

Agreed and changed accordingly.

8340.26. A scientific paper shouldn't really be referencing Wikipedia as information source.

Agreed we removed this reference.

#### 8341.9. Algal growth is another potential mechanism for nutrient retention.

The residence time of water have an impact on all kinds of nutrient retention mechanisms, whether they are biological, chemical or hydrological. This sentence is not meant to given an overview of these kinds of mechanisms. We rephrased this sentence into: "which may impact biogeochemical or hydrological in-stream processes controlling nutrient retention".

#### 8342.15. A confining layer of what? Nearly nil? How long is the main river channel?

We rephrased this sentence into: "The geohydrology of the Flevoland polder area is generally described by a confining clay layer of Holocene origin, with a thickness of less than 0.5 m in the northeast to over 7 m southwest".

#### 8342.19. Is ripening an accepted term? I haven't heard it before.

Soil ripening is, to our knowledge, an accepted term to describe soil formation after land reclamation. A soil ripening index is developed by Kim et al. (1993).

8343.22. Why didn't they do high-resolution monitoring through the spring and summer months? This is a major omission.

See response on major comment.

8344. The method descriptions are overlong and need to be reduced.

We reduced the method description.

8345.7. Change Transparency to turbidity?

The Secchi depth was measured in the field so transparency is to our opinion correct.

8348.14. Seasonal, rather than mid-term?

Agreed and changed accordingly.

8348.20. This is where summer data would really strengthen the paper.

We agree with this, see our reply to the major comment

8349.10. Change to decreased during wet periods to a concentration of approximately.

Agreed and changed accordingly.

8348.15. There is an increase in TP concentration during low flow. What are the sources? This may indicate that there are point inputs. Does the polder receive any sewage effluent from septic tanks and wastewater treatment plants? Whether they are present or not, this should be mentioned in the site description.

See comment before. The effect of the WWTP on the TP concentration at the pumping station seems to be limited. The Lage Vaart channel is with a cross section of 100 m2 rather large compared to the WWTP effluent load. Between the WWTP and the pumping station the discharge from the nature area Oostvaardersplassen enters the Lage Vaart (location 6 in Figure 7). This discharge is three times larger than the discharge of the WWTP. This implies that there is limited flow of the WWTP effluent towards the pumping station during no pumping conditions which is also shown by

the low NO<sub>3</sub> concentrations during no pumping conditions. The increase of TP during no pumping condition can be related to the discharge from the Oostvaardersplassen. This water has relative high TP concentrations (Fig. 7). We added the paragraph below to the discussion section 4.1.1:

"The effect of the WWTP on the nutrient concentration at the pumping station seems to be small. During no pumping conditions there is limited flow of the WWTP effluent towards the pumping station. The discharge load from the channel that drains the nature area Oostvaarderplassen enters the Lage Vaart between the WWTP and the pumping station and is 2 to 3 times higher than the WWTP discharge load. This induces a small water flow in de opposite direction of the pumping station during no pumping conditions. The discharge water from the Oostvaardersplassen has relative high TP concentrations (Fig. 7) and may contribute to the increase in TP concentration at the pumping station during no pumping periods".

8351.3. The increase in TP during cold weather is a really interesting observation. It may also be due to river biofilms detaching from surfaces and entering the water column. This was observed in the River Frome, UK in Bowes, M.J., Smith, J.T., Neal, C., 2009. The value of high-resolution nutrient monitoring: A case study of the River Frome, Dorset, UK. J. Hydrol., 378(1-2): 82-96.

This is an interesting observation and this could be a source of the increase TP concentration but to our opinion this does not influence the  $NO_3$  concentration and conductivity of the channel water in the range that we have measured. Together with the changes in  $NO_3$  and TP concentrations, an increase of the turbidity (from 8 to 57 FTU), a decrease in the TRP concentration (from 0.06 to 0.02 mg P/I) and decrease of the conductivity (from 235 to 122 mS/cm) (Fig. S1) was observed. To our opinion this strongly points to soil surface runoff and transport of particulate P. However, we discussed this in the revised version of the manuscript.

#### 8354.5 Natural or urban areas. Could the decrease be due to denitrification?

This sentence describes the winter situation. Denitrification is limited then.

# 8355.20. Is it really all agricultural? Could there be any other potential NO3 inputs from sewage?

The NO3 load from the WWTP is limited compared to the NO3 load from the polder to the Markermeer. We added this to the manuscript. The low NO3 concentrations during the summer months (April-August) indicate that NO3 input from sewage to the surface water is also limited.

#### 8356.28. Delete levels

Agreed and changed accordingly

8357.10 and 11. Change from half to mid-November.

Agreed and changed accordingly

8357.27. If the nitrate is being transported rapidly via interflow and tube drains, why does it take 5 days to get maximum NO3 concentrations? Doesn't this imply that nitrate delivery to the pumping station is via a much slower route? The Lage Vaart river stretch appears to be only approx 12km long, so the nitrate signal at the pumping point should occur extremely rapidly after rainfall. I'm therefore not sure that your conclusions about tube flow are correct.

This statement might indeed be somewhat confusing. The flow velocities in a polder area are maximised by the capacity of the pumping station. This results in a delay between rainfall and peak

concentrations at the pumping station. The 5 days is the average travel time of the water in the field ditches, sub-channels and main channels. Van den Eertwegh (2002) calculated a mean annual residence times of water in the Lage Vaart main channel of 6.6 days. Catchment mean residence times of water vary strongly upon precipitation events and are much shorter after wet conditions (Van der Velde et al., 2012). As a consequence, the residence time in the main channel is shorter during wet conditions. If we only look at the volume of Lage Vaart main channel and pretend that there are no connecting sub-channels between the pumping station and the agricultural area it took already more than one day with continuous pumping to refresh all the water in the channel stretch of approximately 12 km between the pumping station and the beginning of the agricultural area. We added this statement and this reference to the manuscript.

#### 8362-3. Very wordy. Lots of repetition.

Agreed, we shortened this section

Figure 1 is very unclear and needs improving. The town names are illegible. It is unclear that the area to the north of the map is lake / sea. The numbered monitoring points are not referred to in the text. Do these towns have wastewater treatment works? If so, please add them to the map.

Agreed and changed accordingly

References

Bouwman, A. F., Bierkens, M. F. P., Griffioen, J., Hefting, M. M., Middelburg, J. J., Middelkoop, H., and Slomp, C. P.: Nutrient dynamics, transfer and retention along the aquatic continuum from land to ocean: towards integration of ecological and biogeochemical models, Biogeosciences, 10, 1-22, 10.5194/bg-10-1-2013, 2013.

Kim, D. J., Feyen, J., Vereecken, H., Boels, D., and Bronswijk, J. J. B.: Quantification of physical ripening in an unripe marine clay soil, Geoderma, 58, 67-77, http://dx.doi.org/10.1016/0016-7061(93)90085-Y, 1993.

Van den Eertwegh, G. A. P. H.: Water and Nutrient budgets at field and regional scale, travel times of drainage water and nutrient loads to surface water, PhD thesis Wageningen University, 2002.

van der Velde, Y., Torfs, P. J. J. F., van der Zee, S. E. A. T. M., and Uijlenhoet, R.: Quantifying catchment-scale mixing and its effect on time-varying travel time distributions, Water Resources Research, 48, n/a-n/a, 10.1029/2011WR011310, 2012.

### Reviewer #2

#### General comment

The study evaluates transport processes of TP and nitrate-N in a highly drained lowland catchment using high resolution data. The main concern I have with the manuscript is that it is highly descriptive and several findings are highly vague. Because only water quality data have been used for evaluating the export mechanisms often a serious proof is missing. The main drawback of the study is the short measurement period which does not allow a clear explanation of the seasonal export behavior of the catchment. It is not clear why a half year period has been selected for the study. The study shows some methodological weaknesses because important constitutes like suspended sediments (e.g. via turbidity) have not been measured. This leaves the conclusions somewhat open. Furthermore the used modelling approaches are highly simple and do not provide deeper insight into transport mechanisms. Reading the manuscript was somewhat exhausting because the ratio of new findings to the length of the text was often small. I would not like to recommend the manuscript for publication in HESS.

We agree with reviewer #2 that the half year period of high frequency data are short for allowing a clear explanation of the hydrogeochemical behavior of the polder. The reason behind this half year period was that we started the measurement in Oct. 2014. At time of writing the manuscript, we only had data for a half year. However, we have continued the monitoring during and after writing of the manuscript until Oct 2015. So, at the moment we have a full year of high-frequency nutrient concentration at the polder outlet and we used this data series in the revised manuscript. Shortly, the NO<sub>3</sub> concentrations dropped to almost zero during April and continued to stay low until intensive precipitation events in August. TP concentrations gradually increased from begin June until the end of August and dropped upon the precipitation event in August.

We also have measured suspended sediment continuously (via turbidity) with an OBS sensor combined with SS measurements on grab samples and Total Reactive P during the period Oct. 2014-Oct. 2015. Our original idea was to write second, more hydraulically oriented paper with a focus on erosion and sedimentation of suspended sediment and P from the channel sediment. We realize that not including this data in our manuscript weakens our environmental interpretation of the nutrient behavior in the system and, therefore, added the suspended sediment data and TRP data to the revised version of the manuscript in support of our findings.

We used transfer function-noise modeling to estimate the impact of rainfall on the nitrate concentration. We do not want to say if TFN modeling is a simple approach or not (there is a long record of scientific publication on development and application of TFN models). We are not convinced that modeling should be complicated by definition. Many model concepts exist that deal with nutrient transport. The most mechanistically oriented models are not necessarily the best ones, because they may underperform when applied at larger spatial scales. To our knowledge TFN models have yet not been applied on high-frequency monitoring data of nutrient concentrations. Although we realize that our model is a first step to, we think that TFN modeling is a promising tool to analyze high frequent water quality datasets.

To make our manuscript more quantitative we calculated the statistics of the changes in TP concentrations and turbidity during the pumping events (Table 3) and calculated the event-driven export-TP flux (Fig. 5). For this we used a hydrograph separation method to separate the high-frequency TP concentration data series into short-term TP concentration peaks caused by operation of the pumping station and baseline TP concentration (Fig. S4).

#### Specific comments

#### Page 8344, line 25: please provide correlation measures on that comparison.

We added the  $R^2$  between high frequency TP data and grab sample TP data (0.982) to the text and the scatterplot to the supplement (Fig. S1). We did the same for the turbidity from the OBS sensor and the SS concentration from the grab samples ( $R^2 = 0.965$ ).

Page 8350, line 4: representative for what? Residence time during the period after mid of November? Residence time is the time a water parcel needs to move from rainfall through soil (and groundwater) to the stream or ditch. The fact that nitrate concentration peaks five days after peak discharge does not imply that residence time of water is also five days. That would only be the case if whole nitrate stems from rainfall and nitrate would be a stable tracer. This is of course not the case. The mentioned mean residence time of 5 days is from my point of view unrealistic. The cited literature refers to a residence time of 6.6 days in the main channel and not in the catchment area!

This statement might indeed be somewhat confusing it is. The flow velocities in a polder area are maximised by the capacity of the pumping station. This results in a delay between rainfall and peak concentrations at the pumping station. The 5 days is the average travel time of the water in the field ditches, sub-channels and main channels. Van den Eertwegh (2002) calculated a mean annual residence times of water in the Lage Vaart main channel of 6.6 days. Catchment mean residence times of water vary strongly upon precipitation events and are much shorter after wet conditions (Van der Velde et al., 2012). As a consequence, the residence time in the main channel is shorter during wet conditions. If we only look at the volume of Lage Vaart main channel and pretend that there are no connecting sub-channels between the pumping station and the agricultural area it took already more than one day with continuous pumping to refresh all the water in the channel stretch of approximately 12 km between the pumping station and the beginning of the agricultural area. We added this statement and this reference to the manuscript.

Page 8350, line 17: Are there any measurements on turbidity or sediment concentrations which support this statement? Where should the sediments come from if sediment concentrations can be assumed very low between pumping events? The time series data suggest that the few high DRP concentrations data are mostly associated with high TP concentrations. Therefore high TP concentrations can also be caused by high DRP concentrations. As far as the data suggest PP has not been measured directly during the events and therefor the given explanation that SS are responsible for high TP concentrations are speculative. It is well known that DRP concentrations are often high in surface runoff and may explain also high TP concentrations, at least during freeze-thaw cycles. Without additional data on turbidity/suspended sediments of direct PP measurements it is not possible to identify sediments as a main source of high TP values.

See our reply to the general comments. We added our turbidity measurements to the manuscript. These measurements support our statements that the TP concentration peaks are caused by resuspension of the channel bed sediment. We added the following information to the manuscript. Simultaneously to the TP concentration peak we always measured a peak in turbidity. Compared to the concentration before pumping, the maximum TP concentration was on average a factor 1.83 and 1.3 higher during pumping with two pumps and one pump, respectively. This indicates a dependence of the TP concentration on the flow velocity in the main channel (0.125 m/sec with one pump and 0.5 m/sec with two pump). The TRP concentrations also showed an increase in concentration during pumping. To our opinion, it is plausible that the colorimetric measurement of TRP, which takes place in an acidic solution, can be attributed to the dissolution of particulate inorganic P.

#### Page 8351, line 2: highly speculative, is there any proof on this?

See our reply on the following remark below.

Page 8351, line 3-4: That is not true. Simply high DRP concentrations, which are elevated in surface runoff, can be responsible for high TP concentrations. Here the investigation lacks from missing direct DRP measurements.

Together with the changes in  $NO_3$  and TP concentrations, an increase of the turbidity (from 8 to 57 FTU), a decrease in the TRP concentration (from 0.06 to 0.02 mg P/I) and decrease of the conductivity (from 235 to 122 mS/cm) (Fig. S1) was observed. This strongly points to soil surface runoff and transport of particulate P.

Page 8351, line 10: What does this tell us? It is not surprising that rainfall is related to nitrate concentrations if the soil is saturated (after mid of November). All rainfall is transformed into discharge via transport through the soil and pipe drains. Rainfall becomes not directly discharge but exchanges the soil water rich in nitrate.

As discussed in section 4.1.1 a reduction in NO<sub>3</sub> concentrations coinciding with periods of intensive rainfall is commonly reported in high-frequency monitoring studies in natural catchments and this is attributed to dilution of the surface water by surface run-off. For us, it was somewhat surprising that we didn't see such a dilution phenomenon during rainfall events in our polder catchment. This gives insight in the nutrient transport mechanisms for the agricultural landscape type we studied. It also indicates that soil surface runoff is not an important nutrient transport mechanism in this lowland area. As the relevance of surface runoff on the water quality in such areas is still under debate (e.g. see Van der Salm et al. (2012)) this is valuable information.

Page 8352, line 9: I fully agree. The time series is too short to gain sound information for explaining the export behavior

See our replies before.

Page 8352, line 17: "overestimation" is a wrong term because these loads are calculated with the best available data. Low frequency data underestimate the load!

We considered this during preparation of the manuscript. Originally we used 'overestimation' because load calculation based on grab sampling is common practice and high frequency data

provides addition information. We, however, see the point the reviewer makes here and changed this into underestimation of the grab sampling load. This now gives a small change of the percentages when compared to the original manuscript

We extended Fig. 5 to 1 October 2015 and added the cumulative TP load after separation of the short scale TP concentration peaks during pumping events from the high-frequency dataset. We added a short quantitative description of the results.

Page 8353, line 5: Why discussing it here when it will be discussed one more time later on. Likely is not a clear proof.

Agreed, we removed this sentence

Page 8353, line 14: why are the chloride data presented here?

Chloride is a tracer/indicator for the contribution of deep groundwater to the surface water. The Presenting the Chloride data give support to the interpretation of nutrient dynamics. We explained this in the revised version of the manuscript.

Page 8353, line 25 and ff: these findings are not surprising and can be therefore shortened

Agreed, we shortened this paragraph.

Page 8354, line 8: is there any evidence on that? Has the cited reference conducted the investigation on the same site than this study?

The cited reference provides evidence for shallow pyrite oxidation and is influence on the SO<sub>4</sub> concentration in intensively drained Holocene marine clay polders with the Netherlands. The Lage Afdeling is typically such a polder. The reference also uses data from this polder.

Page 8357, line 10-15: the restriction of the TFN model to less variable (wet) soil moisture conditions allows better model predictions but reveals less information about transport processes within the catchment since only a relatively short duration of several month is captured. State of the art is continues modelling for at least several years. The presented results are not really new as indicated by the discussion.

To our opinion TFN modeling can become a valuable tool for analyzing high frequency water quality data. We searched in the literature for application of TFN model on high-frequency nutrient concentration but we could not find any.

Page 8358, line 20-25: two different reasons are described for the increase of DRP in autumn (change of loading and in-streams processing). Because of missing detailed studies at least of one of these processes the authors are not able to clarify the importance of both possible processes, the statement therefor keeps vague

It is true that we have no quantitative information to separate the groundwater P load and the P load from remobilization from bed sediments. Both process become dominant for the water quality under dryer conditions and are thus difficult to separate. We do not want to speculate too much on this topic.

Page 8359, line 20-25: because suspended sediment P (PP) measurements are missing it is not clear whether the TP concentrations during pump cycles stem from higher PP or DRP concentrations. If resuspension of sediments is the main reason of increased PP concentrations during events than decreasing PP peak concentrations could be expected with subsequent events because of exhausting sediment deposits in the channel. The data do not show this. Due to missing parallel measurements of DRP and TP a clear statement is not possible.

The following sentence was added to the section 3.3: 'The data shows the highest increase of TP concentrations (0.16-0.60 mg P L<sup>-1</sup> during pumping with two pumps after longer periods without pumping (21 Oct, 2 Nov, 8 Dec, 20 Feb., 23 June, 25 July and 15 Aug) and decreasing TP peaks were observed with subsequent events (Fig.3)'.

Page 8360, line 1-23: the discussion starts with a statement which should be part of the problem section. The chapter ends up with a conclusion without referring to the study. No results of the study are discussed.

We agree with this comment and we have rewritten this paragraph. The statement is moved to the introduction.

Page 8360, line 27: I do not see that a NO3 peak concentration of 10.4 mgN/L during a given high flow event is a proof of manure input. During January peak concentrations also reached a range between 8 and 9 mgN/I

This is true if we focus on the absolute height of the peaks. However, if we look at the increase in concentration upon the rainfall event this is almost two times higher than the other TP concentration peaks with similar precipitation (Table 2). Moreover, the residuals in the TFN modeling show that this peak and the following peaks on 27 Febr. and 3 March were different from the peaks before half Febr. which also shows the added value of TFN modeling.

Page 8361, line8-25. The discussion poses more questions than reveals explanations of the measured time series. No clear findings can be presented because of missing supplementary measurements despite the concentration measurements at the outlet. Missing PP or turbidity measurements have already been mentioned.

See our reply to the general comment.

Page 8362, line 1-10: if this information is important for the discussion it should be given in the method section.

Agreed, we moved this to the method section.

#### References

Van den Eertwegh, G. A. P. H.: Water and Nutrient budgets at field and regional scale, travel times of drainage water and nutrient loads to surface water, PhD thesis Wageningen University, 2002.

Van der Salm, C., van den Toorn, A., Chardon, W. J., and Koopmans, G. F.: Water and nutrient transport on a heavy clay soil in a fluvial plain in the Netherlands, Journal of Environmental Quality, 41, 229-241, 2012.

Van der Velde, Y., Torfs, P. J. J. F., van der Zee, S. E. A. T. M., and Uijlenhoet, R.: Quantifying catchment-scale mixing and its effect on time-varying travel time distributions, Water Resources Research, 48, n/a-n/a, 10.1029/2011WR011310, 2012.

# 1 Marked up Manuscript

- 2 High-frequency monitoring reveals nutrient sources and transport processes
- 3 in an agriculture-dominated lowland water system
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11 Abstract

- 12 Many agriculture-dominated lowland water systems worldwide suffer from eutrophication caused
- by high nutrient loads. Insight in the hydrochemical functioning of embanked polder catchments is
- 14 | highly relevant for improving the water quality in such areas. or for reducing export loads to
- 15 downstream water bodies. This paper introduces new insights in nutrient sources and transport
- 16 processes in a low elevated polder in the Netherlands situated below sea level using high-frequency
- 17 monitoring technology at the outlet, where the water is pumped into a higher situated lake,
- 18 combined with a low-frequency water quality monitoring program at six locations within the
- 19 drainage area. Seasonal trends and short scale temporal dynamics in concentrations indicated that
- 20 the NO<sub>3</sub> concentration at the pumping station originated from N-loss from agricultural lands. The
- 21 NO<sub>3</sub> loads appear as losses with drain water dischargevia tube drains after intensive rainfall events
- 22 during the winter months due to preferential flow through the cracked clay soil. Transfer function-
- 23 noise modelling of hourly NO<sub>3</sub> concentrations reveals that a large part of the dynamics in NO<sub>3</sub>
- 24 concentrations during the winter months can be related to rainfall. The total phosphorus (TP)
- 25 concentration <u>and turbidity</u> almost doubled during operation of the pumping station which points to
- 26 resuspension of particulate P from channel bed sediments induced by changes in water flow due to
- 27 pumping. Rainfall events that caused peaks in NO<sub>3</sub> concentrations did not results in TP concentration
- 28 | peaks. The by rainfall induced and NO<sub>3</sub> enriched quick interflow, may also be enriched in TP but this
- 29 is then buffered in the water systemretention of TP due to sedimentation of particulate P then
- 30 <u>results in the absence of rainfall induced TP concentration peaks</u>. Increased TP concentrations

associated with run-off events is only observed during a rainfall event at the end of a freeze-thaw
cycle. All these observations suggest that the P retention potential of polder water systems is
highlyprimarily due to the artificial pumping regime that buffers high flows. As the TP concentration
is affected by operation of the pumping station, timing of sampling relative to the operating hours of
the pumping station should be accounted for when calculating P export loads, determining trends in
water quality or when judging water quality status of polder water systems.

7 Keywords

8 Nitrate, Phosphorus, Nutrient retention, High-frequency monitoring, Time series analysis, Lowland
9 water system, Polder, Nutrient dynamics.

10 1 Introduction

11 Many surface water bodies suffer from eutrophication caused by high nutrient loads. Eutrophication 12 of surface waters can lead to turbid waters with decreased oxygen levels (hypoxia), toxin production 13 by algae and bacteria, and fish kills. (Bouwman et al., 2013a). Policy makers of national governments, 14 the European Union and other authorities aim at improving to improve water quality in surface water 15 bodies that receive nutrient load from agriculture or other sources like sewage effluent (EC, 16 2000)(EC, 2000). A sound assessment of pressures and impacts on the aquatic ecosystem and a 17 reliable assessment of water status in catchments is, therefore, a topic of major importance. If the 18 assessment of pressures is flawed, the action plans will be ill founded and there is a risk that EU 19 member states will not carry out their work where it is most needed and in a cost effective way (EC, 20 2015)(EC, 2015). This holds strongly for the Netherlands where nutrient surpluses and leaching are 21 higher than elsewhere in Europe (van Grinsven et al., 2012)(van Grinsven et al., 2012) and the world 22 (Bouwman et al., 2013)(Bouwman et al., 2013b), due to a highly concentrated and productive 23 agricultural sector.

24 For the evaluation of action programs and pilot studies, water authorities invest heavily in the 25 monitoring of NO<sub>3</sub> and P concentrations in surface water. Regional surface water quality networks in 26 EU member states are commonly sampled 12 times a year (Fraters et al., 2005)(Fraters et al., 2005). 27 However, the interpretation of grab sample data in terms of loads and fluxes is often problematic 28 from such monitoring networks (Rozemeijer et al., 2010). (Rozemeijer et al., 2010). Grab sample 29 frequencies are generally not sufficient to capture the dynamical behavior of surface water quality 30 and hydrological functioning of the catchment (Kirchner et al., 2004; Johnes, 2007) (Kirchner et al., 31 2004; Johnes, 2007). It is increasingly recognized that incidental losses and peak flows play an 32 important role in the nutrient loads of surface water systems in the Netherlands (Van der Salm et al.,

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1 2012;Regelink et al., 2013)(Van der Salm et al., 2012;Regelink et al., 2013) and elsewhere (Withers et 2 al., 2003) (Withers et al., 2003). Such incidental losses are considered to be related to peak flows 3 after heavy rain storms and due to overland flow or quick interflow via drains and cracked clay soils 4 and related leaching of manure and erosion of soil particles (Kaufmann et al., 2014)(Kaufmann et al., 5 2014). Some authors observed a lowering of NO<sub>3</sub> concentrations shortly after peak flow (e.g. Poor and McDonnell, 2007; Shrestha et al., 2013) (e.g. Poor and McDonnell, 2007; Shrestha et al., 2013) 6 7 caused by dilution with NO<sub>3</sub>-poor precipitation water. Others detected concentration peaks in response events (e.g. Rozemeijer and Broers, 2007; Tiemeyer et al., 2008)(e.g. Rozemeijer and Broers, 8 9 2007; Tiemeyer et al., 2008). Therefore, the NO<sub>3</sub> response to rainfall events depends on the 10 hydrochemical properties of the catchment (Rozemeijer et al., 2010) (Rozemeijer et al., 2010). In 11 addition, the capacity of surface water bodies to retain nutrients is spatially and temporally variable 12 (e.g. Withers and Jarvie, 2008:Cirmo and McDonnell, 1997)(e.g. Withers and Jarvie, 2008:Cirmo and 13 McDonnell, 1997). 14 As a consequence of the dynamic behavior of nutrient transfer from land to surface water and 15 instreamin-stream processes that impact nutrient retention combined with increasing demands for 16 sound assessments of the water system, there is an increasing interest in continuous or semi-17 continuous monitoring of water quality at catchment outlets during the last decade (e.g. Bowes et 18 al., 2015; Wade et al., 2012; Jordan et al., 2007; Bieroza et al., 2014; Palmer-Felgate et al., 2008;Rozemeijer et al., 2010;Kirchner et al., 2004;Cassidy and Jordan, 2011;Skeffington et al., 19 20 2015)(e.g. Bowes et al., 2015; Wade et al., 2012; Jordan et al., 2007; Bieroza et al., 2014; Palmer-21 Felgate et al., 2008;Rozemeijer et al., 2010;Kirchner et al., 2004;Cassidy and Jordan, 22 2011;Skeffington et al., 2015). These studies showed catchment dependent non-stationary behavior 23 of the concentration-discharge relationships. High-frequency monitoring has proven to be a 24 powerful tool to improve estimations of annual export loads (e.g. Rozemeijer et al., 2010;Cassidy 25 and Jordan, 2011) (e.g. Rozemeijer et al., 2010; Cassidy and Jordan, 2011), nutrients sources (Bowes 26 et al., 2015) (Bowes et al., 2015) and the hydrochemical functioning of a catchment (e.g. Wade et al., 27 2012;Bieroza et al., 2014;Halliday et al., 2012)(e.g. Wade et al., 2012;Bieroza et al., 2014;Halliday et 28 al., 2012). High-frequency nutrient monitoring has revealed the presence of diurnal nutrient cycles in 29 rivers and streams caused by biological processes or by P and N inputs from sewage treatment 30 works (e.g. Bowes et al., 2015; Halliday et al., 2012; Neal et al., 2012)(e.g. Bowes et al., 2015; Halliday 31 et al., 2012; Neal et al., 2012). Large changes in concentrations or fluxes of materials over relatively 32 short time periods are increasingly recognized as important pathways of nutrient delivery to surface 33 water bodies (Kaushal et al., 2014). In the Netherlands, there is a still debate about the risk of 34 incidental losses associated with manure application (Akkermans and Hermans, 2014). The

1 Netherlands adopted the European Nitrate Directive in 1991 (EC, 1991), which regulates the use of 2 nitrogen in agriculture through national action plans. Among other measures, the regulation 3 includes the period of manure application. To reduce the risk of nutrient leaching to groundwater 4 and surface water, manure application on arable land is allowed from 1 February to 1 August and on 5 grassland from 15 February to 31 August -(LNV, 2009). The potential risk for incidental nutrient 6 losses after manure application in February and March (before the start of the growing season) is 7 not known. High-frequency monitoring is a powerful tool to detect such incidental losses. 8 In many low-lying areas worldwide, water levels are human controlled managed by inlet of diverted 9 river water in dry periods and discharge via pumping stations in wet periods. Such an embanked land 10 form with a human controlled water regime is called a 'polder' (Wikipedia, 2015). with a human 11 controlled water regime is called a 'polder'. In the Netherlands, these regulated polder catchments 12 cover 60% of the land surface (Van de Ven, 2003)(Van de Ven, 2003). The dense network of 13 subsurface drains, ditches, weirs, channels, pumping stations and the dynamic mixing of water from 14 different sources (seepage, precipitation and water inlet) results in a relatively complex hydrology. 15 Many studies on nutrient dynamics in natural catchments showed a relation between nutrient 16 concentrations and discharge, and this significantly improved the insight in the nutrient sources and 17 pathways in the catchment. The water flow in polders is, however, not a function of free discharge 18 but is controlled by pumping stations. The maximum discharge is controlled by the capacity of the 19 pumping stations. Due to the presence of a dense surface water system, the water storage capacity 20 and the residence time of the surface water in a polder is also higher when compared to natural, 21 free drainingdrainage catchments which may impact biogeochemical or hydrological in-stream 22 processes controlling nutrient retention. Insight in the hydrochemical functioning of polder 23 catchments is highly relevant for improving the water quality in the Netherlands. 24 To our knowledge, high-frequency monitoring of surface water quality has not been applied for 25 polder catchments up to now. Discharge-concentration relationships and short scale variation in 26 water quality in polder catchments are still unclear while nutrient sources and pathways are poorly 27 understood (Rozemeijer et al., 2014) (Rozemeijer et al., 2014). High-frequency measurements reveal 28 the short-term variability in solute concentrations which may give valuable insight into the 29 contribution of different sources or different flow routes to the surface water pollution in polders. 30 The general aim of this study is to increase our understanding of the hydrochemical function of an 31 agriculture-dominated water system in a clay polder by analysis of high-frequency monitoring of 32 nutrient concentrations at the polder outlet combined with low-frequency surface water quality 33 data and groundwater quality data from different locations within the polder. The specific objectives

of this study are: (1) to increase insight in dynamics of nutrient concentrations and nutrient sources
 <u>in polder areas</u>(2) to characterize the importance of incidental losses caused by intensive rainfall

3 events whether or not in combination with recent manure application and (3) to assess potential

4 effects of the operational management of the pumping station on the water quality.

#### 5 2 Material and Methods

#### 6 2.1 Study area

7 A continuous monitoring station was established in the Lage Vaart main channel nearby the 8 pumping station Blocq van Kuffeler (A in Fig. 1). This is one of the three pumping stations that 9 control the water level in Lage Afdeling pumped drainage area located within the Flevoland polder, 10 the most recent and at the same time biggest land reclamation project in the Netherland (Groen, 11 1997)(Groen, 1997).- The Flevoland polder consists of two pumped drainage areas, which are each 12 drained by a main channel. The Lage Afdeling drainage area drains into the Lage Vaart main channel 13 (Fig. 1). The size of the Lage Afdeling drainage area is 576  $\rm km^2$ , with altitude ranging between 3 and 5 14 m below mean sea level. The Lage Afdeling drainage area is mainly rural. The land cover is 15 dominated by agriculture (76%), followed by woodlands and moors (18%) and urban or semi-urban 16 areas (6%).

17 The geohydrology of the Flevoland polder area is generally described by a confining layer of 18 Holocene originmarine sediments, with a thickness of nearly nilless than 0.5 m in the northeast to 19 over 7 m southwest, overlying a sandy aquifer deposited in the Pleistocene age. The soils consist for 20 50% of clay soils, for 39% of silty clay loam and for 11% of sandy soils (Van den Eertwegh, 2002)(Van 21 den Eertwegh, 2002). A typical characteristic of the soils in Flevoland is that the clay layer contains 22 permanent and interconnected cracks due to physical and chemical ripening of the soil after 23 reclamation. The shrinkage cracks disappeared in the plough layer by tillage activities, but are 24 permanently present in the subsoil down to about 1.0-1.5 m below the soil surface (Van den 25 Eertwegh, 2002;Groen, 1997)(Van den Eertwegh, 2002;Groen, 1997). From a depth of 1.2 to 1.5 m 26 below the soil surface, clay deposits, if present, are permanently water saturated and thus not 27 ripened, resulting in a low-permeable soil layer. Due to altitudes below mean sea level and below 28 the water level of the surrounding lakes, there is upward groundwater seepage at most locations 29 within the Lage Afdeling drainage area.

The Lage Vaart main channel is connected via a series of secondary channels to a dense network of
 field ditches and tube drains. Tube drains are generally installed at 0.95 m depth. The horizontal
 spacing varies between less than 12 to 48 m, mainly dependent on the soil hydraulic conductivity

17

1 and groundwater seepage rate. The field ditches receive outflow from the tube drain, direct 2 drainage from subsurface flow, regional groundwater seepage and any surface run-off from the 3 connected field area. They drain freely into the secondary channels. The water level in the Lage 4 Afdeling is regulated by 97 weirs and three pumping stations that pump the excess water to the 5 higher situated Markermeer and Ketelmeer. The total pumping capacity is 11-12 mm/ d<sup>-1</sup>. The Lage 6 Vaart main channel has a controlled constant water level of 6.2 m below mean sea level. The 7 pumping station Blocg van Kuffeler has four electrically powered pumps. Two pumps with a capacity 8 of 750 m<sup>3</sup> min<sup>-1</sup> each drain the Lage Afdeling. Operation of the pumping stations with one pump 9 causes a flow velocity in the main channel of approximately 0.125 m sec<sup>-1</sup> and with both pumps the 10 flow velocity is approximately 0.25 m sec<sup>-1</sup>. Up to 2008, the pumping station Blocg van Kuffeler was 11 powered with diesel engines. These diesel engines were replaced with electric engines during two 12 electrically powered pumps with a capacity of 750 m<sup>3</sup>/hr each. The the renovation of the pumping 13 station in the autumn of 2008 and this conversion was finished in the beginning of 2009. Since this 14 renovation, the operational management of the pumping station is automatically controlled by a 15 series of water level pressure sensors in the area. The pumps run predominantly during evening en 16 night hours because of cheaper power supply during these hours. The discharge generated by the 17 pumping stations is measured continuously. The Blocg van Kuffeler pumping station drains the 18 south-western part of the Lage Afdeling drainage area. The flow direction of the water in the 19 channels that are drained by pumping station Blocg van Kuffeler, is illustrated by arrows in Fig. 1. 20 Pumping station B is an emergency pumping station and only operates during extremely wet 21 conditions. Although there is no physical boundary between the area drained by Blocq van Kuffeler 22 and pumping station C, location 5 can be considered as the most upstream location in the Lage Vaart 23 that is drained by the Blocq van Kuffeler pumping station under normal meteorological conditions. 24 There is a sewage treatment plant in the area that discharges its effluent to the Lage Vaart (Fig. 1). 25 The average effluent discharge is 0.35 m<sup>3</sup> min<sup>-1</sup>. The TP concentration in the effluent water is 26 maximal 0.5 mg L<sup>-1</sup> and the maximal NO<sub>3</sub> concentration is 1.5 mg N L<sup>-1</sup>. The TP load to the Lage Vaart 27 in the period October 2014 – October 2015 equals approximately 5400 kg and the NO<sub>3</sub> load 16400 kg 28 N. There are no other sources of sewage discharge to the surface water within the Lage Afdeling 29 drainage area. 30 2.2 Low-frequency monitoring 31 Grab samples were collected every two or four weeks from January 2014 to October 2015 from the 32 polder outlet and 5 other monitoring locations within the part of the Lage Afdeling drainage area

that is drained by the Blocq van Kuffeler pumping station (Fig. 1). Four locations are representative

1 for different types of land use (Table 1). Electrical conductivity, oxygen concentration, transparency, 2 temperature and pH of the samples were measured directly in the field. Sub-samples for 3 determination of dissolved substances were filtered through a 0.45 µm poresize filter. The samples 4 were transported and stored at 4°C. TP, dissolved reactive P (DRP), NO<sub>3</sub>, NH<sub>4</sub> and Cl where 5 determined using standard colorimetric methods (APHA-AWWA-WPCF, 1989). Organic-N was 6 extracted by Kjeldahl extraction and measured by colorimetric method and sulphate was measured 7 using IC (Ion Chromatography). 8 2.3 High-frequency measurements 9 Between October 2014 and AprilOctober 2015 we measured the total-P concentration, (TP), total 10 reactive P (TRP) and NO<sub>3</sub> concentration, turbidity, conductivity and water temperature semi-11 continuously at the polder outlet just before the pumping station. TRP include all P forms that are 12 measured with the molybdenum blue method (Murphy and Riley, 1962) in unfiltered samples, those 13 include acid labile phosphorus containing compounds (inorganic and organic) (Worsfold et al., 2005). 14 The flow regime at the monitoring location is governed almost exclusively by the pumping station. 15 The conductivity-and water temperature was measured continuously with a CTD-diver (Van Essen 16 Instruments, Delft, the Netherlands). 17 The NO<sub>3</sub> concentration was measured using a double wavelength spectrophotometric sensor (DWS), 18 (Nitratax plus sc, Hach Lange GmbH, Düsseldorf, Germany). The DWS measures UV absorbance of 19 dissolved NO<sub>3</sub> at a wavelength of 218 nm at a measuring receiver (EM - element for measuring) and 20 at 228 nm at a reference receiver (ER – element for reference)...). The recorded measurements at 21 two different wavelengths are designed to compensate interference of organic and/or suspended 22 matter by interpreting the difference between the absorbance values at EM and ER. A UV sensor 23 using only one single wavelength is not able to compensate additional interferences (Huebsch et al., 24 2015)(Huebsch et al., 2015). The Nitratax sensor covers a NOx-N detection range of 0.1 to 50.0 mg/4 25  $L^{-1}$ . The NO<sub>3</sub> concentrations were recorded every 5 minutes. There was a small drift in the signal of the Nitratax sensor (max 0.35 mg N<sub>4</sub>  $L^{-1}$  per month). We, therefore, corrected the high-frequency 26 27  $NO_3$  data using the  $NO_3$  concentrations from the biweekly grab samples by calculating a linear drift 28 for the separate maintenance intervals of the sensor. 29 For the total phosphorus (TP) concentration measurements, we installed a Sigmatax sampler and a

30 Phosphax Sigma auto-analyzer (both Hach Lange GmbH, Düsseldorf, Germany). The total-P

31 concentrations were recorded every 20 minutes. The Phosphax Sigma was automatically cleaned

32 and calibrated daily. The Sigmatax was installed for the automated water sample collection and the

1	pretreatment (ultrasonic homogenization <del>) of). Next,</del> the <del>100 ml samples. A 10 ml sub-</del> sample was
2	delivered to the Phosphax Sigma auto-analyzer. This sample was digested using the sulphuric acid-
3	persulphate method (APHA-AWWA-WPCF, 1989)(APHA-AWWA-WPCF, 1989). After mixing and
4	quickly heating and cooling down the sample, molybdate, antimony and ascorbic acid <u>the reagents</u>
5	were automatically added and mixed with the sample and the sample was measured at 880 nm
6	using a LED photometer. The Phosphax Sigma was automatically cleaned and calibrated daily. There
7	was a close agreement between the high-frequency TP data and the TP concentrations of the
8	accompanying two weekly grab samples analyzed by standard laboratory assays $(R^2 = 0.982)$ and,
9	therefore, no need to correct the high-frequency TP data- <u>(Fig. S1).</u>
10	2.3 Low frequency monitoring
11	In addition to the automatic water quality measurements, grab samples were collected every two or
12	four weeks from January 2014 to March <u>The turbidity (FTU) was measured using a OBS (optical back</u>
13	scatter) sensor (SOLITAX t-line sc, Hach Lange GmbH Düsseldorf, Germany) that receives the
14	reflected light from the sediment-laden flow. Instead of directly obtaining the suspended sediment
15	concentration, a turbidity sensor measures the turbidity of flow caused by suspended sediment
16	(Gao, 2008). The FTU data was stored with a time interval of 5 minutes. There was a close
17	agreement between the high-frequency turbidity data (FTU) and the suspended sediment
18	concentrations (mg $L^{-1}$ ) of the grab samples ( $R^2 = 0.965$ ) (Fig. S1).
19	2.4 Background 2.4 Supporting information
20	Precipitation data on an hourly basis for the Lage Afdeling were abstracted from HydroNet
21	(http://portal.hydronet.nl/). This is an online database with precipitation data based on calibrated
22	radar images. The precipitation of the radar pixels were averaged over the Lage Afdeling drainage
23	area. Temperature data were retrieved from the Royal Dutch Meteorological Institute (KNMI, De Bilt,
24	the Netherlands) weather station Lelystad, located in the center of the Lage Afdeling. The Flevoland
25	polder has a moderate maritime climate with an average annual temperature of 9.9°C, an average
26	annual precipitation of 850 mm and an average of 8 days per year with a maximum temperature
27	below 0°C. Groundwater levels were monitored continuously with pressure sensors in five phreatic
28	groundwater wells located within the agricultural area of the Lage Afdeling. (Fig. 1).
29	The groundwater quality data set from Griffioen et al. (2013)Griffioen et al. (2013) was used as
30	background information. This database was assembled from the national database of the TNO
31	Geological Survey of the Netherlands and contains complete groundwater analyses down to a depth
32	of about 30 m with sampling dates later than 1945. The groundwater in the Lage Afdeling is

1 characterized as anoxic fresh to saline and P-rich with low NO<sub>3</sub> concentrations, (CI concentrations

2 between 7 and 4500 mg/4 L<sup>-1</sup>) and P-concentrations-rich (TP between 0.01 and 3.6 mg P/4 L<sup>-1</sup>) with

- 3 <u>Iow NO<sub>3</sub> concentrations (between 0 and 7 mg NO<sub>3</sub> L<sup>-1</sup>)</u> (Fig. \$1\$2).
- 4 2.5 Transfer function-noise modelling

5 To increase insight in the driving forces of measured dynamics of nutrient concentrations, 6 preliminary research was done on the application of time series analysis, and more specifically 7 transfer function-noise (TFN) modelling, to estimate the impact of rainfall on NO<sub>3</sub> concentrations. 8 TFN models are very popular for describing dynamic causal relationships between time series and 9 have been widely applied in the field of groundwater modelling (e.g. Berendrecht et al., 10 2003;Knotters and van Walsum, 1997)(e.g. Berendrecht et al., 2003;Knotters and van Walsum, 1997). 11 Although a small number of studies has used TFN models to relate streamflow data to nutrient 12 concentrations (Schoch et al., 2009; Worrall et al., 2003) (Schoch et al., 2009; Worrall et al., 2003) or 13 relate precipitation data to high-frequency observation of dissolved organic carbon (Jones et al., 14 2014), to our knowledge TFN models have not been applied yet on high-frequency monitoring data 15 of nutrients such as available in this study. Therefore, as a first step, we tried to relate the time 16 series of hourly NO<sub>3</sub> concentration measurements to rainfall using the following linear TFN model: 17  $\log(NO_3) = \theta(B)p_t + \mu + n_t$ (1)

18 and

19  $n_t = \phi n_{t-1} + \varepsilon_t$ 

20 with  $p_t$  the precipitation at time t,  $\theta(B) = \theta_0 + \theta_1 B + \dots + \theta_r B^r$  the transfer function (B is 21 backward shift operator,  $B^i p_t = p_{t-i}$ ,  $\mu$  is the reference or baseline level,  $n_t$  a stochastic first-order 22 autoregressive process,  $\phi$  the autoregressive coefficient (**0** <  $\phi$  < **1**), and  $\varepsilon_t$  a zero-mean normally 23 distributed process (Box and Jenkins, 1970) (Box and Jenkins, 1970). As  $\varepsilon_t$  is assumed to be normally 24 distributed, the time series of NO<sub>3</sub> data was log-transformed to better satisfy this assumption. For 25 reasons of flexibility and model parsimony, we used a predefined transfer function as described by 26 (von Asmuth et al., 2002) von Asmuth et al. (2002), which has the form of a Gamma distribution 27 28 2.6 Export loads calculations and trend analysis

(2)

29 True NO<sub>3</sub> and TP export loads from the drainage area into the Markermeer were based on our high-

- 30 frequency concentration measurements and discharge data of the pumping station. In addition NO<sub>3</sub>
- 31 and TP loads were estimated from linear interpolation of the low-frequency grab sample data

1 combined with the discharge data. Although advanced methods have been developed to improve 2 load estimates from low-frequency concentration data, none of the methods clearly outperformed the methods that were based on simple linear or stepwise interpolation (Rozemeijer et al., 2010). 3 Long term TP and NO<sub>2</sub> concentration measurements were available for the polder outlet. We used 4 5 two frequently applied methods for trend analysis of concentration-time series: (1) Theil-Sen robust line (Hirsch et al., 1982) and (2) locally weighted scatterplot smoothing (LOWESS) trend lines 6 7 (Cleveland, 1979). These methods are relatively insensitive to extreme values and missing data in the 8 time series. The Theil Sen method is a robust non parametric trend slope estimator. The LOWESS 9 trend lines were used to examine possible changes in trend slopes within the concentration time-10 series period.

$$\theta_t = A^* t^{n-1} e^{-at}, \quad A^* = A \frac{a^n}{\Gamma(n)}$$

where the parameters A\*, a, n and the stochastic model parameter α are estimated using a log likelihood function, and Γ(n) is the gamma function.

13 <u>2.6 Export loads calculations and trend analysis</u>

14 True NO<sub>3</sub> and TP export loads from the drainage area into the Markermeer were based on our high-15 frequency concentration measurements and discharge data of the pumping station. In addition NO<sub>3</sub> 16 and TP loads were estimated from linear interpolation of the low-frequency grab sample data 17 combined with the discharge data. Although advanced methods have been developed to improve 18 load estimates from low-frequency concentration data, none of the methods clearly outperformed 19 the methods that were based on simple linear or stepwise interpolation (Rozemeijer et al., 2010). To 20 guantify the event-driven TP export load generated by changes in the water flow due to pumping, a 21 hydrograph separation method was used to separate the high-frequency TP concentration data 22 series into short-term TP concentration peaks and baseline TP concentration. In this study we used 23 the same method as applied by Rozemeijer and Broers (2007). This method, originally developed by 24 (Hewlett and Hibbert, 1963), separates the baseline concentration and the peak concentration by a 25 separation line with a constant slope (Fig. S4). This line starts whenever the slope of the 26 concentration series exceeds a specified constant separation slope. The separation line ends when it 27 intersects the falling limb of the concentration series. For this study, a constant separation slope of 0.02 mg P L<sup>-1</sup> d<sup>-1</sup> was used. With this relatively low slope value, concentration peaks were also 28 29 separated from the baseline concentration during situations of upward trends in TP concentrations.

- Long term TP and NO<sub>3</sub> concentration measurements were available for the polder outlet. We used
   two frequently applied methods for trend analysis of concentration-time series: (1) seasonal Mann-
- 3 Kendall tests (Hirsch and Slack, 1984) (2) Theil-Sen robust line (Hirsch et al., 1982) and (3) locally
- 4 weighted scatterplot smoothing (LOWESS) trend lines (Cleveland, 1979). These methods are
- 5 relatively insensitive to extreme values and missing data in the time series. The seasonal Mann-
- 6 Kendall trend test is a robust, non-parametric test on the significance of an upward or downward
- 7 trend. The Theil-Sen method is a robust non-parametric trend slope estimator. The LOWESS trend
- 8 lines were used to examine possible changes in trend slopes within the concentration time-series
- 9 period. We refer to Rozemeijer et al. (2014) for details on the statistical methods.

# 10 3 Results

11 The results of the high-frequency monitoring at the pumping station Blocq van Kuffeler and low-

- 12 frequency monitoring within the Lage Afdeling drainage area will be presented in the next sections.
- 13 First, we shortly describe the water discharge from the polder. Next, the general seasonal trends and
- 14 short time-scale dynamics in the high-frequency nutrient concentrations will be presented. Finally,
- 15 we present a general description of water quality in the Lage Afdeling based on low-frequency

# 16 monitoring.

# 17 3.1 Water discharge

18 The Blocg van Kuffeler pumping station responds rapidly to rainfall events in the drainage area by 19 automatically switching on one or two pumps (Fig. 2). The interval in which the pumping station is in 20 operation decreased during the autumn months. During the winter months the pumping station 21 runs almost at a daily basis and continuously for several days during very wet periods. There was a 22 strong decline of the daily pumping hours from mid-April to the end of July. A wet period from mid-23 August to mid-September resulted in an increase of pumping hours. The pumping station pumped 24 almost 70x10<sup>6</sup> m<sup>3</sup> water from the polder into the Markermeer during the period from October 2014 25 until March 2015- and 30x10<sup>6</sup> m<sup>3</sup> during the period from April 2015 until October 2015. This 26 corresponds to approximately 350 mm distributed across the entire drainage area- for the winter 27 half year (Oct-March) and 150 mm for the summer half year (April-Sept.). The sum of the 28 precipitation during this period equaled 470 mm was 455 mm and 517 mm for the winter half year 29 and summer half year, respectively.

30 3.2 Mid-termSeasonal trends in high-frequency nutrient data

1 The high-frequency NO<sub>3</sub> concentration measured at the Blocg van Kuffeler pumping station ranged from 0.4501 to 10.4 mg N/4 L<sup>-1</sup> and the total phosphorus (TP) concentration ranged from 0.07 to 2 3 0.571.16 mg P/4 L<sup>-1</sup>. (Fig. 2). The NO<sub>3</sub> and TP concentrations from the biweekly grab samples and the 4 accompanying one day antecedent precipitation and flow data are shown in Fig. 2 as well. Although 5 the data do not cover a whole year, the The high-frequency NO<sub>3</sub> data showshowed a seasonal 6 pattern and a response to rainfall. The NO<sub>3</sub> concentrations were low at the start of the monitoring in 7 October 2014 and stayed low until the rainfall event on 15-17 November. Precipitation events 8 before mid-November only had a minor influence on the NO<sub>3</sub> concentration. The NO<sub>3</sub> concentration increased from a level of 1 mg N4<u>L</u><sup>1</sup> to a maximum concentration of 9 mg N4L<sup>1</sup> from mid-9 10 November to the third week of January. Major increases of the NO<sub>3</sub> concentration occurred during 11 pumping from 18 to 21 November, 16 to 23 December and 13 to 18 January which showed that the 12 NO<sub>3</sub> concentration responded to rainfall during this period. The concentration slightly decreased 13 during dryer periods after these individual wet periods. During the dry period in the first three weeks 14 of February, the NO<sub>3</sub> concentration decreased to a level of 1 mg N<sub>4</sub> L<sup>-1</sup>. Next, the concentration 15 reached a maximum of 10.4 mg N<sub>4</sub> L<sup>-1</sup> at 24-25 February and gradually decreased towards the end of March where it showed an increase again to high concentrations during the first 10 days of April. 16 17 During April the concentration declined to a level around 0.5 mg N L<sup>-1</sup> or below and stayed at this 18 low level until mid-August. The NO<sub>3</sub> concentration rapidly increased to approximately 3 mg N L<sup>-1</sup> 19 after a wet period in mid-August. The concentration peaked with 4.6 mg N  $L^{-1}$  on 2 September and gradually decreased towards the end of the monitoring period. 20 21 The high-frequency total-P (TP) data showshowed a seasonal variation, a response to rainfall and a 22 response to pumping as well. The TP concentration was, with concentrations that ranged from 0.25 23 to 0.4 mg P4 L<sup>-1</sup>, high during the first three weeks of the monitoring period. In October and 24 November, the TP concentration decreased uponduring wet periods to a concentration level 25 around of approximately 0.15-0.2 mg P/4 L<sup>-1</sup> and increased again during the dryer periods to levels 26 around 0.3 to 0.4 mg P.4 L<sup>-1</sup>. During the first two weeks of December, the TP concentration 27 decreased to a level around 0.1 mg P4 L<sup>-1</sup>. This baseline level remained at this level until halfway 28 February. During the relatively dry period in February and March there was a gradual increase of the 29 TP concentration to a level around 0.2 mg P/<del>I. The</del> L<sup>-1</sup>. It remained at this level until mid-June. During 30 the period from mid-June to mid-August the TP concentration gradually increased and peaked with a concentration of 1.2 mg P L<sup>1</sup> during a wet period in mid-August. After this wet period in mid-August 31 32 the TP concentration decreased to a level of approximately 0.1-0.2 mg P L<sup>-1</sup>. Towards the end of the 33 monitoring period the TP concentration peaked once more at a level of approximately 0.6 mg P L<sup>-1</sup>. The high-frequency total-reactive P (TRP) data and the dissolved reactive P (DRP) data from the low-34

24

- 1 | frequency monitoring program showed relatively a high concentration untilrather high
- 2 <u>concentrations from the start of the monitoring to</u> early December <u>2014</u> and then declined to
- 3 concentration below 0.051 mg P4L<sup>1</sup>. The <u>TRP and</u> DRP concentration remained at this low level
- 4 until the end of the monitoring program.second half of May. During the period from mid-May to
- 5 mid-August the TRP and DRP concentrations followed the trend of the increasing TP concentrations.

#### 6 3.3 Short scale dynamics in high-frequency nutrient data

- 7 Significant increases of the NO<sub>3</sub> concentration up to 8 mg N/4 L<sup>-1</sup> in short time scales appeared during 8 pumping within five days after major rainfall events on 15-18 November, 10-12 December, 19-20 9 December, 7-9 January, 12-14 January, 21-22 February-and, 29 March-2 April, 14-18 August and 26-10 31 August (Fig. 23 and Table 2). The precipitation during these events peaked around 20 mm or 11 above (Fig. 2 and Fig. 3). The increase in NO<sub>3</sub> concentration did not appear after the precipitation 12 events on 20-23 October-and, 3-4 November 17-23 June and 27-29 July. As it will be discussed in 13 section 4, this is likely due to the absence of tube drain discharge upon these precipitation events. 14 For the events after from mid-November to early April, it applies that the response of the NO<sub>3</sub> 15 concentration to rainfall was delayed and occurred about five days after the rainfall event. After this 16 NO<sub>3</sub> concentration peak, the concentration declined during pumping. The period of five days 17 between rainfall event and peak in the NO<sub>3</sub> concentration at the pumping station is representative 18 for the average residence time of water in the Lage Afdeling drainage area. This during wet 19 conditions. Catchment mean residence times are much shorter during wet periods compared dry 20 periods (Van der Velde et al., 2012). The five days travel time of the water in the field ditches, sub-21 channels and main channel during wet conditions is in line with model calculated mean annual 22 residence times of water in the Lage Vaart main channel of 6.6 days for the period 1988 1998 (Van 23 den Eertwegh, 2002) (Van den Eertwegh, 2002). 24 There is a structural response of the TP concentration and the turbidity on operation of the pumping 25 station. The TP concentration and turbidity always peaked directly after the start of the pumping-26 engines and decreased again during the period of pumping and afterwards (Fig. 2 and Fig. 3). The 27 maximum TP concentration during pumping was a factor 1.5 to 2 higher than the concentration 28 before pumping. The abruptPumping events with one pump resulted in an average increase of the 29 TP concentration as caused by of 0.06 mg  $L^{-1}$  while events with two pumps resulted in an average increase of 0.13 mg L<sup>-1</sup> (Table 3). The TP concentration was on average a factor of 1.30 and 1.83 30 31 higher during pumping with one pump and two pumps, respectively, compared to the concentration
- 32 <u>before pumping. The increase of the TP concentration and turbidity during</u> operation of the pumping
- 33 station and the larger increase during pumping with two pumps compared to one pump (Table 3)

1	indicates that the additional TP (increase of the TP concentration during pumping compared to the
2	concentration before pumping) is related to resuspension of particulate P (PP)P from bed sediments
3	due to increased flow velocities. Due to low flow conditions The TRP concentrations also showed an
4	increase in concentration during pumping. As the colorimetric measurement of TRP takes place in an
5	acidic solution it is plausible to attribute the increase of the TRP concentration during pumping to
6	the dissolution of particulate Fe or Ca bound inorganic P. The data shows the largest increase of TP
7	concentrations (0.16-0.60 mg P L <sup>-1-</sup> ) during pumping with two pumps after longer periods without
8	pumping (21 Oct, 2 Nov, 8 Dec, 20 Feb., 23 June, 25 July and 15 Aug) and decreasing TP peaks were
9	observed with subsequent events (Fig.3). This indicates that during no-pumping conditions, an
10	erodible layer builds up by sedimentation of PP.particulate P. When the water flow velocities in the
11	main channel increase upon pumping, the PPP becomes suspended and transported downstream.
12	Short-term declines of the TP concentrations to values below the pre-pumping concentration were
13	observed during pumping or shortly after pumping induced by rainfall periods in October, June and
14	August (Fig. 3).
15	A significant short-term change in NO <sub>3</sub> and TP concentrations and the conductivity during a period
16	without pumping appeared on 26 January (Fig. 2 and Fig. 3). The decrease in the NO <sub>3</sub> concentration
17	(from 6.1 to 1.5 mg N/4 $L^{-1}$ ) and increase in the TP concentration (from 0.0709 to 0.21 mg P/4 $L^{-1}$ ) as
18	observed on 26 January cannot be explained by operation of the pumping station or by antecedent
19	precipitation (5.5 mm on 24 January and 2.1 mm on 25-26 January). <u>Together with the changes in</u>
20	$NO_3$ and TP concentrations, an increase of the turbidity (from 8 to 57 FTU), a decrease in the TRP
21	concentration (from 0.06 to 0.02 mg P L <sup>-1</sup> ) and decrease of the conductivity (from 235 to 122 mS cm <sup>-</sup>
22	<sup>1</sup> ) (Fig. S3) were observed. A cold period with daily average temperatures below 0 °C started at 20
23	January and ended on 24 January (Fig. 3). As a consequence the top soil was frozen, the precipitation
24	during the night of 24 January fell asconsisted of snow and this resulted in a snow cover of a few
25	centimeters. Soil freeze-thaw processes significantly increase the potential erosion during run-off
26	events that follow thaw in hill slope areas (Ferrick and Gatto, 2005) (Ferrick and Gatto, 2005) but also
27	in relatively flat areas (Gentry et al., 2007). Where under normal conditions rainfall infiltrates into
28	the soil, the thaw and precipitation on 25 January likely resulted in run-off. This temporally diluted
29	the NO <sub>3</sub> concentration and <u>conductivity and</u> increased the TP concentration, <u>Thus, and turbidity This</u>
30	strongly indicates that the increase of the TP concentration must bewas caused by erosion of soil
31	surface particles. The TRP did not increase during this event, suggesting the TP largely existed of
32	non-liable organic P.

33 3.4 Decomposition of high-frequency nitrate data

1 As shown in section 3.2, NO<sub>3</sub> concentrations were low from the start of the monitoring period until 2 the rainfall event on 15 November and precipitationduring April the NO<sub>3</sub> concentrations decreased 3 again. Precipitation events before mid-November and after April only had a minor influence on the 4 NO<sub>3</sub> concentration. For the period after 15between15 November and 30 April a transfer function-5 noise modelling of hourly NO<sub>3</sub> concentrations reveals that the model can relate guite a large part of 6 the dynamics to rainfall: the coefficient of determination  $R^2 = 0.7$ . The measured time series 7 together with the model simulation and the residual series are shown in Fig. 4. 8 Overall, the transfer model describes slow dynamics well; high frequencyshort-term dynamics 9 cannot be related to rainfall with the transfer model and are described by the stochastic model. The 10 estimated autoregressive coefficient ( $\phi = 0.98$ ) is quite low given the high sampling interval of 1 11 hour, indicating that most of the temporal structure in the time series has been captured by the 12 transfer model. 13 The results in Fig. 4 show that during no-rain periods the decline in concentration is modelled well. 14 The various periods of rainfall show different results: in December the increase in concentration is 15 modelled well, in January the concentration is overestimated, while in February4 and March the 16 concentration is underestimated. The overestimation in January can be explained by dilution while 17 recent manure application is a plausible explanation for the underestimation of modelled 18 concentrations in February  $\neq$  and March (see section 4). The largest negative residuals appeared 19 during the thaw event on 26 January (see section 3.3) while the largest positive residuals appeared 20 on 24-25 February. 21 The estimated model parameters and their standard deviation are given in Table S1. The estimated 22 impulse response function for transferring an impulse of 1 mm rainfall into  $\log$ -NO<sub>3</sub> concentration is 23 given in Fig. <u>\$2</u>\$5. The smooth character of the function is due to predefined structure of the 24 function, which is the Gamma distribution function. The time to peak is 5.54 days with a response of 25  $0.033 \log(\text{mg NO}_3\text{H-N mg L}^1)$ , while 95% of the total response happens within 43 days. The time to 26 peak as revealed by the TFN model matches well with the delay of approximately five days between

- 27 | rainfall eventevents and peak concentrations (Fig. 2).
- 28 The estimated reference or baseline level is follows from the model estimation and has a value of  $\mu$
- 29 = -1.13, or back-transformed from logarithm:  $e^{-1.13} = 0.5432$  mg NO<sub>2</sub>/4,N L<sup>-1</sup> which means that after
- 30 a long no-rain period, the NO<sub>3</sub> concentration will decline to 0.5432 mg/l. A longer time series (at
- 31 least 1 year) would be necessary to give any physical interpretation of this value (e.g. estimate of
- 32 background concentration). <u>N L<sup>-1</sup></u>. The current time series does not include seasonal patterns; during

1	spring and summer season the NO $_3$ concentration cannot be related to rainfall only <del>, so other driving</del>
2	forces have to be included. As it will be discussed in section 4,. The groundwater levels drop below
3	the tube drain levels (i.e. precipitation may not lead to discharge) and denitrification or in-stream
4	nutrient uptake processes reduce the NO $_3$ concentration and rainfall may not lead to discharge, so
5	other driving forces and non-linearity have to be included in the TFN model for modelling the
6	summer season.
7	3.5 Nutrient loads and fluxes at polder outlet
8	Cumulative loads at the polder outlet based on either linear interpolation within the low-frequency
9	<del>data set<u>dataset</u> or the high-frequency <del>data set<u>dataset</u> are given in Fig. 5. <u>The total measuredFor TP</u></del></del>
10	the cumulative 'baseline' load calculated from the high frequency dataset after separation of the
11	pumping event-driven short-term TP peaks are given in Fig. 5 as well. The annual loads based on the
12	high-frequency dataset <del>from 1 Oct 2014 to 1 April 2015 were 10<u>equaled 19</u>,500 kg for P<u>TP</u> and</del>
13	$\frac{308,000}{388,500}$ kg for NO <sub>3</sub> -N. These The TP load during the winter months (October – March) was
14	almost equal to the load during the summer months (April – September) while for NO $_3$ almost 80%
15	of the annual load occurred during the winter months. The annual loads overestimate the TP load
16	calculated from the low-frequency data <del>by 20 %<u>e</u>qualed 18200 for TP</del> and <del>underestimate<u>372500 kg</u></del>
17	for NO <sub>3</sub> -N. The annual baseline TP load after separation of the TP concentration peaks was 15400 kg.
18	The difference between the total load and the baseline load equaled 4100 kg, i.e., 21 % of the annual
19	TP load can be attributed to resuspension of TP due to changes in water flow induced by the
20	pumping station.
21	During the period from 1 Oct 2014 to 1 April 2015 the cumulative TP load calculated from the low-
22	frequency NO <sub>2</sub> -data matched the baseline TP load and underestimated the high frequency load with
23	<u>17%. The low-frequency NO<sub>3</sub> load overestimated the high-frequency load by 56.5%. From April to</u>
24	mid-August 2015 there was almost no NO <sub>3</sub> export load. During the period from April 2015 to
25	October 2015 the difference between the baseline load and grab sample load increase. The annual
26	grab sample load underestimated the best available data load with 6%.
27	Time series of TP and NO $_3$ concentrations in grab samples at the Blocq van Kuffeler pumping-station
28	over the period 2000-2015 are given in Fig. 6. The red lines in Fig. 6 show the LOWESS trend line and
29	the black lines show the Theil-Sen slope over the period 2000-2015. The $NO_3$ concentration showed
30	no <u>significant</u> upward or downward trend over the period 2000-2015. The time series of TP
31	concentration showed different trends over the period 2000-2015. After a period with minor
32	increase for 2000 to 2009, the LOWESS trend line reveals a decline in TP concentrations in the period

- 1 2009-2010 followed by an increase from 2011 to 2015. The Theil-Sen slope showed a decline of TP
- concentration (-0.0053 mg P4<u>L<sup>-1</sup></u> per year) over the years 2000-2015. <u>This downward trend was</u>
   <u>significant according the seasonal Mann-Kendall trend tests.</u>
- 4 The blue and green lines give the Theil-Sen slopes for the periods 2000-2008 and 2009-2015,
- 5 respectively. As it will be discussed in section 4, the pumping-station was renovated in the autumn
- 6 of 2008 and this likely had an impact on the TP dataset time series., before and after renovation of
- 7 the pumping station. Where the Theil-Sen slope showed a decline of TP concentration over the years
- 8 2000-2015, it showed upward trends of 0.0023 mg P $4L^{-1}$  per year and 0.0088011 mg P $4L^{-1}$  per year
- 9 over the separate periods 2000-2008 and 2009-2015, respectively. <u>The upward trend for the period</u>
- 10 <u>2009-2015 was significant according the seasonal Mann-Kendall trend tests.</u> The NO<sub>3</sub>
- 11 **concentration**<u>concentrations</u> showed no<u>significant</u> upward or downward trend over the separate

12 periods 2000-2008 and 2009-2015.

13 3.6 Water quality within Lage Afdeling drainage area

- 14 The low frequency dataset of <u>1¼ yearalmost two years</u> with analyses from 6 locations within the
- 15 Lage Afdeling drainage area showed spatial differences in water quality related to land use and
- 16 subsurface characteristics. High chloride concentrations were observed at monitoring locations 1, 3
- 17 and 5, where location 1 and 3 showed higher concentrations during summer than during winter (Fig.
- 18 7). The salinityChloride is an indicator for the contribution of deep groundwater to the surface water
- 19 was high with CI concentrations above approximatly 250 mg/I when the groundwater in the vicinity
- 20 of the monitoring location had high Cl concentrations. Chloride concentrations above 500 mg/4 L<sup>-1</sup>
- 21 were commonly observed in the <u>deeper</u> groundwater in the area upstream of location 3 and 5 (Fig.
- 22 S1). S2). Location 3 shows an inverse relation between the NO<sub>3</sub> and CI concentrations ( $R^2 = -0.67$ )
- 23 <u>which illustrates the soil and shallow groundwater as source of NO<sub>3</sub> in the surface water.</u> The Lage
- 24 Vaart channel acts as a drainage channel for groundwater under the confining Holocene layer, which
- 25 is often brackish/saline (Van den Eertwegh, 2002)(Van den Eertwegh, 2002). This explains the
- 26 relatively high Cl concentrations of location 1 during summer.
- 27 Low NO<sub>3</sub> concentrations were observed in discharge water from the nature area
- 28 Oostvaardersplassen (location 6) throughout the year whereas high NO<sub>3</sub> concentrations were
- 29 observed in water from the agricultural areas Lepelaartocht and Gruttotocht (location 3 and 4) in the
- 30 | winter. The overall highest NO<sub>3</sub> concentrations of (8.3 and 13 mg N/I were observed at these
- 32 water (location 2) did not exceed 2 mg N/l and showed only a minor seasonal variation  $L^{-1}$ . The NO<sub>3</sub>

1 concentrations of the Lage Vaart channel water at the pumping station (location 1) during the winter 2 months were lower compared to the  $NO_3$  concentrations at the outlet of the agricultural areas. This 3 indicating someAs denitrification is limited during winter time, this indicates dilution of the 4 agriculture-dominated water with water from nature areas or urban areas. This is confirmed by the 5 SO₄ data that demonstrate some dilution of the agriculture-dominated water as well. The locations 6 with high SO<sub>4</sub> concentrations exhibit an inverse pattern with the CI concentration,  $(R^2 = -0.45 \text{ for})$ 7 location 3). This shows the occurrence of pyrite oxidation in the shallow subsurface (Grifficen et al., 8 2013)(Grifficen et al., 2013) in the Lage Afdeling drainage area except for location 6 that drains the 9 Oostvaarderplassen which has no tube drains and high groundwater levels throughout the year. The 10 N-Kjeldahl concentrations varied between 0.77 and 5.8 mg N/4 L<sup>-1</sup> but showed little variation over 11 the year for the individual agriculture-dominated and urban-dominated sampling locations. The N-12 Kjeldahl concentration in the water from the Gruttotocht (location 3) was almost twice as high as 13 from the Lepelaartocht (location 4). 14 The TP concentration of the low-frequency monitoring program varied between 0.05 and 0.72 mg 15  $P4L^{-1}$  (Fig. 7). From all sampling locations within the Lage Afdeling, the water from the 16 Oostvaardersplassen (location 6) had the highest TP concentrations. The TP concentration of this 17 water ranged between 0.37 and 0.72 mg P4 L<sup>-1</sup> from January to July 2014. The concentration 18 dropped to a level around 0.3 mg P4 L<sup>-1</sup> or lower in August 2014 and stayed at this level until April 19 2015. From April 2015 to mid-September 2015 the end of the monitoring programTP concentration 20 ranged between 0.35 and 0.74 mg P L<sup>-1</sup>. The TP concentration at the Oostvaarderplassen and Blocq 21 van Kuffeler were higher during the first months of 2014 compared with the same period in 2015. 22 The long-term data series for Blocg van Kuffeler showed high TP concentrations during the first 23 months of 2014 as well compared with concentrations in other recent years (Fig. 6.). We do not 24 have a clear explanation for this observation. Together with a decrease of the TP concentration at 25 the Oostvaardersplassen. The DRP concentrations were low during the first half year of 2014 and 26 Blocg van Kuffeler, there 2015. There was an increase of the DRP concentration, in July 2014 and July 27 2015. During the first half year of 2014 and 2015 the TP concentration was dominated (> 90 %) by 28 particulate P while in the second half year of 2014-about 50% of the TP concentration consisted of 29 DRP. The DRP concentration dropped again to levels around the detection limit during the winter of 30 2015.

The seasonal variation of the DRP concentrations of the Lage Vaart channel water at the pumping station (location 1) followed the trend of the Oostvaardersplassen. Although less pronounced, this seasonal variation applied as well for the agriculture-dominated water (location 3 and 4) and the urban water (location 2). The TP concentrations were higher during the summer months than during
 winter months. The groundwater within the Lage Afdeling drainage area has relatively high dissolved
 P concentrations (Fig. \$152)

4 4 Discussion

5 4.1 Identification of nutrients sources and dynamics in nutrient concentrations

6 The first objective of our study was gaining insight in the dynamics of nutrient concentrations and

7 nutrient sources of a typical agriculture-dominated lowland water system. We examine the added

8 value of TFN modelling of high-frequency NO<sub>3</sub> data for identification of NO<sub>3</sub> sources and dynamics

9 and, in addition, combining high-frequency monitoring data at the polder outlet with low-frequency

10 surface water quality data and groundwater data from the drainage area.

11 *4.1.1 Nitrate* 

12 Given the low  $NO_3$  concentrations in groundwater (Fig. <u>\$152</u>) and the high  $NO_3$  concentrations in the

13 surface water at the outlet of the agriculture-dominated areas during winter months (Fig. 7), it is

14 clear that almost all NO<sub>3</sub> in the surface water at the polder outlet has an agricultural source. The

15 high-frequency monitoring data at the Blocq van Kuffeler pumping stations additionally provides

16 insights in the processes and dynamics of NO<sub>3</sub> delivery to the surface water.

17 The high-frequency NO<sub>3</sub> data showed a seasonal trend with a gradually increase from half-mid-18 November to half-mid-January. An increase of NO<sub>3</sub> concentrations from summer to winter is 19 observed in a large majority of agriculture-dominated headwater in The Netherlands (Rozemeijer et 20 al., 2014)(Rozemeijer et al., 2014) and natural catchments elsewhere (Wade et al., 2012)(Wade et al., 21 2012). Catchments where NO<sub>3</sub> concentrations are controlled by a combination of effluent loads from 22 sewage treatment works and dilution by rainfall commonly show a decline in  $NO_3$  from summer to 23 winter (Bowes et al., 2015; Wade et al., 2012) (Bowes et al., 2015; Wade et al., 2012). The NO<sub>3</sub> pattern 24 is therefore thought to be due to a combination of interflow or shallow draining groundwater with 25 high fertilizer or manure inputs and NO<sub>3</sub> enrichment during autumn and winter. Increased crop 26 uptake of NO<sub>3</sub> during the growing season combined with the effect of instreamin-stream processes 27 result in declined NO<sub>3</sub> concentrations during the summer months. 28 The annual NO<sub>3</sub> load from the WWTP to the Lage Vaart is approximately 4 % of the NO<sub>3</sub> export load 29 at the polder outlet. The low NO<sub>3</sub> concentrations during the summer months and the rapid increase

30 after a very wet period during August additionally indicate that the influence of sewage effluent on

31 the NO<sub>3</sub> concentrations is limited. The discharge from the channel that drains the nature area

1 Oostvaarderplassen (location 6) enters the Lage Vaart between the WWTP and the pumping station 2 and is 2 to 3 times higher than the discharge from the WWTP. This implies that there is limited flow 3 of the WWTP effluent towards the pumping station during no pumping conditions. 4 Beside the seasonal variation, we structurally observed an increase of NO<sub>3</sub> concentrations after 5 intensive rainfall events, except for the rainfall event during the thaw on 24-25 January. A reduction 6 in NO<sub>3</sub> concentrations coinciding with periods of intensive rainfall is commonly reported in high-7 frequency monitoring studies in natural catchments and attributed to dilution of the surface water 8 by run-off (Bowes et al., 2015;Rozemeijer et al., 2010)(Bowes et al., 2015;Rozemeijer et al., 2010). 9 Our structurally observed I increase implies that run-off, which dilutes the NO<sub>3</sub> concentration of the 10 surface water does not commonly occur in the polder. It, therefore, indicates that rainfall initiates a 11 sudden increase of quick interflow via subsurface tube drains, cracks or other macropores to the 12 Lage Vaart channel water. This is confirmed by the TFN model which showed that quite a large part 13 of the NO<sub>3</sub> dynamics during the winter months can be related to rainfall. Meinardi and Van der 14 Eertwegh (1997)Meinardi and Van den Eertwegh (1997) ran a monitoring program on tube drain 15 water composition at 14 farms in the Flevoland polder during 1992-1995 and reported 16 concentrations between 5 - 25 mg N/4 L<sup>-1</sup>. Another monitoring program on nutrient concentration of 17 tube drain water at 6 farms in Flevoland from 2004 to 2008 gave farm-average NO<sub>3</sub> concentrations 18 of 14 - 18 mg N/4 L<sup>-1</sup> (van Boekel et al., 2012)(van Boekel et al., 2012). These concentrations levels 19 can only explain the observed  $NO_3$  concentration at the pumping station when tube drain water is a 20 dominant source of the Lage Vaart channel water. Groundwater levels within the polder are 21 commonly low and tube drainage is rare during the summer and early autumn (Van den Eertwegh, 22 2002;Groen, 1997) (Van den Eertwegh, 2002;Groen, 1997). In autumn, when evapotranspiration 23 decreases, the groundwater levels rise upon rainfall events to around or above the level of the tube 24 drains, which are present at a depth of 0.95 m below the soil surface, and this initiates drain

discharge. This is illustrated by the measured groundwater levels within the Lage Afdeling drainage 26 area (Fig. S3S6) that shows a direct response of the groundwater level on rainfall combined with a 27 seasonal trend that shows increasing rising groundwater levels during the months October and 28 November and quite stable levels from December to March. Rainfall events unit half-between the 29 start of the monitoring and mid-November and between April and mid-August did not result in tube 30 drain discharge and the. The low NO<sub>3</sub> concentration of the surface water until half November 31 is, during these periods, are thus, explained by the absence of tube drain discharge. Extensive rainfall 32 during the second half of August resulted in a rising of the groundwater level close to the tube drain

25

33 level (Fig. S6) and thus to leaching of  $NO_3$ , stored in the soil profile, to the surface water. This is also

34 the reason that we started the TFN model on 15 November. As rainfall is not a driving force for the NO<sub>3</sub> concentration before mid-November <u>and after April</u>, starting the TFN model on 1 October<u>and</u>
 <u>continuing after 1 May</u> would serenely be unfavorable for the transfer model.

3 The presence of cracked clay soils results in a rapid response of drainage to rainfall events in winter 4 (Groen, 1997; Van den Eertwegh, 2002) (Groen, 1997; Van den Eertwegh, 2002). Preferential 5 transport of water and nutrients through cracks and macropores is known to play an important role in heavy clay soils (e.g. Van der Salm et al., 2012)(e.g. Van der Salm et al., 2012), which explains the 6 7 quick response of NO<sub>3</sub> concentration of the surface water to rainfall events. Due to regular plowing 8 rainwater easily infiltrates into the top soil layer where exchange of NO<sub>3</sub> from manure, fertilizers and 9 plant debris occurs. The top soil or plough layer is commonly well aerated, and therefore, guite 10 optimal for conversion of organic nitrogen and ammonium to NO<sub>3</sub>. After leaching of this water from 11 the plough layer to the cracked soil layer it quickly contributes to tube drain discharge. Due to short 12 residence time of this water in the soil, the influence of denitrification on the NO<sub>3</sub> concentration is 13 limited. This implies that the NO<sub>3</sub> concentration at the polder outlet and the related export load 14 from the polder are strongly controlled by quick interflow including tube drain discharge during the 15 winter months.

#### 16 4.1.2 Phosphorus

17 In contrast to the  $NO_3$  concentration, the TP concentration at the pumping station decreased after 18 the wet periods in the autumn of 2014- and the late summer of 2015 (Fig. 2). The interflow discharge 19 via subsurface tube drains, cracks or other macropores that resulted in an increase of  $NO_3$ 20 concentrations diluted the TP concentration.concentrations. Likely this can be attributed to the 21 relative decrease of the groundwater contribution to the channel water during periods of increased 22 interflow discharge. This indicates that the sources of TP in the channel water at the polder outlet 23 can largely be attributed to exfiltration of dissolved-P-rich groundwater that occurs throughout the 24 year, presumably combined with effluent loads from the WWTP and biogeochemical remobilization 25 of P from channel sediments induring the summer and autumn. The low DRP:TP ratio of the surface 26 water within the Lage Afdeling as observed during the first half year of 2014 and the winter of 2015 27 (Fig. 7) can be explained by transition of dissolved P to particulate P at the groundwater-surface 28 water interface. This commonly occurs after exfiltration of anaerobic groundwater into surface 29 water due to oxidation processes (e.g. van der Grift et al., 2014; Baken et al., 2015)(e.g. van der Grift 30 et al., 2014;Baken et al., 2015).

The decrease of annual TP load from the groundwater contribution WWTP to the channel water due
 to an increase in interflow discharge during autumn, results in a decline Lage Vaart is approximately

- 1 27 % of the TP export load at the polder outlet. As discussed previously for  $NO_3$ , the effect of the 2 WWTP on the  $NO_3$  concentration in the channel water. at the pumping station seems to be small. 3 For TP, however, the WWTP load cannot be neglected. The discharge water from the 4 Oostvaardersplassen has relatively high TP concentrations (Fig. 7) and may contribute to the 5 increase in TP concentration at the pumping station during no pumping periods. The source of the 6 TP in the Oostvaardersplassen is groundwater and feces of wildlife. The Oostvaardersplassen is an 7 important wintering area for birds that import nutrients from elsewhere. 8 Additional to this groundwater input signal, the high DRP:TP ratios of the low-frequency monitoring 9 program during the second half year of 2014 and the summer of 2015 indicates that mineralization 10 of organic P from algae or plant debris, or release of DRP from bed sediments can be considered as a 11 second P source during summer and autumn-when the TP concentration reached a maximum level between 0.8 and 1.2 mg P L<sup>-1</sup>. Mineralization of organic P mainly occurs after the growing season and 12 13 the release of DRP from bed sediments is reported during summer and autumn due to temperature 14 and redox dependent biogeochemical remobilization processes for lakes (e.g. Lavoie and Auclair, 15 2012;Boers and van Hese, 1988)(e.g. Lavoie and Auclair, 2012;Boers and van Hese, 1988), wetlands, 16 fens and floodplain soils <del>(e.g. Zak et al., 2006;Loeb et al., 2008)</del>(e.g. Zak et al., 2006;Loeb et al., 2008) 17 but also for streams and rivers (e.g. Duan et al., 2012; Jarvie et al., 2008)(e.g. Duan et al., 2012; Jarvie 18 et al., 2008). Low  $O_2$  concentrations in the water column are reported as an indicator for 19 remobilization of P from bed sediments (Geurts et al., 2013) (Geurts et al., 2013). The decline of the 20 O<sub>2</sub> concentrations in the surface water at low-frequency monitoring locations during the summer 21 and autumn months (Fig. 7), thus, indicates that biogeochemical remobilization may occur in the 22 channels of the Lage Afdeling. 23 As a result of resuspension of particulate P from bed sediments due to increased flow velocities, we 24 structurally observed an increase of TP concentrations during pumping. Resuspension of particulate 25 P retained by sediments during high discharge events is an important transport mechanism in 26 natural catchments (e.g. Evans et al., 2004; Mulholland et al., 1985; Nyenje et al., 2014; Haygarth et al., 27 2005;Palmer-Felgate et al., 2008)(e.g. Evans et al., 2004;Mulholland et al., 1985;Nyenje et al., 28 2014; Haygarth et al., 2005; Palmer-Felgate et al., 2008). Our data shows that this mechanism is also 29 relevant for P transport in polders where flow velocities vary more abruptly and are maximized by 30 the capacity of the pumping station. The changes in TP concentration during pumping are, however, 31 significantly lower than reported during peak water discharge amongst storms in natural catchments. 32 For an agriculture-dominated lowland catchment in the Netherlands, Rozemeijer et al. 33 (2010) Rozemeijer et al. (2010) reported a mean increase in TP concentration during discharge from
  - 34

1	0.15 to 0.95 mg P <del>/I comming L<sup>-1</sup> coming</del> from 47 rainfall events over a year. Particulate P (PP)
2	increases up to a factor <u>of</u> 100 were reported by <del>Stutter et al. (2008)<u>Stutter et al. (2008)</u> in response</del>
3	to storm events. Evans et al. (2004)Evans et al. (2004) measured PP concentrations up to 3.93 mg P/4
4	$\underline{L}^1$ in al lowland stream during high discharge conditions while the mean concentration equaled 0.1
5	mg P/ <u>4 L<sup>-1</sup></u> . <del>Haygarth et al. (2005)Haygarth et al. (2005)</del> reported 10 to 20 times higher mean TP
6	concentrations during storm flow conditions compared to base flow conditions. With data from 76
7	storms Correll et al. (1999)Correll et al. (1999) showed that concentrations of PP increased up to
8	three orders of magnitude during storms. These changes are significantly higher than the factor 1.5
9	to 2 that we observed at the pumping station but with 79 pump cycles during the period October
10	2014 – March 2015, discharge-related changes that lead to resuspension of particulate P appear
11	more frequent in polders compared to natural catchments. Total P export loads from polders can
12	thus showed that concentrations of PP increased up to three orders of magnitude during storms.
13	These changes are all considerably larger than the average factor of 1.30 and 1.83 that we observed
14	at the pumping station during pumping with one and two pumps, respectively. The P export from
15	natural catchments during pulses at high flow in less than 10% of the time may amount to about 80%
16	of the annual export (Kaushal et al., 2014). For our polder catchment we calculated that only 21% of
17	the annual TP export load can be related to resuspension of TP due to changes in water flow induced
18	by the pumping station. With 143 pumping events during the period from October 2014 to October
19	2015, discharge-related changes that lead to resuspension of P appear more frequent in polders
20	compared to natural catchments. The TP concentrations that increase during dry periods in the
21	summer and autumn, likely as a result of DRP release from the bed sediments additionally
22	contributes the TP export loads. Therefore, it can be concluded that total P export loads from polder
23	catchment can be characterized as less incidental and less peak flow controlled than those from
24	natural catchments.
25	4.2 Incidental nutrient losses to surface water after manure application
26	The second objective of our study was to determine the relevance of incidental nutrient losses
27	caused by intensive rainfall events whether or not in combination with recent manure application.
28	The Netherlands adopted the European Nitrate Directive in 1991 (EC, 1991), which regulates the use
29	of nitrogen in agriculture through national action plans. The second objective of our study was to
30	determine the relevance of incidental nutrient losses caused by intensive rainfall events in
31	combination with recent manure application.
32	Among other measures, the regulation includes the period of manure application. To reduce the risk
33	of nutrient leaching to groundwater and surface water, manure application on arable land is allowed

1 from 1 February to 1 August and on grassland from 15 February to 31 August (LNV, 2009). There is 2 still debate about potential effects of manure application in February and March (before the start of 3 the growing season) on the water guality. Several studies ask attention for elevated nutrient 4 concentrations in guickflow within a few weeks after application of fertilizers or liquid farm manure. 5 However, the individual conditions varied between those studies: high losses were reported after 6 installation of drains following application of liquid farm manure (Hodgkinson et al., 2002), with a 7 rainfall event after P fertilizer application on frozen soil (Gentry et al., 2007), in drain water with a 8 rainfall event after fertilizer application on clayey grassland (Simard et al., 2000), in drain water after 9 harvest and superphosphate fertilizer application on clay soil (Diodiic et al., 2000), in drain and trench water after application of fertilizer or cattle manure (Van der Salm et al., 2012). The 10 11 associated incidental loss may even amount to about 50% of the annual loss. Next, the guestion 12 arises if this affects water quality at a more regional scale. High-frequency monitoring is a powerful 13 tool to detect such incidental losses. 14 The NO<sub>3</sub> concentration peaked at the polder outlet on 24 February, four days after an intensive 15 rainfall event that marked the end of a relative dry period that started early February. The increase 16 of the NO<sub>3</sub> concentration is almost two times higher compared to the other peaks in NO<sub>3</sub> 17 concentration after a rainfall event (Table 2). This suggests that the NO<sub>3</sub> peak of 10.4 mg N<sub>4</sub> L<sup>-1</sup> was 18 caused by an incidental loss after recent-manure application- that started on 1 February. The TFN 19 model revealed high residual NO<sub>3</sub> concentrations up to almost 8 mg N4 $L^1$  during this NO<sub>3</sub> peak that 20 cannot be explained by rainfall (Fig. 4). The NO<sub>3</sub> concentration peaks on 27 February and 3 March 21 also showed highlarge positive residuals of -4.2 and 3.4 mg N/4 L<sup>-1</sup>, respectively. The wet period in 22 January resulted, however, in predicted NO<sub>3</sub> concentrations that were higher than the measured concentrations. There was probably some degree of dilution during this period. A plausible 23 24 explanation for this behavior The negative residuals in January can be explained by leaching of the NO<sub>3</sub> stored in the soil profile during the winter season in combination with the appearance of some 25 26 degree of dilution of the remaining  $NO_3$  by precipitation water during this period. Dilution of the  $NO_3$ 27 concentration upon rainfall events commonly observed in catchments (e.g. Rozemeijer et al., 28 2010; Wade et al., 2012). A plausible explanation for the large positive residuals in February and 29 March is recent manure application that started on 1 February and temporary soil storage of applied 30 N during the first dry weeks of February. 31 The TP concentration peaked on 21 February. It is, however, not likely that this peak was caused by 32 an incidental loss after manure application. This peak appeared during the beginning of the rainfall

33 event, simultaneously with <u>a turbidity peak after</u> the start-up of the pumps <u>afterfollowing upon</u> a

1 relatively dry period. Therefore, it is of more likelythan one week without pumping (Fig. 3). It is, 2 therefore, not likely that this peak was caused by an incidental loss after manure application but 3 caused by hydrodynamic resuspension of the Lage Vaart bed sediment. The absence of a TP peak 4 after the rainfall event on 21-22 February can be attributed to the soil characteristics of the area. We 5 already discussed that the water quality at the polder outlet is strongly controlled by quick interflow 6 via tube drains or cracks and that surface run-off only influenced the water quality when it rained 7 during the end of a freeze-thaw cycle. Although it is known that tube drain discharge after rainfall 8 events in combination with recent manure application on cracked clay soils may contain significant 9 TP concentrations (Van der Salm et al., 2012)(Van der Salm et al., 2012), these peaks did not appear 10 at the polder outlet., these peaks did not appear at the polder outlet. Several other studies ask 11 attention for elevated TP concentrations in drain and trench flow within a few weeks after 12 application of fertilizers or liquid farm manure (Hodokinson et al., 2002; Simard et al., 2000; Diodiic et 13 al., 2000). It is unknown if these peaks appear after rainfall events in the tube drain discharge or in 14 the receiving field ditches in the Lage Afdeling drainage area. Therefore, it is unclear if the absence 15 of TP peaks simultaneously with the NO<sub>3</sub> peaks at the polder outlet can be attributed to 16 sedimentation of PP from agricultural sources in the field ditches or sub-channels where it may 17 become a source for DRP release from bed sediments during the summer and autumn months or 18 that there is almost no particulate or dissolved P leaching from the top-soil to the surface water due 19 to the sorption capacity of the top-soil. From other areas it is known that the dissolved P loads to 20 surface water from tube drains and shallow groundwater discharge are low due to precipitation with 21 Fe hydroxides with a high affinity to retain P, at the oxic/anoxic interface around the tube drains and 22 ditch sediment (van der Grift et al., 2014; Baken et al., 2015) (van der Grift et al., 2014; Baken et al., 23 2015). It is unknown if The relevance of this process is relevant in the Lage Afdeling is unknown. 24 4.3 Water quality affected by the operational management of the pumping station 25 The third objective of our study was to assess the potential effects of the operational management 26 of the pumping station on the water quality. Since Up to 2008, the pumping station Blocq van 27 Kuffeler was powered with diesel engines. These diesel engines were replaced with electric engines 28 during the renovation of the pumping station in the autumn of 2008 and this conversion was 29 finished in the beginning of 2009. Since this transition, the pumping station, it runs typically 30 overnight during normal meteorological conditions, because night power supply is as reason of 31 cheaper-than daytime power supply. The low-frequency sampling is always performed during 32 daytime. The distribution of pumping hours and sampling moments over the day during the period 33 October 2014 – MarchSeptember 2015 and boxplots of measured TP concentrations over the day

1 during the months January and February 2015 are shown in Fig. <u>\$4\$7</u>. These two months were 2 selected because boxplots for longer time series are dominated by the seasonal trends in the TP 3 concentration. The median, quartile and maximum TP concentrations were higher during night hours 4 than during daytime. As a result, the monitoring program systematically misses the TP peak that 5 occurs during pumping hours and consequently does not measure diurnal cycles in water quality 6 caused by the operation of the pumping station. The reported time series from the low-frequency 7 sampling program is, thus, not fully representative for the TP concentration at the polder outlet. As a 8 consequence, export fluxes from the polder as calculated from low-frequency sample data 9 underestimate the true export P-loads (Fig. 5). Similar results have been reported for load 10 calculations in natural catchments with rapid run-off (e.g. Rozemeijer et al., 2010;Cassidy and Jordan, 11  $\frac{2011}{100}$ . The NO<sub>3</sub> concentration showed no structural response on pumping, further illustrating the 12 importance of resuspension of particulate P by pumping.

The preferred timing of sampling during regular working-hours is also critical for trend detection in the resulted dataset time series (Fig. 6). Trend analysis before and after replacement of the diesel engines compared with trend analysis over the years 2000-2015 indicates that the trend of slightly decreasing concentrations over the years 2000-2015 ismay be caused by the sudden decrease of concentrations after renovation of the pumping station which is an artifact of a change in pumping regimes. It means that the routine of water sampling at the pumping station between 9 AM and 3 PM result in a dataset time series that is not fully representative of the actual trends in water quality.

20 The number of diesel powered pumping stations in the Netherlands has rapidly declined during the 21 last decades. There were around 200 diesel or hybrid (diesel + electric) powered pumping stations in 22 operation in 1990. Currently, there are only 40 remaining and these pumping stations have mainly a 23 function for emergency situations (Gemalen, 2015Gemalen, 2015)(Gemalen, 2015). During the same 24 period, electric powered pumping stations have been equipped with automatic switching systems. 25 Nowadays, a large majority of pumping stations operates predominantly during night hours. As the 26 pumping station is the outlet of a (artificial) water system it is often a monitoring location for surface 27 water quality as well. The renovation of pumping stations may thus have had a substantial impact on 28 reported trends in water quality on a regional or even a national scale.

29 5 Conclusions

30 High-frequency monitoring at the outlet of an agriculture-dominated lowland water system in

31 combination with low-frequency monitoring within the area significantly improves insight in nutrient

32 sources and transport processes.

1	Discharge water from subsurface drains, likely in combination with quick interflow via clay cracks,
2	has a dominant contribution to NO $_3$ loads to surface water, mainly originating from N-losses from
3	agricultural lands during the winter. Transfer function-noise modelling of hourly $NO_3$ concentrations
4	reveals that quite a large part of the dynamics in $NO_3$ concentrations during the winter months can
5	be related to rainfall once groundwater tables have risen aboveclose to the tube drain levels. The
6	$NO_3$ loads appear as incidental losses upon intensive rainfall events and cause high $NO_3$
7	concentrations at the polder outlet within approximately five days after the rainfall event. Such
8	dynamics are difficult to detect with grab samples.
	Total Despert he linked to a dominant source. The TD concentration decreases in removes to wat
9	Total P cannot be linked to a dominant source. The TP concentration decreases in response to wet
10 11	periods, this implies that groundwater seepage is an important source of TP during dry periods. High
11	DRP/TP ratios in the grab samples from different location within the polder in the summer and
12	autumn months further suggest that biogeochemical remobilization from bed sediments or
13	mineralization of organic P from algae of plant debris additionally attributes <u>contributed</u> to the TP
14	concentration. The effluent load of a wastewater treatment plant finally attributes the TP
15	concentration. Agriculture did not seem to be a direct source of the TP concentration at the polder
16	outlet. At the moments when water at the polder outlet was enriched in NO <sub>3</sub> , originated from the
17	agricultural land, it had low TP concentrations.
18	Short-scale responses of the NO $_3$ and TP concentration on rainfall events indicate that run-off is not
19	an important process that controls nutrient export from the polder. WaterA decline of the NO $_3$
20	concentration of the channel water (caused by dilution with NO <sub>3</sub> -poor run-off water) in combination
20	
20 21	with an increase in the TP concentration and turbidity (by surface erosion and associated particulate
	with an increase in the TP concentration and turbidity (by surface erosion and associated particulate P transport) was only observed at the polder outlet during a rainfall event at the end of a freeze-
21	
21 22	P transport) was only observed at the polder outlet during a rainfall event at the end of a freeze-
21 22 23	P transport) was only observed at the polder outlet during a rainfall event at the end of a freeze- thaw cycle. Under non-freezing conditions, rainfall infiltrates into the soil where it gets enriched in
21 22 23 24	<u>P transport) was only observed at the polder outlet during a rainfall event at the end of a freeze- thaw cycle. Under non-freezing conditions, rainfall infiltrates into the soil where it gets enriched in NO<sub>3</sub> and contributes to tube drain discharge due to preferential flow through the cracked clay soil.</u>
21 22 23 24 25	P transport) was only observed at the polder outlet during a rainfall event at the end of a freeze- thaw cycle. Under non-freezing conditions, rainfall infiltrates into the soil where it gets enriched in NO <sub>3</sub> and contributes to tube drain discharge due to preferential flow through the cracked clay soil. This drain discharge may also be enriched in TP but this is then buffered in the water system due to
21 22 23 24 25 26	P transport) was only observed at the polder outlet during a rainfall event at the end of a freeze- thaw cycle. Under non-freezing conditions, rainfall infiltrates into the soil where it gets enriched in NO <sub>3</sub> and contributes to tube drain discharge due to preferential flow through the cracked clay soil. This drain discharge may also be enriched in TP but this is then buffered in the water system due to sedimentation of particulate P where it may become a source for DRP release from bed sediments
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21 22 23 24 25 26 27 28 29	P transport) was only observed at the polder outlet during a rainfall event at the end of a freeze- thaw cycle. Under non-freezing conditions, rainfall infiltrates into the soil where it gets enriched in NO <sub>3</sub> and contributes to tube drain discharge due to preferential flow through the cracked clay soil. This drain discharge may also be enriched in TP but this is then buffered in the water system due to sedimentation of particulate P where it may become a source for DRP release from bed sediments during the summer and autumn months. High-frequency monitoring shows that the water discharge from the polder- <del>as</del> generated by the pumping station initiates <u>short-scale</u> hydrodynamic resuspension of particulate P from the channel
21 22 23 24 25 26 27 28 29 30	P transport) was only observed at the polder outlet during a rainfall event at the end of a freeze- thaw cycle. Under non-freezing conditions, rainfall infiltrates into the soil where it gets enriched in NO <sub>3</sub> and contributes to tube drain discharge due to preferential flow through the cracked clay soil. This drain discharge may also be enriched in TP but this is then buffered in the water system due to sedimentation of particulate P where it may become a source for DRP release from bed sediments during the summer and autumn months. High-frequency monitoring shows that the water discharge from the polder-as generated by the pumping station initiates <u>short-scale</u> hydrodynamic resuspension of particulate P from the channel bed sediment and thus an increase of the TP concentration in the surface water during pumping.

1 suggest that the P retention capacity of polder water systems is high because flow velocities are

- 2 maximized by the power of the pumping station. This result in a large P retention compared with
- 3 natural catchments where incidental losses during peak flow conditions control the export load.

4 Short-scale responses of the NO<sub>2</sub> and TP concentration on rainfall events indicate that run-off is not 5 an important process that controls nutrient export from the polder.-A decline of the NO<sub>3</sub> 6 concentration of the channel water (caused by dilution with NO<sub>2</sub> poor run off water) in combination 7 with an increase in the TP concentration (by surface erosion and associated particulate P transport) 8 was only observed at the polder outlet during a rainfall event at the end of a freeze thaw cycle. 9 Under non freezing conditions, rainfall infiltrates into the soil where it gets enriched in NO<sub>2</sub>-and 10 contributes to tube drain discharge due to preferential flow through the cracked clay soil. This drain 11 discharge may also be enriched in TP but this is then buffered in the water system due to 12 sedimentation of particulate P. 13 A change in pumping regime caused by a transformation of the pumping station from powering with 14 diesel engines to electric engines leads to a trend suggesting decreasing TP concentrations in the 15 surface water that now should be considered artificial. Our data suggest increasing TP 16 concentrations when the individual time series before and after the transformation. The timing of 17 sampling relative to the operating hours of the pumping station affects the concentration and this 18 should be accounted for when calculating P export loads, determining trends in water quality or 19 when judging water quality against ecological thresholds and standards. High-frequency monitoring

20 appears to be an effective tool to reveal this kind of difficult to notice artificial responses in surface

21 water quality.

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28 References

- 29 APHA AWWA WPCF: Standard Methods for the Examination of Water and Waste Water, edited by:
- 30 Clesceri, G., Trussell, American Public Health Association, Washington, D.C, 1989.
- 31 Baken, S., Verbeeck, M., Verheyen, D., Diels, J., and Smolders, E.: Phosphorus losses from agricultural
- 32 land to natural waters are reduced by immobilization in iron-rich sediments of drainage ditches,
- 33 Water Research, 71, 160-170, 2015.

1 Berendrecht, W. L., Heemink, A. W., van Geer, F. C., and Gehrels, J. C.; Decoupling of modeling and 2 measuring interval in groundwater time series analysis based on response characteristics, Journal of Hydrology, 278, 1 16, http://dx.doi.org/10.1016/S0022 1694(03)00075 1, 2003. 3 Bieroza, M. Z., Heathwaite, A. L., Mullinger, N. J., and Keenan, P. O.: Understanding nutrient 4 5 biogeochemistry in agricultural catchments: The challenge of appropriate monitoring frequencies, Environmental Sciences: Processes and Impacts, 16, 1676 1691, 10.1039/c4em00100a, 2014. 6 7 Boers, P. C. M., and van Hese, O.: Phosphorus release from the peaty sediments of the Loosdrecht 8 Lakes (The Netherlands), Water Research, 22, 355-363, 1988. 9 Bouwman, L., Goldewijk, K. K., Van Der Hoek, K. W., Beusen, A. H. W., Van Vuuren, D. P., Willems, J., 10 Rufino, M. C., and Stehfest, E.: Exploring global changes in nitrogen and phosphorus cycles in 11 agriculture induced by livestock production over the 1900–2050 period, Proceedings of the National 12 Academy of Sciences, 110, 20882 20887, 10.1073/pnas.1012878108, 2013. 13 Bowes, M. J., Jarvie, H. P., Halliday, S. J., Skeffington, R. A., Wade, A. J., Loewenthal, M., Gozzard, E., Newman, J. R., and Palmer Felgate, E. J.: Characterising phosphorus and nitrate inputs to a rural river 14 15 using high-frequency concentration-flow relationships, Science of The Total Environment, 511, 608-16 620, http://dx.doi.org/10.1016/j.scitotenv.2014.12.086, 2015. Box, G. E. P., and Jenkins, G. M.: Time Series Analysis: Forecasting and Control, Holden Day, San 17 18 Francisco, 575 pp., 1970. 19 Cassidy, R., and Jordan, P.: Limitations of instantaneous water guality sampling in surface-water catchments: Comparison with near continuous phosphorus time series data, Journal of Hydrology, 20 405, 182-193, http://dx.doi.org/10.1016/j.jhydrol.2011.05.020, 2011. 21 22 Cirmo, C. P., and McDonnell, J. J.: Linking the hydrologic and biogeochemical controls of nitrogen 23 transport in near stream zones of temperate forested catchments: a review, Journal of Hydrology, 199, 88-120, http://dx.doi.org/10.1016/S0022-1694(96)03286-6, 1997. 24 25 Cleveland, W. S.: Robust locally weighted regression and smoothing scatterplots, Journal of the 26 American Statistical Association, 74, 829-836, 1979. 27 Correll, D. L., Jordan, T. E., and Weller, D. E.: Transport of nitrogen and phosphorus from Rhode River watersheds during storm events, Water Resources Research, 35, 2513, 2521, 1999. 28 29 Diodiic, F., Ulén, B., and Bergström, L.: Temporal and spatial variations of phosphorus losses and drainage in a structured clay soil, Water Research, 34, 1687-1695, http://dx.doi.org/10.1016/S0043-30 1354(99)00312 7, 2000. 31 32 Duan, S., Kaushal, S. S., Groffman, P. M., Band, L. E., and Belt, K. T.: Phosphorus export across an 33 urban to rural gradient in the Chesapeake Bay watershed, Journal of Geophysical Research: 34 Biogeosciences, 117, 10.1029/2011JG001782, 2012. 35 Evans, D. J., Johnes, P. J., and Lawrence, D. S.: Physico-chemical controls on phosphorus cycling in 36 two lowland streams. Part 2-The sediment phase, Science of The Total Environment, 329, 165-182, 37 10.1016/j.scitotenv.2004.02.023, 2004. 38 Ferrick, M. G., and Gatto, L. W .: Quantifying the effect of a freeze thaw cycle on soil erosion: Laboratory experiments, Earth Surface Processes and Landforms, 30, 1305-1326, 10.1002/esp.1209, 39 40 2005. Fraters, B., Kovar, K., Willems, W., Stockmarr, J., and Grant, R.: Monitoring effectiveness of the EU 41 42 Nitrates Directive Action Programmes. Results of the international MonNO3 workshop in the 43 Netherlands, 11-12 June 2003, RIVM, Bilthoven, The Netherlands, 2005. 44 Gemalen: Available from: http://www.gemalen.nl/ (Accessed 12 May 2015), 2015. 45 Gentry, L. E., David, M. B., Royer, T. V., Mitchell, C. A., and Starks, K. M.: Phosphorus Transport 46 Pathways to Streams in Tile-Drained Agricultural Watersheds, J. Environ. Qual., 36, 408-415, 47 10.2134/jeg2006.0098, 2007. 48 Geurts, J. J. M., Hetjens, H., and Lamers, L. P. M.: Remobilization of nutrients after un deepening of

49 lakes (in dutch), Radbouduniversiteit Nijmegen,, 2013.

1	Griffioen, J., Vermooten, S., and Janssen, G.: Geochemical and palaeohydrological controls on the
2	composition of shallow groundwater in the Netherlands, Applied Geochemistry, 39, 129-149,
3	http://dx.doi.org/10.1016/j.apgeochem.2013.10.005, 2013.
4	Groen, K. P.: Pesticide leaching in polders, Field and model studies on cracked clays and loamy sand,
5	Van land tot zee, Ministerie van Verkeer en Waterstaat, Directoraat-Generaal Rijkswaterstaat,
6	Lelystad, 1997.
7	Halliday, S. J., Wade, A. J., Skeffington, R. A., Neal, C., Reynolds, B., Rowland, P., Neal, M., and Norris,
8	D.: An analysis of long-term trends, seasonality and short-term dynamics in water quality data from
9	Plynlimon, Wales, Science of The Total Environment, 434, 186-200,
10	http://dx.doi.org/10.1016/j.scitotenv.2011.10.052, 2012.
11	Haygarth, P. M., Wood, F. L., Heathwaite, A. L., and Butler, P. J.: Phosphorus dynamics observed
12	through increasing scales in a nested headwater to river channel study, Science of The Total
13	Environment, 344, 83-106, <u>http://dx.doi.org/10.1016/j.scitotenv.2005.02.007</u> , 2005.
14	Hirsch, R. M., Slack, J. R., and Smith, R. A.: Techniques of trend analysis for monthly water quality
15	data, Water Resources Research, 18, 107-121, 10.1029/WR018i001p00107, 1982.
16	Hodgkinson, R. A., Chambers, B. J., Withers, P. J. A., and Cross, R.: Phosphorus losses to surface
17	waters following organic manure applications to a drained clay soil, Agricultural Water Management,
18	57, 155-173, http://dx.doi.org/10.1016/S0378-3774(02)00057-4, 2002.
19	Huebsch, M., Grimmeisen, F., Zemann, M., Fenton, O., Richards, K. G., Jordan, P., Sawarieh, A., Blum,
20	P., and Goldscheider, N.: Technical Note: Field experiences using UV/VIS sensors for high resolution
21	monitoring of nitrate in groundwater, Hydrol. Earth Syst. Sci., 19, 1589-1598, 10.5194/hess-19-1589-
22	<del>2015, 2015.</del>
23	Jarvie, H. P., Mortimer, R. J. G., Palmer Felgate, E. J., Quinton, K. S., Harman, S. A., and Carbo, P.:
24	Measurement of soluble reactive phosphorus concentration profiles and fluxes in river-bed
25	sediments using DET gel probes, Journal of Hydrology, 350, 261-273, 2008.
26	Johnes, P. J.: Uncertainties in annual riverine phosphorus load estimation: Impact of load estimation
27	methodology, sampling frequency, baseflow index and catchment population density, Journal of
	methodology, sumpling requency, suscinow mack and susciment population density, southar or
28	Hydrology, 332, 241–258, <u>http://dx.doi.org/10.1016/j.jhydrol.2006.07.006</u> , 2007.
28 29	
	Hydrology, 332, 241-258, http://dx.doi.org/10.1016/j.jhydrol.2006.07.006, 2007.
29	Hydrology, 332, 241–258, <u>http://dx.doi.org/10.1016/j.jhydrol.2006.07.006</u> , 2007. Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrology and Earth System Sciences, 11, 372–381, 2007.
29 30	Hydrology, 332, 241–258, <u>http://dx.doi.org/10.1016/j.jhydrol.2006.07.006</u> , 2007. Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrology and Earth System Sciences, 11, 372–381, 2007. Kaufmann, V., Pinheiro, A., and Castro, N. M. d. R.: Simulating transport of nitrogen and phosphorus
29 30 31	Hydrology, 332, 241–258, <u>http://dx.doi.org/10.1016/j.jhydrol.2006.07.006</u> , 2007. Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrology and Earth System Sciences, 11, 372–381, 2007. Kaufmann, V., Pinheiro, A., and Castro, N. M. d. R.: Simulating transport of nitrogen and phosphorus in a Cambisol after natural and simulated intense rainfall, Journal of Contaminant Hydrology, 160,
29 30 31 32 33 34	<ul> <li>Hydrology, 332, 241–258, http://dx.doi.org/10.1016/j.jhydrol.2006.07.006, 2007.</li> <li>Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrology and Earth System Sciences, 11, 372–381, 2007.</li> <li>Kaufmann, V., Pinheiro, A., and Castro, N. M. d. R.: Simulating transport of nitrogen and phosphorus in a Cambisol after natural and simulated intense rainfall, Journal of Contaminant Hydrology, 160, 53–64, http://dx.doi.org/10.1016/j.jconhyd.2014.02.005, 2014.</li> </ul>
29 30 31 32 33 34 35	<ul> <li>Hydrology, 332, 241–258, http://dx.doi.org/10.1016/j.jhydrol.2006.07.006, 2007.</li> <li>Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrology and Earth System Sciences, 11, 372–381, 2007.</li> <li>Kaufmann, V., Pinheiro, A., and Castro, N. M. d. R.: Simulating transport of nitrogen and phosphorus in a Cambisol after natural and simulated intense rainfall, Journal of Contaminant Hydrology, 160, 53–64, http://dx.doi.org/10.1016/j.jconhyd.2014.02.005, 2014.</li> <li>Kirchner, J. W., Feng, X., Neal, C., and Robson, A. J.: The fine structure of water-quality dynamics: the</li> </ul>
29 30 31 32 33 34 35 36	<ul> <li>Hydrology, 332, 241–258, <u>http://dx.doi.org/10.1016/j.jhydrol.2006.07.006</u>, 2007.</li> <li>Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrology and Earth System Sciences, 11, 372–381, 2007.</li> <li>Kaufmann, V., Pinheiro, A., and Castro, N. M. d. R.: Simulating transport of nitrogen and phosphorus in a Cambisol after natural and simulated intense rainfall, Journal of Contaminant Hydrology, 160, 53–64, <u>http://dx.doi.org/10.1016/j.jconhyd.2014.02.005</u>, 2014.</li> <li>Kirchner, J. W., Feng, X., Neal, C., and Robson, A. J.: The fine structure of water-quality dynamics: the (high-frequency) wave of the future, Hydrological Processes, 18, 1353-1359, 10.1002/hyp.5537,</li> </ul>
29 30 31 32 33 34 35 36 37	<ul> <li>Hydrology, 332, 241–258, http://dx.doi.org/10.1016/j.jhydrol.2006.07.006, 2007.</li> <li>Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrology and Earth System Sciences, 11, 372–381, 2007.</li> <li>Kaufmann, V., Pinheiro, A., and Castro, N. M. d. R.: Simulating transport of nitrogen and phosphorus in a Cambisol after natural and simulated intense rainfall, Journal of Contaminant Hydrology, 160, 53–64, http://dx.doi.org/10.1016/j.jconhyd.2014.02.005, 2014.</li> <li>Kirchner, J. W., Feng, X., Neal, C., and Robson, A. J.: The fine structure of water-quality dynamics: the (high-frequency) wave of the future, Hydrological Processes, 18, 1353-1359, 10.1002/hyp.5537, 2004.</li> </ul>
29 30 31 32 33 34 35 36 37 38	<ul> <li>Hydrology, 332, 241–258, http://dx.doi.org/10.1016/j.jhydrol.2006.07.006, 2007.</li> <li>Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrology and Earth System Sciences, 11, 372–381, 2007.</li> <li>Kaufmann, V., Pinheiro, A., and Castro, N. M. d. R.: Simulating transport of nitrogen and phosphorus in a Cambisol after natural and simulated intense rainfall, Journal of Contaminant Hydrology, 160, 53–64, http://dx.doi.org/10.1016/j.jconhyd.2014.02.005, 2014.</li> <li>Kirchner, J. W., Feng, X., Neal, C., and Robson, A. J.: The fine structure of water-quality dynamics: the (high-frequency) wave of the future, Hydrological Processes, 18, 1353-1359, 10.1002/hyp.5537, 2004.</li> <li>Knotters, M., and van Walsum, P. E. V.: Estimating fluctuation quantities from time series of water-</li> </ul>
29 30 31 32 33 34 35 36 37 38 39	<ul> <li>Hydrology, 332, 241–258, http://dx.doi.org/10.1016/j.jhydrol.2006.07.006, 2007.</li> <li>Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrology and Earth System Sciences, 11, 372–381, 2007.</li> <li>Kaufmann, V., Pinheiro, A., and Castro, N. M. d. R.: Simulating transport of nitrogen and phosphorus in a Cambisol after natural and simulated intense rainfall, Journal of Contaminant Hydrology, 160, 53–64, http://dx.doi.org/10.1016/j.jconhyd.2014.02.005, 2014.</li> <li>Kirchner, J. W., Feng, X., Neal, C., and Robson, A. J.: The fine structure of water-quality dynamics: the (high-frequency) wave of the future, Hydrological Processes, 18, 1353-1359, 10.1002/hyp.5537, 2004.</li> <li>Knotters, M., and van Walsum, P. E. V.: Estimating fluctuation quantities from time series of water-table depths using models with a stochastic component, Journal of Hydrology, 197, 25-46,</li> </ul>
29 30 31 32 33 34 35 36 37 38 39 40	<ul> <li>Hydrology, 332, 241–258, http://dx.doi.org/10.1016/j.jhydrol.2006.07.006, 2007.</li> <li>Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrology and Earth System Sciences, 11, 372–381, 2007.</li> <li>Kaufmann, V., Pinheiro, A., and Castro, N. M. d. R.: Simulating transport of nitrogen and phosphorus in a Cambisol after natural and simulated intense rainfall, Journal of Contaminant Hydrology, 160, 53–64, http://dx.doi.org/10.1016/j.jconhyd.2014.02.005, 2014.</li> <li>Kirchner, J. W., Feng, X., Neal, C., and Robson, A. J.: The fine structure of water-quality dynamics: the (high-frequency) wave of the future, Hydrological Processes, 18, 1353-1359, 10.1002/hyp.5537, 2004.</li> <li>Knotters, M., and van Walsum, P. E. V.: Estimating fluctuation quantities from time series of water-table depths using models with a stochastic component, Journal of Hydrology, 197, 25-46, http://dx.doi.org/10.1016/S0022-1694(96)03278-7, 1997.</li> </ul>
29 30 31 32 33 34 35 36 37 38 39 40 41	<ul> <li>Hydrology, 332, 241–258, <u>http://dx.doi.org/10.1016/j.jhydrol.2006.07.006</u>, 2007.</li> <li>Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrology and Earth System Sciences, 11, 372–381, 2007.</li> <li>Kaufmann, V., Pinheiro, A., and Castro, N. M. d. R.: Simulating transport of nitrogen and phosphorus in a Cambisol after natural and simulated intense rainfall, Journal of Contaminant Hydrology, 160, 53–64, <u>http://dx.doi.org/10.1016/j.jconhyd.2014.02.005</u>, 2014.</li> <li>Kirchner, J. W., Feng, X., Neal, C., and Robson, A. J.: The fine structure of water-quality dynamics: the (high-frequency) wave of the future, Hydrological Processes, 18, 1353-1359, 10.1002/hyp.5537, 2004.</li> <li>Knotters, M., and van Walsum, P. E. V.: Estimating fluctuation quantities from time series of water-table depths using models with a stochastic component, Journal of Hydrology, 197, 25-46, <u>http://dx.doi.org/10.1016/S0022-1694(96)03278-7</u>, 1997.</li> <li>Lavoie, M., and Auclair, JC.: Phosphorus Mobilization at the Sediment–Water Interface in Softwater</li> </ul>
29 30 31 32 33 34 35 36 37 38 39 40 41 42	<ul> <li>Hydrology, 332, 241–258, <u>http://dx.doi.org/10.1016/j.jhydrol.2006.07.006</u>, 2007.</li> <li>Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrology and Earth System Sciences, 11, 372–381, 2007.</li> <li>Kaufmann, V., Pinheiro, A., and Castro, N. M. d. R.: Simulating transport of nitrogen and phosphorus in a Cambisol after natural and simulated intense rainfall, Journal of Contaminant Hydrology, 160, 53–64, <u>http://dx.doi.org/10.1016/j.jconhyd.2014.02.005</u>, 2014.</li> <li>Kirchner, J. W., Feng, X., Neal, C., and Robson, A. J.: The fine structure of water quality dynamics: the (high-frequency) wave of the future, Hydrological Processes, 18, 1353-1359, 10.1002/hyp.5537, 2004.</li> <li>Knotters, M., and van Walsum, P. E. V.: Estimating fluctuation quantities from time series of water-table depths using models with a stochastic component, Journal of Hydrology, 197, 25-46, <u>http://dx.doi.org/10.1016/S0022-1694(96)03278-7</u>, 1997.</li> <li>Lavoie, M., and Auclair, J. C.: Phosphorus Mobilization at the Sediment–Water Interface in Softwater Shield Lakes: the Role of Organic Carbon and Metal Oxyhydroxides, Aquatic Geochemistry, 18, 327</li> </ul>
29 30 31 32 33 34 35 36 37 38 39 40 41 42 43	<ul> <li>Hydrology, 332, 241 258, http://dx.doi.org/10.1016/j.jhydrol.2006.07.006, 2007.</li> <li>Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrology and Earth System Sciences, 11, 372-381, 2007.</li> <li>Kaufmann, V., Pinheiro, A., and Castro, N. M. d. R.: Simulating transport of nitrogen and phosphorus in a Cambisol after natural and simulated intense rainfall, Journal of Contaminant Hydrology, 160, 53-64, http://dx.doi.org/10.1016/j.jconhyd.2014.02.005, 2014.</li> <li>Kirchner, J. W., Feng, X., Neal, C., and Robson, A. J.: The fine structure of water-quality dynamics: the (high frequency) wave of the future, Hydrological Processes, 18, 1353-1359, 10.1002/hyp.5537, 2004.</li> <li>Knotters, M., and van Walsum, P. E. V.: Estimating fluctuation quantities from time series of water-table depths using models with a stochastic component, Journal of Hydrology, 197, 25-46, http://dx.doi.org/10.1016/S0022-1694(96)03278-7, 1997.</li> <li>Lavoie, M., and Auclair, J. C.: Phosphorus Mobilization at the Sediment–Water Interface in Softwater Shield Lakes: the Role of Organic Carbon and Metal Oxyhydroxides, Aquatic Geochemistry, 18, 327-341, 10.1007/s10498-012-9166-3, 2012.</li> </ul>
29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44	<ul> <li>Hydrology, 332, 241-258, <u>http://dx.doi.org/10.1016/j.jhydrol.2006.07.006</u>, 2007.</li> <li>Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrology and Earth System Sciences, 11, 372-381, 2007.</li> <li>Kaufmann, V., Pinheiro, A., and Castro, N. M. d. R.: Simulating transport of nitrogen and phosphorus in a Cambisol after natural and simulated intense rainfall, Journal of Contaminant Hydrology, 160, 53-64, <u>http://dx.doi.org/10.1016/j.jconhyd.2014.02.005</u>, 2014.</li> <li>Kirchner, J. W., Feng, X., Neal, C., and Robson, A. J.: The fine structure of water-quality dynamics: the (high-frequency) wave of the future, Hydrological Processes, 18, 1353-1359, 10.1002/hyp.5537, 2004.</li> <li>Knotters, M., and van Walsum, P. E. V.: Estimating fluctuation quantities from time series of water-table depths using models with a stochastic component, Journal of Hydrology, 197, 25-46, <u>http://dx.doi.org/10.1016/S0022-1694(96)03278-7</u>, 1997.</li> <li>Lavoie, M., and Auclair, J. C.: Phosphorus Mobilization at the Sediment–Water Interface in Softwater Shield Lakes: the Role of Organic Carbon and Metal Oxyhydroxides, Aquatic Geochemistry, 18, 327-341, 10.1007/s10498-012-9166-3, 2012.</li> <li>LNV: Fourth Dutch Action Programme (2010-2013) concerning the Nitrates Directive; 91/676/EEC,</li> </ul>
29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45	<ul> <li>Hydrology, 332, 241–258, http://dx.doi.org/10.1016/j.jhydrol.2006.07.006, 2007.</li> <li>Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrology and Earth System Sciences, 11, 372–381, 2007.</li> <li>Kaufmann, V., Pinheiro, A., and Castro, N. M. d. R.: Simulating transport of nitrogen and phosphorus in a Cambisol after natural and simulated intense rainfall, Journal of Contaminant Hydrology, 160, 53–64, http://dx.doi.org/10.1016/j.jconhyd.2014.02.005, 2014.</li> <li>Kirchner, J. W., Feng, X., Neal, C., and Robson, A. J.: The fine structure of water-quality dynamics: the (high-frequency) wave of the future, Hydrological Processes, 18, 1353–1359, 10.1002/hyp.5537, 2004.</li> <li>Knotters, M., and van Walsum, P. E. V.: Estimating fluctuation quantities from time series of water-table depths using models with a stochastic component, Journal of Hydrology, 197, 25-46, http://dx.doi.org/10.1016/S0022-1694(96)03278-7, 1997.</li> <li>Lavoie, M., and Auclair, J. C.: Phosphorus Mobilization at the Sediment–Water Interface in Softwater Shield Lakes: the Role of Organic Carbon and Metal Oxyhydroxides, Aquatic Geochemistry, 18, 327-341, 10.1007/s10498-012-9166-3, 2012.</li> <li>LNV: Fourth Dutch Action Programme (2010-2013) concerning the Nitrates Directive; 91/676/EEC., The Hague, 2009.</li> </ul>
29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46	<ul> <li>Hydrology, 322, 241-258, http://dx.doi.org/10.1016/j.jhydrol.2006.07.006, 2007.</li> <li>Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrology and Earth System Sciences, 11, 372-381, 2007.</li> <li>Kaufmann, V., Pinheiro, A., and Castro, N. M. d. R.: Simulating transport of nitrogen and phosphorus in a Cambisol after natural and simulated intense rainfall, Journal of Contaminant Hydrology, 160, 53-64, http://dx.doi.org/10.1016/j.jconhyd.2014.02.005, 2014.</li> <li>Kirchner, J. W., Feng, X., Neal, C., and Robson, A. J.: The fine structure of water-quality dynamics: the (high frequency) wave of the future, Hydrological Processes, 18, 1353-1359, 10.1002/hyp.5537, 2004.</li> <li>Knotters, M., and van Walsum, P. E. V.: Estimating fluctuation quantities from time series of water-table depths using models with a stochastic component, Journal of Hydrology, 197, 25-46, http://dx.doi.org/10.1016/S0022-1694(96)03278-7, 1997.</li> <li>Lavoie, M., and Auclair, JC.: Phosphorus Mobilization at the Sediment–Water Interface in Softwater Shield Lakes: the Role of Organic Carbon and Metal Oxyhydroxides, Aquatic Geochemistry, 18, 327-341, 10.1007/s10498-012-9166-3, 2012.</li> <li>LNV: Fourth Dutch Action Programme (2010-2013) concerning the Nitrates Directive; 91/676/EEC., The Hague, 2009.</li> <li>Loeb, R., Lamers, L. P. M., and Roelofs, J. G. M.: Prediction of phosphorus mobilisation in inundated</li> </ul>
29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47	<ul> <li>Hydrology, 332, 241–258, http://dx.doi.org/10.1016/j.jhydrol.2006.07.006, 2007.</li> <li>Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrology and Earth System Sciences, 11, 372–381, 2007.</li> <li>Kaufmann, V., Pinheiro, A., and Castro, N. M. d. R.: Simulating transport of nitrogen and phosphorus in a Cambisol after natural and simulated intense rainfall, Journal of Contaminant Hydrology, 160, 53–64, http://dx.doi.org/10.1016/j.jconhyd.2014.02.005, 2014.</li> <li>Kirchner, J. W., Feng, X., Neal, C., and Robson, A.J.: The fine structure of water-quality dynamics: the (high-frequency) wave of the future, Hydrological Processes, 18, 1353–1359, 10.1002/hyp.5537, 2004.</li> <li>Knotters, M., and van Walsum, P. E. V.: Estimating fluctuation quantities from time series of water-table depths using models with a stochastic component, Journal of Hydrology, 197, 25-46, http://dx.doi.org/10.1016/S0022-1694(96)03278-7, 1997.</li> <li>Lavoie, M., and Auclair, J. C.: Phosphorus Mobilization at the Sediment–Water Interface in Softwater Shield Lakes: the Role of Organic Carbon and Metal Oxyhydroxides, Aquatic Geochemistry, 18, 327-341, 10.1007/s10498-012-9166-3, 2012.</li> <li>LNV: Fourth Dutch Action Programme (2010-2013) concerning the Nitrates Directive; 91/676/EEC, The Hague, 2009.</li> <li>Loob, R., Lamers, L. P. M., and Roelofs, J. G. M.: Prediction of phosphorus mobilisation in inundated floodplain soils, Environmental Pollution, 156, 325-331, 10.1016/j.envpol.2008.02.006, 2008.</li> </ul>
29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48	<ul> <li>Hydrology, 332, 241–258, http://dx.doi.org/10.1016/j.jhydrol.2006.07.006, 2007.</li> <li>Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrology and Earth System Sciences, 11, 372–381, 2007.</li> <li>Kaufmann, V., Pinheiro, A., and Castro, N. M. d. R.: Simulating transport of nitrogen and phosphorus in a Cambisol after natural and simulated intense rainfall, Journal of Contaminant Hydrology, 160, 53–64, http://dx.doi.org/10.1016/j.jconhyd.2014.02.005, 2014.</li> <li>Kirchner, J. W., Feng, X., Neal, C., and Robson, A.J.: The fine structure of water-quality dynamics: the (high-frequency) wave of the future, Hydrological Processes, 18, 1353–1359, 10.1002/hyp.5537, 2004.</li> <li>Knotters, M., and van Walsum, P. E. V.: Estimating fluctuation quantities from time series of water-table depths using models with a stochastic component, Journal of Hydrology, 197, 25-46, http://dx.doi.org/10.1016/S0022-1694(96)03278-7, 1997.</li> <li>Lavoie, M., and Auclair, J. C.: Phosphorus Mobilization at the Sediment–Water Interface in Softwater Shield Lakes: the Role of Organic Carbon and Metal Oxyhydroxides, Aquatic Geochemistry, 18, 327-341, 10.1007/s10498-012-9166-3, 2012.</li> <li>LNV: Fourth Dutch Action Programme (2010-2013) concerning the Nitrates Directive; 91/676/EEC, The Hague, 2009.</li> <li>Loob, R., Lamers, L. P. M., and Roelofs, J. G. M.: Prediction of phosphorus mobilisation in inundated floodplain soils, Environmental Pollution, 156, 325-331, 10.1016/j.envpol.2008.02.006, 2008.</li> <li>Meinardi, C. R., and Van der Eertwegh, G. A. P. H.: Investigations on tile drains in clayey regions of</li> </ul>
29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47	<ul> <li>Hydrology, 332, 241–258, http://dx.doi.org/10.1016/j.jhydrol.2006.07.006, 2007.</li> <li>Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrology and Earth System Sciences, 11, 372–381, 2007.</li> <li>Kaufmann, V., Pinheiro, A., and Castro, N. M. d. R.: Simulating transport of nitrogen and phosphorus in a Cambisol after natural and simulated intense rainfall, Journal of Contaminant Hydrology, 160, 53–64, http://dx.doi.org/10.1016/j.jconhyd.2014.02.005, 2014.</li> <li>Kirchner, J. W., Feng, X., Neal, C., and Robson, A.J.: The fine structure of water-quality dynamics: the (high-frequency) wave of the future, Hydrological Processes, 18, 1353–1359, 10.1002/hyp.5537, 2004.</li> <li>Knotters, M., and van Walsum, P. E. V.: Estimating fluctuation quantities from time series of water-table depths using models with a stochastic component, Journal of Hydrology, 197, 25-46, http://dx.doi.org/10.1016/S0022-1694(96)03278-7, 1997.</li> <li>Lavoie, M., and Auclair, J. C.: Phosphorus Mobilization at the Sediment–Water Interface in Softwater Shield Lakes: the Role of Organic Carbon and Metal Oxyhydroxides, Aquatic Geochemistry, 18, 327-341, 10.1007/s10498-012-9166-3, 2012.</li> <li>LNV: Fourth Dutch Action Programme (2010-2013) concerning the Nitrates Directive; 91/676/EEC, The Hague, 2009.</li> <li>Loob, R., Lamers, L. P. M., and Roelofs, J. G. M.: Prediction of phosphorus mobilisation in inundated floodplain soils, Environmental Pollution, 156, 325-331, 10.1016/j.envpol.2008.02.006, 2008.</li> </ul>

51 Spiralling in a Woodland Stream: Seasonal Variations, Ecology, 66, 1012-1023, 1985.

1	Neal, C., Reynolds, B., Rowland, P., Norris, D., Kirchner, J. W., Neal, M., Sleep, D., Lawlor, A., Woods,
2	C., Thacker, S., Guyatt, H., Vincent, C., Hockenhull, K., Wickham, H., Harman, S., and Armstrong, L.:
3	High frequency water quality time series in precipitation and streamflow: From fragmentary signals
4	to scientific challenge, Science of The Total Environment, 434, 3-12,
5	http://dx.doi.org/10.1016/j.scitotenv.2011.10.072, 2012.
6	Nyenje, P. M., Meijer, L. M. G., Foppen, J. W., Kulabako, R., and Uhlenbrook, S.: Phosphorus
7	transport and retention in a channel draining an urban, tropical catchment with informal
8	settlements, Hydrol. Earth Syst. Sci., 18, 1009-1025, 10.5194/hess-18-1009-2014, 2014.
9	Palmer Felgate, E. J., Jarvie, H. P., Williams, R. J., Mortimer, R. J. G., Loewenthal, M., and Neal, C.:
10	Phosphorus dynamics and productivity in a sewage-impacted lowland chalk stream, Journal of
11	Hydrology, 351, 87-97, http://dx.doi.org/10.1016/j.jhydrol.2007.11.036, 2008.
12	Poor, C. J., and McDonnell, J. J.: The effects of land use on stream nitrate dynamics, Journal of
13	Hydrology, 332, 54-68, <u>http://dx.doi.org/10.1016/j.jhydrol.2006.06.022</u> , 2007.
14	Regelink, I. C., Koopmans, G. F., van der Salm, C., Weng, L., and van Riemsdijk, W. H.:
15	Characterization of Colloidal Phosphorus Species in Drainage Waters from a Clay Soil Using
16	Asymmetric Flow Field-Flow Fractionation, J. Environ. Qual., 42, 464-473, 10.2134/jeq2012.0322,
17	<del>2013.</del>
18	Rozemeijer, J. C., and Broers, H. P.: The groundwater contribution to surface water contamination in
19	a region with intensive agricultural land use (Noord-Brabant, The Netherlands), Environmental
20	Pollution, 148, 695 706, 10.1016/j.envpol.2007.01.028, 2007.
21	Rozemeijer, J. C., Van Der Velde, Y., Van Geer, F. C., De Rooij, G. H., Torfs, P. J. J. F., and Broers, H. P.:
22	Improving load estimates for NO3 and P in surface waters by characterizing the concentration
23	response to rainfall events, Environmental Science and Technology, 44, 6305-6312, 2010.
24	Rozemeijer, J. C., Klein, J., Broers, H. P., Van Tol-Leenders, T. P., and Van Der Grift, B.: Water quality
25	status and trends in agriculture-dominated headwaters; a national monitoring network for assessing
26	the effectiveness of national and European manure legislation in The Netherlands, Environmental
27	Monitoring and Assessment, 10.1007/s10661-014-4059-0, 2014.
28	Schoch, A. L., Schilling, K. E., and Chan, K. S.: Time series modeling of reservoir effects on river
29	nitrate concentrations, Advances in Water Resources, 32, 1197-1205,
30	<u>http://dx.doi.org/10.1016/j.advwatres.2009.04.002, 2009.</u>
31	Shrestha, R. R., Osenbrück, K., and Rode, M.: Assessment of catchment response and calibration of a
32	hydrological model using high-frequency discharge nitrate concentration data, Hydrology Research,
33	44, <del>995-1012, 10.2166/nh.2013.087, 2013.</del>
34	Simard, R. R., Beauchemin, S., and Haygarth, P. M.: Potential for preferential pathways of
35	phosphorus transport, Journal of Environmental Quality, 29, 97-105, 2000.
36	Skeffington, R. A., Halliday, S. J., Wade, A. J., Bowes, M. J., and Loewenthal, M.: Using high-frequency
37	water quality data to assess sampling strategies for the EU Water Framework Directive, Hydrol. Earth
38	<del>Syst. Sci., 19, 2491-2504, 10.5194/hess 19-2491-2015, 2015.</del>
39	Stutter, M. I., Langan, S. J., and Cooper, R. J.: Spatial contributions of diffuse inputs and within-
40	channel processes to the form of stream water phosphorus over storm events, Journal of Hydrology,
41	<del>350, 203-214, 10.1016/j.jhydrol.2007.10.045, 2008.</del>
42	Tiemeyer, B., Lennartz, B., and Kahle, P.: Analysing nitrate losses from an artificially drained lowland
43	catchment (North-Eastern Germany) with a mixing model, Agriculture, Ecosystems & Environment,
44	<del>123, 125-136, <u>http://dx.doi.org/10.1016/j.agee.2007.05.006</u>, 2008.</del>
45	van Boekel, E. M. P. M., Roelsma, J., Massop, H. T. L., Hendriks, R. F. A., Goedhart, P. W., and Jansen,
46	P. C.: Nitraatconcentraties in het drainwater in zeekleigebieden : oriënterend onderzoek naar de
47	oorzaken van de verhoogde nitraatconcentraties, Alterra-rapport;2360, Alterra Wageningen UR,
48	Wageningen, 2012.
49	Van de Ven, G. P.: Man-made lowlands, history of water management and land reclamation in the
50	Netherlands, Uitgeverij Matrijs, Utrecht, 2003.

1	Van den Eertwegh, G. A. P. H.: Water and Nutrient budgets at field and regional scale, travel times of
2	drainage water and nutrient loads to surface water, PhD thesis Wageningen University, 2002.
3	van der Grift, B., Rozemeijer, J. C., Griffioen, J., and van der Velde, Y.: Iron oxidation kinetics and
4	phosphate immobilization along the flow-path from groundwater into surface water, Hydrol. Earth
5	Syst. Sci., 18, 4687-4702, 10.5194/hess-18-4687-2014, 2014.
6	Van der Salm, C., van den Toorn, A., Chardon, W. J., and Koopmans, G. F.: Water and nutrient
7	transport on a heavy clay soil in a fluvial plain in the Netherlands, Journal of Environmental Quality,
8	41, 229-241, 10.2134/jeq2011.0292, 2012.
9	van Grinsven, H. J. M., ten Berge, H. F. M., Dalgaard, T., Fraters, B., Durand, P., Hart, A., Hofman, G.,
10	Jacobsen, B. H., Lalor, S. T. J., Lesschen, J. P., Osterburg, B., Richards, K. G., Techen, A. K., Vertès, F.,
11	Webb, J., and Willems, W. J.: Management, regulation and environmental impacts of nitrogen
12	fertilization in northwestern Europe under the Nitrates Directive; a benchmark study,
13	Biogeosciences, 9, 5143-5160, 10.5194/bg-9-5143-2012, 2012.
14	von Asmuth, J. R., Bierkens, M. F. P., and Maas, K.: Transfer function noise modeling in continuous
15	time using predefined impulse response functions, Water Resources Research, 38, 23-21-23-12,
16	10.1029/2001WR001136, 2002.
17	Wade, A. J., Palmer Felgate, E. J., Halliday, S. J., Skeffington, R. A., Loewenthal, M., Jarvie, H. P.,
18	Bowes, M. J., Greenway, G. M., Haswell, S. J., Bell, I. M., Joly, E., Fallatah, A., Neal, C., Williams, R. J.,
19	Gozzard, E., and Newman, J. R.: Hydrochemical processes in lowland rivers: Insights from in situ,
20	high resolution monitoring, Hydrology and Earth System Sciences, 16, 4323-4342, 10.5194/hess 16-
21	4323-2012, 2012.
22	Polder, Available from: <u>http://en.wikipedia.org/wiki/Polder</u> (Accessed 12 May 2014), 2015.
23	Withers, P. J. A., Ulén, B., Stamm, C., and Bechmann, M.: Incidental phosphorus losses are they
24	significant and can they be predicted?, Journal of Plant Nutrition and Soil Science, 166, 459-468,
25	<del>10.1002/jpln.200321165, 2003.</del>
26	Withers, P. J. A., and Jarvie, H. P.: Delivery and cycling of phosphorus in rivers: A review, Science of
27	The Total Environment, 400, 379-395, 2008.
28	Worrall, F., Swank, W. T., and Burt, T. P.: Changes in stream nitrate concentrations due to land
29	management practices, ecological succession, and climate: Developing a systems approach to
30	integrated catchment response, Water Resources Research, 39, HWC11-HWC114, 2003.
31	Zak, D., Kleeberg, A., and Hupfer, M.: Sulphate mediated phosphorus mobilization in riverine
32	sediments at increasing sulphate concentration, River Spree, NE Germany, Biogeochemistry, 80, 109-
33	<del>119, 2006.</del>
34	
34	
35	APHA-AWWA-WPCF: Standard Methods for the Examination of Water and Waste Water, edited by:
36	Clesceri, G., Trussell, American Public Health Association, Washington, D.C, 1989.
37	Baken, S., Verbeeck, M., Verheyen, D., Diels, J., and Smolders, E.: Phosphorus losses from agricultural
38	land to natural waters are reduced by immobilization in iron-rich sediments of drainage ditches,
39	Water Research, 71, 160-170, 2015.
40	Berendrecht, W. L., Heemink, A. W., van Geer, F. C., and Gehrels, J. C.: Decoupling of modeling and
40	measuring interval in groundwater time series analysis based on response characteristics, Journal of
42	Hydrology, 278, 1-16, http://dx.doi.org/10.1016/S0022-1694(03)00075-1, 2003.
72	<u>nyarology, 270, 1 10, mp. / ax.aoi.org/10.1010/30022 10/4(03/00073 1, 2003.</u>
43	Bieroza, M. Z., Heathwaite, A. L., Mullinger, N. J., and Keenan, P. O.: Understanding nutrient
44	biogeochemistry in agricultural catchments: The challenge of appropriate monitoring frequencies,
45	Environmental Sciences: Processes and Impacts, 16, 1676-1691, 10.1039/c4em00100a, 2014.
14	Poors D.C.M. and you Hose O. Describer in relaces from the posty addiments of the Locadresht
46 47	Boers, P. C. M., and van Hese, O.: Phosphorus release from the peaty sediments of the Loosdrecht
47	Lakes (The Netherlands), Water Research, 22, 355-363, 1988.
1	

1	Bouwman, A. F., Bierkens, M. F. P., Griffioen, J., Hefting, M. M., Middelburg, J. J., Middelkoop, H.,
2	and Slomp, C. P.: Nutrient dynamics, transfer and retention along the aquatic continuum from land
3	to ocean: towards integration of ecological and biogeochemical models, Biogeosciences, 10, 1-22,
4	10.5194/bg-10-1-2013, 2013a.
5	Bouwman, L., Goldewijk, K. K., Van Der Hoek, K. W., Beusen, A. H. W., Van Vuuren, D. P., Willems, J.,
6	Rufino, M. C., and Stehfest, E.: Exploring global changes in nitrogen and phosphorus cycles in
7	agriculture induced by livestock production over the 1900–2050 period, Proceedings of the National
8	Academy of Sciences, 110, 20882-20887, 10.1073/pnas.1012878108, 2013b.
9 10 11 12	Bowes, M. J., Jarvie, H. P., Halliday, S. J., Skeffington, R. A., Wade, A. J., Loewenthal, M., Gozzard, E., Newman, J. R., and Palmer-Felgate, E. J.: Characterising phosphorus and nitrate inputs to a rural river using high-frequency concentration–flow relationships, Science of The Total Environment, 511, 608-620, http://dx.doi.org/10.1016/j.scitotenv.2014.12.086, 2015.
13	Box, G. E. P., and Jenkins, G. M.: Time Series Analysis: Forecasting and Control, Holden-Day, San
14	Francisco, 575 pp., 1970.
15	Cassidy, R., and Jordan, P.: Limitations of instantaneous water quality sampling in surface-water
16	catchments: Comparison with near-continuous phosphorus time-series data, Journal of Hydrology,
17	405, 182-193, http://dx.doi.org/10.1016/j.jhydrol.2011.05.020, 2011.
18	<u>Cirmo, C. P., and McDonnell, J. J.: Linking the hydrologic and biogeochemical controls of nitrogen</u>
19	<u>transport in near-stream zones of temperate-forested catchments: a review, Journal of Hydrology,</u>
20	<u>199, 88-120, http://dx.doi.org/10.1016/S0022-1694(96)03286-6, 1997.</u>
21	<u>Cleveland, W. S.: Robust locally weighted regression and smoothing scatterplots, Journal of the</u>
22	<u>American Statistical Association, 74, 829-836, 1979.</u>
23 24	Correll, D. L., Jordan, T. E., and Weller, D. E.: Transport of nitrogen and phosphorus from Rhode River watersheds during storm events, Water Resources Research, 35, 2513-2521, 1999.
25 26 27	Djodjic, F., Ulén, B., and Bergström, L.: Temporal and spatial variations of phosphorus losses and drainage in a structured clay soil, Water Research, 34, 1687-1695, http://dx.doi.org/10.1016/S0043-1354(99)00312-7, 2000.
28	Duan, S., Kaushal, S. S., Groffman, P. M., Band, L. E., and Belt, K. T.: Phosphorus export across an
29	urban to rural gradient in the Chesapeake Bay watershed, Journal of Geophysical Research:
30	Biogeosciences, 117, G01025, 10.1029/2011JG001782, 2012.
31 32 33	Evans, D. J., Johnes, P. J., and Lawrence, D. S.: Physico-chemical controls on phosphorus cycling in two lowland streams. Part 2–The sediment phase, Science of The Total Environment, 329, 165-182, 10.1016/j.scitotenv.2004.02.023, 2004.
34	Ferrick, M. G., and Gatto, L. W.: Quantifying the effect of a freeze-thaw cycle on soil erosion:
35	Laboratory experiments, Earth Surface Processes and Landforms, 30, 1305-1326, 10.1002/esp.1209,
36	2005.
37	Fraters, B., Kovar, K., Willems, W., Stockmarr, J., and Grant, R.: Monitoring effectiveness of the EU
38	Nitrates Directive Action Programmes. Results of the international MonNO3 workshop in the
39	Netherlands, 11-12 June 2003, RIVM, Bilthoven, The Netherlands, 2005.
40 41	Gao, P.: Understanding watershed suspended sediment transport, Progress in Physical Geography, 32, 243-263, 2008.

1	Gemalen: Available from: http://www.gemalen.nl/ (Accessed 12 May 2015), 2015.
2	<u>Geurts, J. J. M., Hetjens, H., and Lamers, L. P. M.: Remobilization of nutrients after un-deepening of</u>
3	<u>lakes (in dutch), Radbouduniversiteit Nijmegen,, Nijmegen, 2013.</u>
4	<u>Griffioen, J., Vermooten, S., and Janssen, G.: Geochemical and palaeohydrological controls on the</u>
5	composition of shallow groundwater in the Netherlands, Applied Geochemistry, 39, 129-149,
6	http://dx.doi.org/10.1016/j.apgeochem.2013.10.005, 2013.
7	<u>Groen, K. P.: Pesticide leaching in polders, Field and model studies on cracked clays and loamy sand,</u>
8	<u>Van land tot zee, Ministerie van Verkeer en Waterstaat, Directoraat-Generaal Rijkswaterstaat,</u>
9	<u>Lelystad, 1997.</u>
10	Halliday, S. J., Wade, A. J., Skeffington, R. A., Neal, C., Reynolds, B., Rowland, P., Neal, M., and Norris,
11	D.: An analysis of long-term trends, seasonality and short-term dynamics in water quality data from
12	Plynlimon, Wales, Science of The Total Environment, 434, 186-200,
13	http://dx.doi.org/10.1016/j.scitotenv.2011.10.052, 2012.
14	Haygarth, P. M., Wood, F. L., Heathwaite, A. L., and Butler, P. J.: Phosphorus dynamics observed
15	through increasing scales in a nested headwater-to-river channel study, Science of The Total
16	Environment, 344, 83-106, http://dx.doi.org/10.1016/j.scitotenv.2005.02.007, 2005.
17 18	Hewlett, J. D., and Hibbert, A. R.: Moisture and energy conditions within a sloping soil mass during drainage, Journal of Geophysical Research, 68, 1081-1087, 1963.
19 20	Hirsch, R. M., Slack, J. R., and Smith, R. A.: Techniques of trend analysis for monthly water quality data, Water Resources Research, 18, 107-121, 10.1029/WR018i001p00107, 1982.
21	Hirsch, R. M., and Slack, J. R.: A Nonparametric Trend Test for Seasonal Data With Serial Dependence,
22	Water Resources Research, 20, 727-732, 10.1029/WR020i006p00727, 1984.
23 24 25	Hodgkinson, R. A., Chambers, B. J., Withers, P. J. A., and Cross, R.: Phosphorus losses to surface waters following organic manure applications to a drained clay soil, Agricultural Water Management, 57, 155-173, http://dx.doi.org/10.1016/S0378-3774(02)00057-4, 2002.
26	Huebsch, M., Grimmeisen, F., Zemann, M., Fenton, O., Richards, K. G., Jordan, P., Sawarieh, A., Blum,
27	P., and Goldscheider, N.: Technical Note: Field experiences using UV/VIS sensors for high-resolution
28	monitoring of nitrate in groundwater, Hydrol. Earth Syst. Sci., 19, 1589-1598, 10.5194/hess-19-1589-
29	2015, 2015.
30	Jarvie, H. P., Mortimer, R. J. G., Palmer-Felgate, E. J., Quinton, K. S., Harman, S. A., and Carbo, P.:
31	Measurement of soluble reactive phosphorus concentration profiles and fluxes in river-bed
32	sediments using DET gel probes, Journal of Hydrology, 350, 261-273, 2008.
33	Johnes, P. J.: Uncertainties in annual riverine phosphorus load estimation: Impact of load estimation
34	methodology, sampling frequency, baseflow index and catchment population density, Journal of
35	Hydrology, 332, 241-258, http://dx.doi.org/10.1016/j.jhydrol.2006.07.006, 2007.
36	Jones, T. D., Chappell, N. A., and Tych, W.: First Dynamic Model of Dissolved Organic Carbon Derived
37	Directly from High-Frequency Observations through Contiguous Storms, Environmental Science &
38	Technology, 48, 13289-13297, 10.1021/es503506m, 2014.
39 40 41	Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrology and Earth System Sciences, 11, 372-381, 2007.

1	Kaufmann, V., Pinheiro, A., and Castro, N. M. d. R.: Simulating transport of nitrogen and phosphorus
2	in a Cambisol after natural and simulated intense rainfall, Journal of Contaminant Hydrology, 160,
3	53-64, http://dx.doi.org/10.1016/j.jconhyd.2014.02.005, 2014.
4	Kaushal, S. S., Mayer, P. M., Vidon, P. G., Smith, R. M., Pennino, M. J., Newcomer, T. A., Duan, S.,
5	Welty, C., and Belt, K. T.: Land use and climate variability amplify carbon, nutrient, and contaminant
6	pulses: A review with management implications, Journal of the American Water Resources
7	Association, 50, 585-614, 10.1111/jawr.12204, 2014.
8 9 10	Kirchner, J. W., Feng, X., Neal, C., and Robson, A. J.: The fine structure of water-quality dynamics: the (high-frequency) wave of the future, Hydrological Processes, 18, 1353-1359, 10.1002/hyp.5537, 2004.
11	Knotters, M., and van Walsum, P. E. V.: Estimating fluctuation quantities from time series of water-
12	table depths using models with a stochastic component, Journal of Hydrology, 197, 25-46,
13	http://dx.doi.org/10.1016/S0022-1694(96)03278-7, 1997.
14	Lavoie, M., and Auclair, JC.: Phosphorus Mobilization at the Sediment–Water Interface in Softwater
15	Shield Lakes: the Role of Organic Carbon and Metal Oxyhydroxides, Aquatic Geochemistry, 18, 327-
16	341, 10.1007/s10498-012-9166-3, 2012.
17	LNV: Fourth Dutch Action Programme (2010-2013) concerning the Nitrates Directive; 91/676/EEC. ,
18	The Hague, 2009.
19 20	Loeb, R., Lamers, L. P. M., and Roelofs, J. G. M.: Prediction of phosphorus mobilisation in inundated floodplain soils, Environmental Pollution, 156, 325-331, 10.1016/j.envpol.2008.02.006, 2008.
21	<u>Meinardi, C. R., and Van den Eertwegh, G. A. P. H.: Investigations on tile drains in clayey regions of</u>
22	the Netherlands, Part II: Interpretation of data, RIVM, Bilthoven, The Netherlands, 1997.
23	Mulholland, P. J., Newbold, J. D., Elwood, J. W., Ferren, L. A., and Jackson, R. W.: Phosphorus
24	Spiralling in a Woodland Stream: Seasonal Variations, Ecology, 66, 1012-1023, 1985.
25 26	Murphy, J., and Riley, J. P.: A modified single solution method for the determination of phosphate in natural waters, Analytica Chimica Acta, 27, 31-36, 1962.
27	Neal, C., Reynolds, B., Rowland, P., Norris, D., Kirchner, J. W., Neal, M., Sleep, D., Lawlor, A., Woods,
28	C., Thacker, S., Guyatt, H., Vincent, C., Hockenhull, K., Wickham, H., Harman, S., and Armstrong, L.:
29	High-frequency water quality time series in precipitation and streamflow: From fragmentary signals
30	to scientific challenge, Science of The Total Environment, 434, 3-12,
31	http://dx.doi.org/10.1016/j.scitotenv.2011.10.072, 2012.
32	Nyenje, P. M., Meijer, L. M. G., Foppen, J. W., Kulabako, R., and Uhlenbrook, S.: Phosphorus
33	transport and retention in a channel draining an urban, tropical catchment with informal
34	settlements, Hydrol. Earth Syst. Sci., 18, 1009-1025, 10.5194/hess-18-1009-2014, 2014.
35	Palmer-Felgate, E. J., Jarvie, H. P., Williams, R. J., Mortimer, R. J. G., Loewenthal, M., and Neal, C.:
36	Phosphorus dynamics and productivity in a sewage-impacted lowland chalk stream, Journal of
37	Hydrology, 351, 87-97, http://dx.doi.org/10.1016/j.jhydrol.2007.11.036, 2008.
38 39	Poor, C. J., and McDonnell, J. J.: The effects of land use on stream nitrate dynamics, Journal of Hydrology, 332, 54-68, http://dx.doi.org/10.1016/j.jhydrol.2006.06.022, 2007.
40	Regelink, I. C., Koopmans, G. F., van der Salm, C., Weng, L., and van Riemsdijk, W. H.:
41	Characterization of Colloidal Phosphorus Species in Drainage Waters from a Clay Soil Using

1 2	Asymmetric Flow Field-Flow Fractionation, J. Environ. Qual., 42, 464-473, 10.2134/jeq2012.0322, 2013.
3 4 5	Rozemeijer, J. C., and Broers, H. P.: The groundwater contribution to surface water contamination in a region with intensive agricultural land use (Noord-Brabant, The Netherlands), Environmental Pollution, 148, 695-706, 10.1016/j.envpol.2007.01.028, 2007.
6 7 8	Rozemeijer, J. C., Van der Velde, Y., Van Geer, F. C., De Rooij, G. H., Torfs, P. J. J. F., and Broers, H. P.: Improving load estimates for NO3 and P in surface waters by characterizing the concentration response to rainfall events, Environmental Science and Technology, 44, 6305-6312, 2010.
9 10 11 12	Rozemeijer, J. C., Klein, J., Broers, H. P., Van Tol-Leenders, T. P., and Van Der Grift, B.: Water quality status and trends in agriculture-dominated headwaters; a national monitoring network for assessing the effectiveness of national and European manure legislation in The Netherlands, Environmental Monitoring and Assessment, 186, 8981-8995, 10.1007/s10661-014-4059-0, 2014.
13 14 15	Schoch, A. L., Schilling, K. E., and Chan, KS.: Time-series modeling of reservoir effects on river nitrate concentrations, Advances in Water Resources, 32, 1197-1205, http://dx.doi.org/10.1016/j.advwatres.2009.04.002, 2009.
16 17 18	Shrestha, R. R., Osenbrück, K., and Rode, M.: Assessment of catchment response and calibration of a hydrological model using high-frequency discharge nitrate concentration data, Hydrology Research, 44, 995-1012, 10.2166/nh.2013.087, 2013.
19 20	Simard, R. R., Beauchemin, S., and Haygarth, P. M.: Potential for preferential pathways of phosphorus transport, Journal of Environmental Quality, 29, 97-105, 2000.
21 22 23	Skeffington, R. A., Halliday, S. J., Wade, A. J., Bowes, M. J., and Loewenthal, M.: Using high-frequency water quality data to assess sampling strategies for the EU Water Framework Directive, Hydrol. Earth Syst. Sci., 19, 2491-2504, 10.5194/hess-19-2491-2015, 2015.
24 25 26	Stutter, M. I., Langan, S. J., and Cooper, R. J.: Spatial contributions of diffuse inputs and within- channel processes to the form of stream water phosphorus over storm events, Journal of Hydrology, 350, 203-214, 10.1016/j.jhydrol.2007.10.045, 2008.
27 28 29	Tiemeyer, B., Lennartz, B., and Kahle, P.: Analysing nitrate losses from an artificially drained lowland catchment (North-Eastern Germany) with a mixing model, Agriculture, Ecosystems & Environment, 123, 125-136, http://dx.doi.org/10.1016/j.agee.2007.05.006, 2008.
30 31 32 33	van Boekel, E. M. P. M., Roelsma, J., Massop, H. T. L., Hendriks, R. F. A., Goedhart, P. W., and Jansen, P. C.: Nitraatconcentraties in het drainwater in zeekleigebieden : oriënterend onderzoek naar de oorzaken van de verhoogde nitraatconcentraties, Alterra-rapport;2360, Alterra Wageningen UR, Wageningen, 2012.
34 35	<u>Van de Ven, G. P.: Man-made lowlands, history of water management and land reclamation in the Netherlands, Uitgeverij Matrijs, Utrecht, 2003.</u>
36 37	Van den Eertwegh, G. A. P. H.: Water and Nutrient budgets at field and regional scale, travel times of drainage water and nutrient loads to surface water, PhD thesis Wageningen University, 2002.
38 39 40	van der Grift, B., Rozemeijer, J. C., Griffioen, J., and van der Velde, Y.: Iron oxidation kinetics and phosphate immobilization along the flow-path from groundwater into surface water, Hydrol. Earth Syst. Sci., 18, 4687-4702, 10.5194/hess-18-4687-2014, 2014.

1 2 3	Van der Salm, C., van den Toorn, A., Chardon, W. J., and Koopmans, G. F.: Water and nutrient transport on a heavy clay soil in a fluvial plain in the Netherlands, Journal of Environmental Quality, 41, 229-241, 2012.
4 5 6	Van der Velde, Y., Torfs, P. J. J. F., van der Zee, S. E. A. T. M., and Uijlenhoet, R.: Quantifying catchment-scale mixing and its effect on time-varying travel time distributions, Water Resources Research, 48, n/a-n/a, 10.1029/2011WR011310, 2012.
7 8 9 10 11	van Grinsven, H. J. M., ten Berge, H. F. M., Dalgaard, T., Fraters, B., Durand, P., Hart, A., Hofman, G., Jacobsen, B. H., Lalor, S. T. J., Lesschen, J. P., Osterburg, B., Richards, K. G., Techen, A. K., Vertès, F., Webb, J., and Willems, W. J.: Management, regulation and environmental impacts of nitrogen fertilization in northwestern Europe under the Nitrates Directive; a benchmark study, Biogeosciences, 9, 5143-5160, 10.5194/bg-9-5143-2012, 2012.
12 13 14	von Asmuth, J. R., Bierkens, M. F. P., and Maas, K.: Transfer function-noise modeling in continuous time using predefined impulse response functions, Water Resources Research, 38, 23-21-23-12, 10.1029/2001WR001136, 2002.
15 16 17 18 19	Wade, A. J., Palmer-Felgate, E. J., Halliday, S. J., Skeffington, R. A., Loewenthal, M., Jarvie, H. P., Bowes, M. J., Greenway, G. M., Haswell, S. J., Bell, I. M., Joly, E., Fallatah, A., Neal, C., Williams, R. J., Gozzard, E., and Newman, J. R.: Hydrochemical processes in lowland rivers: Insights from in situ, high-resolution monitoring, Hydrology and Earth System Sciences, 16, 4323-4342, 10.5194/hess-16- 4323-2012, 2012.
20 21 22	Withers, P. J. A., Ulén, B., Stamm, C., and Bechmann, M.: Incidental phosphorus losses – are they significant and can they be predicted?, Journal of Plant Nutrition and Soil Science, 166, 459-468, 10.1002/jpln.200321165, 2003.
23 24	<u>Withers, P. J. A., and Jarvie, H. P.: Delivery and cycling of phosphorus in rivers: A review, Science of The Total Environment, 400, 379-395, 2008.</u>
25 26 27	Worrall, F., Swank, W. T., and Burt, T. P.: Changes in stream nitrate concentrations due to land management practices, ecological succession, and climate: Developing a systems approach to integrated catchment response, Water Resources Research, 39, HWC11-HWC114, 2003.
28 29 30 31	Worsfold, P. J., Gimbert, L. J., Mankasingh, U., Omaka, O. N., Hanrahan, G., Gardolinski, P. C. F. C., Haygarth, P. M., Turner, B. L., Keith-Roach, M. J., and McKelvie, I. D.: Sampling, sample treatment and quality assurance issues for the determination of phosphorus species in natural waters and soils, Talanta, 66, 273-293, 2005.
32 33 34	Zak, D., Kleeberg, A., and Hupfer, M.: Sulphate-mediated phosphorus mobilization in riverine sediments at increasing sulphate concentration, River Spree, NE Germany, Biogeochemistry, 80, 109-119, 2006.
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36	
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- 1 Tables
- 2 Table 1. Locations of the low-frequency monitoring program in Lage Afdeling pumped drainage area
- 3 that is drained by the Blocq van Kuffeler pumping station.

location	Description			
1	Lage Vaart main-channel at pumping station "Blocq van Kuffeler"; outlet of the			
	Lage Afdeling drainage area			
2	Outlet of sub-channel that drains the urban area of the city "Almere"			
3	Outlet of sub-channel that drains the agricultural "Gruttotocht"			
4	Outlet of sub-channel that drains the agricultural "Lepelaartocht"			
5	Far end of Lage Vaart main channel that is drained by the pumping station "Blocq van Kuffeler"			
6	Outlet of channel that drains the nature area "Oostvaardersplassen"			

## 5 | Table 2. Rainfall events and response of NO<sub>3</sub> concentration (in mg $N4L^{-1}$ ).

Delinfall	data		NO concentration	
Rainfall	date	mm	NO <sub>3</sub> concentration	MaximalMaximum
event			before event	NO <sub>3</sub> concentration
				after event
1	20-23 Oct	31	0.7	0.8
	<u>3-4 Nov</u>	<u>16</u>	<u>0.8</u>	<u>0.9</u>
2	15-18 Nov	23	0.8	4.6
3	10-12 Dec	29	1.0	5.3
4	19-20 Dec	24	2.4	5.9
5	7-9 Jan	14	3.0	5.8
6	12-14 Jan	24	4.1	9.0
7	20-21 Feb	26	0.8	10.4
8	29 Mar-2-Apr	43	0.8	6.1
	<u>17-23 June</u>	<u>40</u>	<u>0.2</u>	<u>0.5</u>
	<u>27-29 July</u>	<u>47</u>	<u>0.5</u>	<u>0.7</u>
<u>9</u>	<u>14-18 Aug</u>	<u>87</u>	<u>0.6</u>	<u>3.4</u>
<u>10</u>	<u>26-31 Aug</u>	<u>59</u>	<u>2.4</u>	<u>4.7</u>

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Table 3. Summary of TP and turbidity peaks, calculated as difference between the maximum value

during the peak minus the value before the peak, induced by the pumping station

	$\Delta$ TP (mg L <sup>-1</sup> )	<u>∆ turbidity (FTU)</u>	$\Delta$ TP (mg L <sup>-1</sup> )	<u>∆ turbidity (FTU)</u>
	<u>1 pump</u>	<u>1 pump</u>	<u>2 pumps</u>	<u>2 pumps</u>
<u>n peaks</u>	<u>72</u>	<u>79</u>	<u>59</u>	<u>60</u>
<u>average</u>	<u>0.06</u>	<u>4.4</u>	<u>0.13</u>	<u>22.1</u>
<u>median</u>	<u>0.04</u>	<u>4.4</u>	<u>0.10</u>	<u>21.1</u>
<u>P25</u>	<u>0.01</u>	<u>1.8</u>	<u>0.07</u>	<u>14.0</u>
<u>P75</u>	<u>0.08</u>	<u>8.3</u>	<u>0.14</u>	<u>29.2</u>
max	<u>0.58</u>	<u>26.2</u>	<u>0.61</u>	<u>52.0</u>
min	<u>-0.01</u>	<u>-1.5</u>	<u>0.03</u>	<u>5.9</u>

## 1 Figures



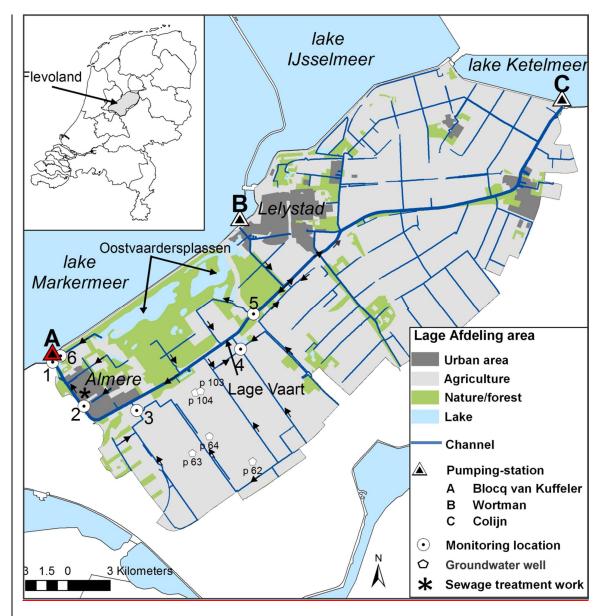
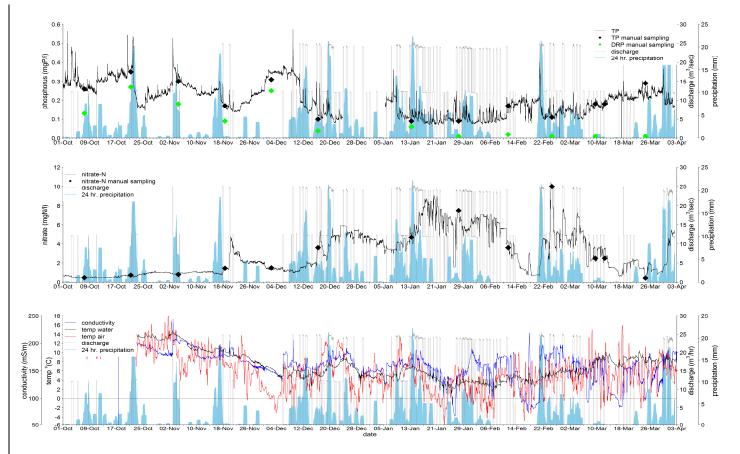
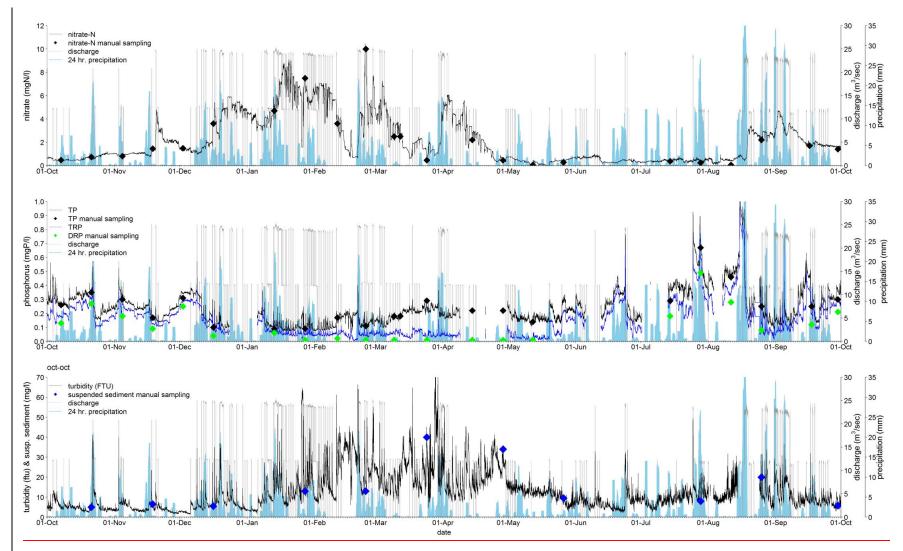
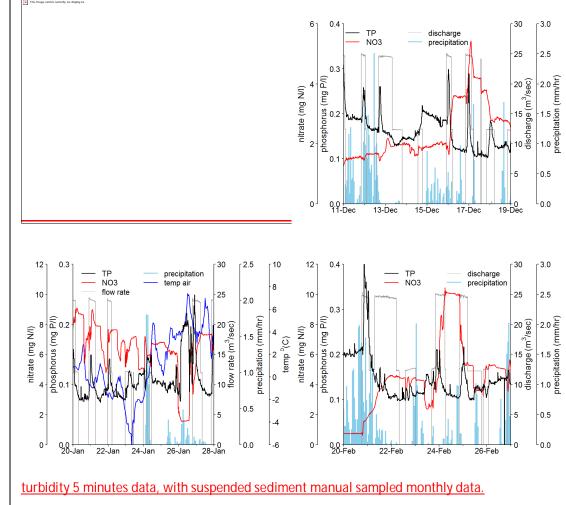


Figure 1. -Map of the Lage Afdeling pumped drainage area, <u>the continuous monitoring station at</u> <u>location A, the low-frequency surface water monitoring locations and the groundwater level</u> <u>monitoring locations</u>. The flow direction of the water in the channels that are drained by pumping station Blocq van Kuffeler is illustrated by arrows.

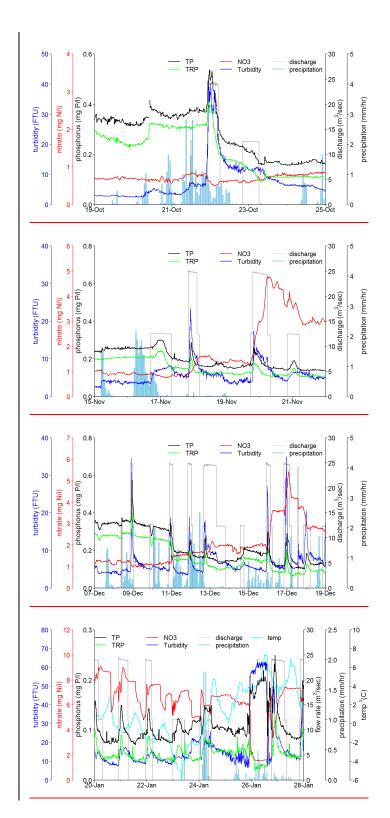




- 1 Figure 2. High-frequency monitoring data for the Lage Vaart channel at the pumping station Blocq van Kuffeler together with the 1 day antecedent
- 2 precipitation and the pumping regime: (top) total phosphorus 20 minutes data, with TP and DRP manual sampled biweekly data, precipitation data and
- 3 discharge as generated by the pumping station; (middle: (top) nitrate-N 5 minutes data, with NO<sub>3</sub>-N manual sampled biweekly data; (middle) total
- 4 phosphorus and total reactive phosphorus 20 minutes data, with TP and DRP manual sampled biweekly data; (bottom) conductivity, air temperature (from
- 5 KNMI weather station Lelystad) and water temperature.







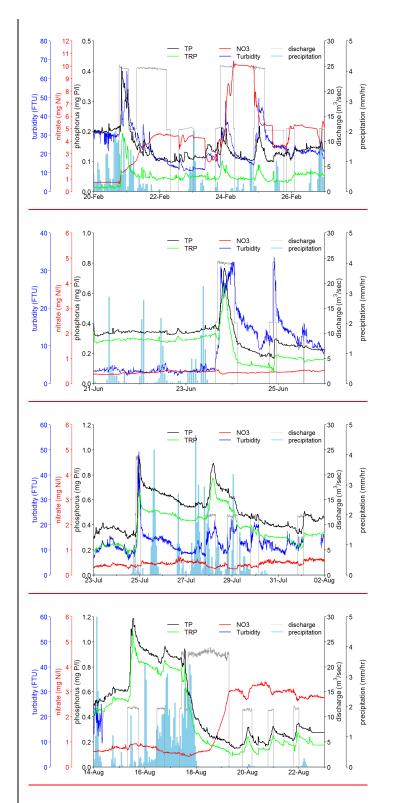
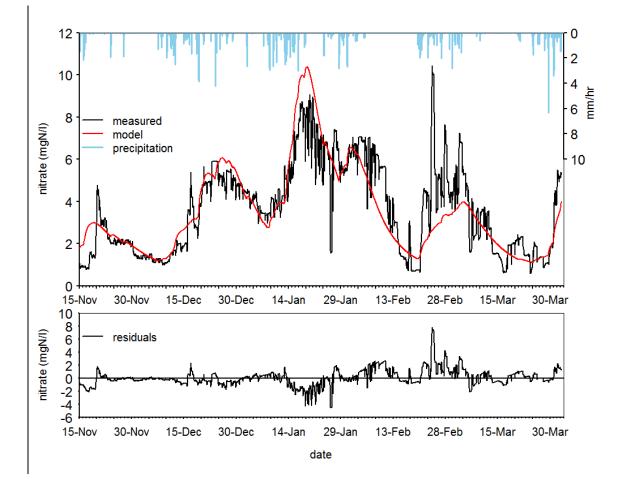


Figure 3. Examples <u>of</u> surface water NO<sub>3</sub>, <u>TP</u> and <u>TPturbidity</u> dynamics at the pumping station Blocq van Kuffeler during meteorological events between <u>NovemberOctober</u> 2014 and <u>FebruaryAugust</u> 2015 together with the pumping regime and precipitation (in  $mm_{-}^{+}hr^{-1}$ ). The January event

demonstrates the effect of freeze-thaw on the nutrient concentrations while the other events show the nutrient dynamics upon rainfall events.



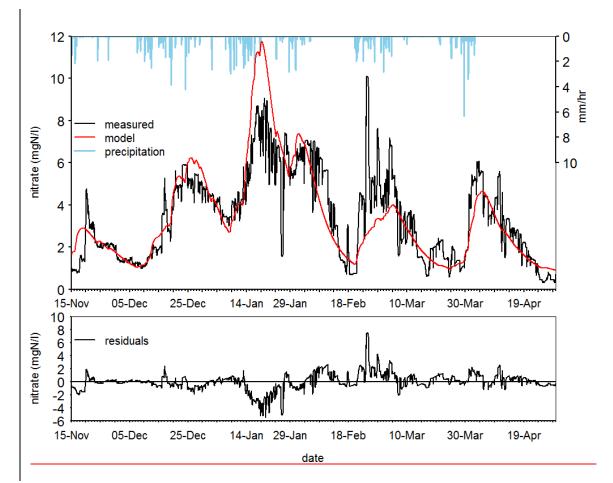


Figure 4. Measured and simulated NO<sub>3</sub> concentrations and rainfall data (top); and residual NO<sub>3</sub> series (bottom).

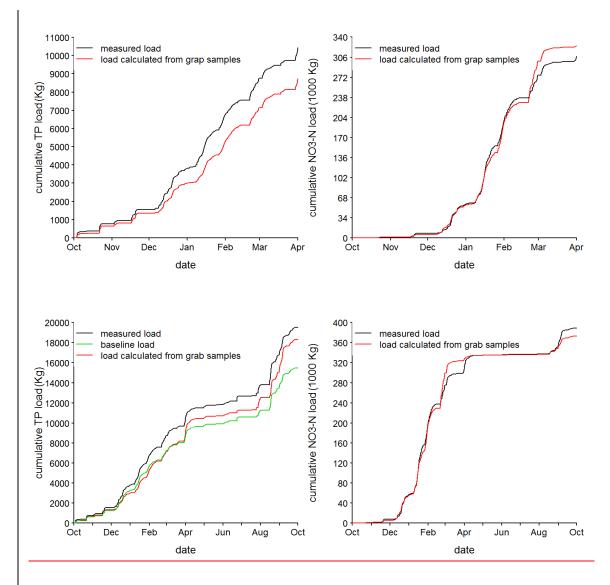
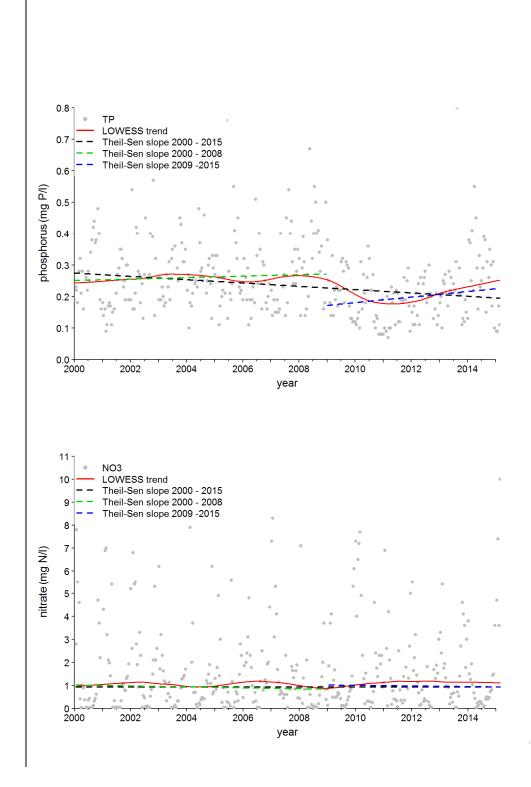


Figure 5: Measured and calculated PTP and NO<sub>3</sub> loads at the pumping station Blocq van Kuffeler<u>, the</u> baseline load was calculated with the high-frequency TP data after separation of the short-scale concentration peaks generated by the pumping station.



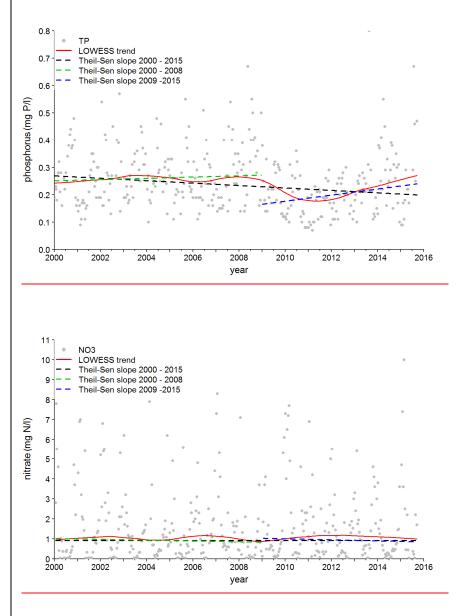
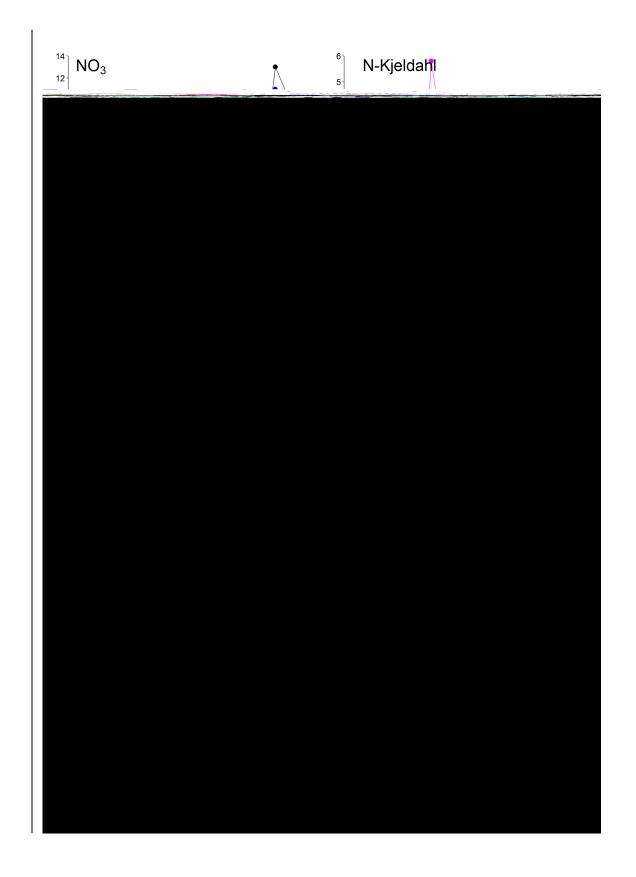


Figure 6: Trends in TP and NO<sub>3</sub> concentrations over the period 2000-2015 at location 1 (Blocq van Kuffeler).



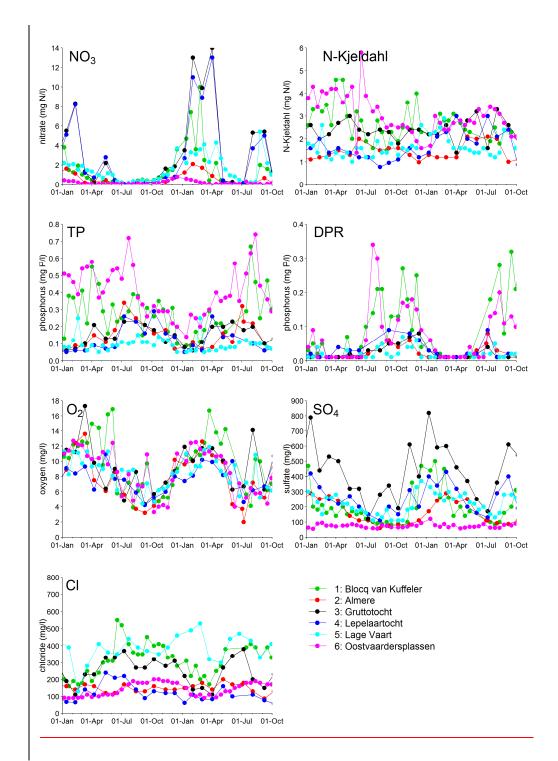


Figure 7. Low-frequency time series of NO<sub>3</sub>, N-kjeldahl, TP, DRP, O<sub>2</sub>, SO<sub>4</sub> and Cl concentration at surface water sampling location in the Lage Afdeling drainage area during the period January 2014 to <u>MarchOctober</u> 2015. Fig. 1 forshows the positions of the monitoring locations.